DESIGN, FABRICATION AND CHARACTERIZATION OF EPITAXIAL AND NON-EPITAXIAL THERMO-PHOTOVOLTAIC CELLS

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by

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DISSERTATION

Submitted in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy
Optical Science and Engineering

The University of New Mexico
Albuquerque, New Mexico

May, 2014
DEDICATION

To my devoted mom and dad

&

To my beloved husband

Their support, encouragement, and constant love have sustained me throughout my life
ACKNOWLEDGEMENTS

I would like to thank my advisor, Prof. Luke Lester, for not only teaching me research strategies but also many history facts. As a thesis supervisor, Professor Luke Lester supported me in all stages of this work. He is the initiator of this project and he always gave me constant encouragement and advice, despite his busy agenda. Without a coherent and illuminating instruction, this dissertation would not have reached its present form. I thank him for having managed to support me even after he left the University of New Mexico for Virginia Tech University as a head of electrical engineering department. I will not forget our very frequent teleconferences during which he gave me advice and encouragement.

I express my sincerest gratitude to my current advisor Prof. Ganesh Balakrishnan that kindly supported my research after Prof. Lester joined VTU, from whom I have learned advanced materials science and its application to engineering. I am especially grateful for his trust in me and the freedom he gave me to do this work. His great desire to explore novel ideas governed me through multiple publications. Thank you both my advisors, I have learned a great deal from you.

I am deeply grateful to the committee members, Prof. Olga Lavrova and Prof. Andrea Mammoli for taking time to read this manuscript and for agreeing to participate in the dissertation defense.

I would like to acknowledge the assistance of Dr. Tito Busani who offered me valuable suggestions whenever I had problems during the study and generously shared his time and expertise. During the preparation of the dissertation, he spent much time to improve publications and provide me relevant advice.

I wish to express my gratitude to Sr. research engineer Chris Hains, who helped me to learn photoluminescence measurement in his laboratory. He also helped me to revise my papers many times along with new ideas to overcome challenges during my research. I am also very grateful to Dr. Tom Rotter for his guidance and help with MBE growth quality improvement and defect study.

I extend my sincere thanks to all members of the Center for High Technology Materials (CHTM), and all those who contributed directly or indirectly to the dissertation. In particular, I wish to thank
Andrew Aragon, Orlando Romero, Emma Renteria, Somayeh Imani, Sadhvikas Addamane and Mahmoud Behzadirad for their valuable help and friendship.

Without the support of all members of my family, I would never finish this dissertation and I would never find the courage to overcome all these difficulties during this work. My thanks go to my parents for their support and their love during all these years. I would especially like to express my gratitude to my husband, Mohammad Arbabshirani, who has always supported me and helped me overcoming the difficulties without complaining. If my work has sometimes prevented us from sharing important moments of life, know that I never stopped thinking about you.

This material is based upon work supported in part by the National Science Foundation (NSF) and the Department of Energy (DOE) under NSF CA No. EEC-1041895 and U.S. Army Research Laboratory (ARL) Micro Autonomous Systems and Technology (MAST) program. Any opinions, findings and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect those of NSF, DOE or ARL.
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ABSTRACT

Thermophotovoltaics (TPVs) have significant potential in efficiently converting thermal energy to electrical energy. These applications include conversion from internal combustion engines, small nuclear sources and even portable fuel-based sources. Group-III antimonide semiconductors have been identified as the material of choice for such TPV devices due to the possibility of growing materials with the bandgap energies of 0.51 eV (GaInAsSb quaternary) to 0.72 eV (GaSb binary) that are correspond to commonly available heat sources. The quaternary alloys are grown epitaxially while the binary GaSb devices can be realized through non-epitaxial techniques.

In this work, we have pursued fabrication and design methods that will allow us to realize large area GaSb-based diode technology for TPV applications. TPV yield is a serious issue in such large area devices. Functional TPV cells using epitaxial GaSb, epitaxial GaInAsSb, and implanted GaSb with areas up to 1 square cm are realized.
The epitaxial cells fabricated in this study allow for the engineering of the bandgap in the structure and also allows for the tailoring of the absorber in the cell to 2.4 µm which is a blackbody wavelength of interest. These cells however are not straightforward to scale in dimension due to the presence of large epitaxy related defects that end up shorting the devices. We have identified and mitigated the effect of such shunt defects that were limiting the yield of the epitaxial TPVs on GaSb. The Non-epitaxial TPV cells are realized using beryllium ion implantation into an n-type GaSb substrate. Through the use of rapid thermal annealing a pn junction is formed. The ion-implanted approach is intended to maximize shunt resistance compared to the epitaxial technique. The presentation will involve in-depth characterization and analysis of the materials from the quality of the semiconductor materials and interfaces to the ohmic contacts. Extensive analysis of the material using transmission electron microscopy, electron dispersive spectroscopy and secondary ion mass spectroscopy will be presented and correlated to electrical characterization results.
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CHAPTER 1

INTRODUCTION
1. **INTRODUCTION**

Nowadays most of the consumed energy for transportation, building and industry comes from fossil fuels, which are the primary energy sources. Overusing fossil fuels has caused lots of concern world-wide regarding the limitation of supplies, increasing energy needs and environmental and global effects. For example overusing fossil fuels can cause acid rain and climate change. These consequences have created more interest in people to explore non-fossil fuel resources and decrease the use of fossil fuels, or at least efficiently use it.

Thermo-photovoltaics (TPV) cells convert heat directly into electricity. This is useful for non-fossil fuel energy resources like solar energy, nuclear, and biomass and the efficient use of fossil fuel by converting the waste heat to energy. TPV cells are promising for the conversion of heat into electricity, which makes this very attractive to existing technologies for electricity generation. To date, researchers have not shown high efficiencies for TPV systems and apparently it is unclear what a practical TPV system efficiency is. However, even considering low efficiency, TPV systems can be very useful for efficient fossil fuel usage. For example, it can be used in systems like portable power and waste heat recovery and combined heat and power systems (CHP). At the present time, existing TPV systems are mostly developed to use in fossil fuel powered combustion applications. This is not very favorable for fossil fuel substitution, but useful from an energy savings aspect. Nevertheless, TPV systems are very flexible in terms of their fuel sources and this may allow us to change from fossil fuels to bio fuels in near future. So, TPV systems should develop to generate more energy from wasted heat from thermal sources (fossil or non-fossil), if market and technology challenges can be solved.

This work presents different novel approaches to improve TPV systems by improving PV cells and contacts. It was started as a part of large research project funded by the US Army Research Laboratory in the Micro-Autonomous Systems Technology (MAST) effort. In this chapter, the basic TPV system is discussed starting from history down to its physics and applications. Second, the main funded project as a whole picture is explained briefly and the goals are stated.
1.1 THERMPHOTOVOLTAIC (TPV) ENERGY CONVERSION CONCEPT

The thermophotovoltaic (TPV) energy conversion system is a direct conversion process wherein heat energy is first converted by some sort of absorber/emitter into photon radiation, which in turn is converted into electrical energy. The concept is demonstrated in Figure 1.1. This shows a basic thermophotovoltaic system that consists of a photovoltaic diode cell and a thermal emitter. In more developed TPV designs there are cooling systems for diode cells and a photonic crystal for bandgap filtering.

There are different thermal sources shown in Figure 1.1 Thermal energy from these sources is supplied to an emitter, and then the radiation from the emitter is directed to the photovoltaic (PV) cells. This radiation converts to electrical energy in these PV cells using semiconductors photocurrent generation properties.

For different systems, the thermal emitter temperatures can vary from 900 °C to about 1400 °C. However, in theory TPV systems can generate energy from any heater that emits photons with energies greater than the PV cell bandgap.

In a TPV system, a piece of solid material or a specially engineered structure can perform as a thermal emitter. Thermal emission, which is mainly at near infrared and infrared frequencies, is the spontaneous emission of photons that is due to thermal motion of charges in the material. The TPV diode is capable of absorbing these photons and converting them to free carriers, which are collected to provide electricity. In the most elementary case, a conventional solar cell can be thought of as a TPV in which the sun is the thermal emitter.

In order to produce electricity and have an efficient TPV system, the emitted photons’ energy from the heater should be greater than the bandgap energy of the PV. How can this be accomplished? One way of making an efficient TPV system is to shape the radiation in the spectral domain. This is accomplished in different ways:

One strategy is to use a selective emitter with low emittance for photon energies below the bandgap and high emittance for photons with energies greater than the PV cell bandgap.

The second strategy is to use a gray body emitter that has a constant emittance and a band pass filter. This system works in a way that the band pass filter should have a transmittance for photon energies greater than PV cell bandgap and high reflectance for low energy photons. To make this system more efficient a back surface reflector on the PV array can
be very useful. There is a great possibility to combine all these strategies together and boost TPV system efficiency [1].

![Diagram of Thermophotovoltaic (TPV) energy conversion concept](image)

*Figure 1.1. Thermophotovoltaic (TPV) energy conversion concept [1].*

1.2 **SHORT HISTORY OF TPV ENERGY CONVERSION [2]**

Thermophotovoltaic technology initiation is not very clear. The very first event regarding TPV invention is attributed to Dr Henry H Kolm [3] at MIT’s Lincoln Laboratory that invented the basic TPV system in 1956. He made an emitter using a simple Coleman camping lantern with an incandescent gas mantle. The PV cell that he used was a silicon solar cell as a photoconverter to electricity. After recording the power of the solar cell he extrapolated the power output of the whole system, which was approximately 1 watt. He proposed some improvements to his design later, which increased the theoretical conversion energy by 5 to 10%. After this achievement, Lincoln Laboratory wasn’t very active in TPV research. However, more literature [4, 5] attributes the invention of the TPV to Professor Pierre Aigrain rather than Kolm of MIT.

One of the important early advances that came from the GM research laboratory was the idea of a photoconverter back surface reflector [7] to implement spectral control in a TPV system.
The US Army de-emphasized TPV technology in the mid-1970s and switched to thermoelectric technology to convert power sources. This slowed down TPV technology progress significantly. The reason for this decision by the Army was the very new and unknown TPV technology in comparison to thermoelectric systems that were more mature and reliable. This even expanded to GM research labs and they stopped TPV technology exploration.

In late 1970s two events revived TPV technology research. One was governmental regulations on emissions reduction, and second was confronting increasing foreign competition for energy sources. Also, an energy crisis happened in the 1970s, which was in beneficial to TPV development. In this period, all types of renewable energy including TPV systems became attractive; among all, solar energy received prime attention.

In the 1980s, TPV systems research was continued in the US by different groups. One of these groups was Woolf [8] at GA Technologies in San Diego, CA. He suggested that it is possible to use InGaAs photoconverters in TPV systems. This new photoconverter resulted in an improvement in the performance compared to crystalline Si photoconverters. Also, about the same decade, the Gillette Company in Boston, MA were developing selective fibrous rare earth oxide emitters [9] that were applicable to TPV systems. At NASA-Lewis, selective emitters were built by Chubb [10] to use in space power systems.

In 1990s, two former Boeing engineers Horne and Fraas left the company and started new companies. These companies were named EDTEK Inc. (Kent, WA) and JX Crystals Inc (Issaquah, WA). The first one belonged to Horne and the second one was Fraas’s. The JX Crystal Incorporation licensed Zn-diffused GaSb cell technology that was developed earlier at Boeing and started making commercial TPVs.

There was another company in San Diego, CA named Quantum Group Inc. that started to develop TPV systems later along with its carbon monoxide sensor business. Also, AstroPower, Inc., NREL, Sarnoff Corporation and MIT Lincoln Laboratory started to investigate TPV technologies very seriously about the same time. The reason for the unexpected interest was an undisclosed military application that was discovered. Narrow bandgap cells for TPV application was the most important researcher’s interest at these companies. Among all these, NREL performed the most essential role in the TPV
technology progress. They sponsored a series of conferences regarding TPV technologies, collected data and published the conference proceedings [11].

In the recent decade, research on TPV systems has focused on two different areas:

1. Using InGaAs and InAsP epitaxial structures to fabricate TPV devices on InP substrates. This research has been pursued at different sites like NREL, NASA-Glenn Research Center, Bechtel Bettis and Ohio State University.

2. Using InGaAsSb epitaxial structures on GaSb substrates to fabricate TPV devices. This work was conducted at MIT Lincoln Labs, Sarnoff Labs, Sandia National Laboratories, KAPL/Lockheed-Martin, the Ioffe Institute and the Fraunhofer Institute [12].

1.3 TPV APPLICATIONS

The TPV history shows that the technology has started since 1960s, but the great progress is made in recent years. Today there are lots of developments on emitter type and technology and PV cells.

There are many applications for TPV systems and the interest on this technology is resurgent. These systems are portable, simple and have a potential of achieving high efficiencies. Also, they don’t have a moving part but just a fan or pump for cooling the PV cells.

The TPV system components consist of a PV cell, thermal source, emitter, filter, the waste heat rejection system and cooling system. Among all these components, the PV cells and filter are the most complicated parts and the rest are in the solid state.

Besides simplicity of the TPV system and achievable high efficiency, it can be coupled with variety of thermal sources. These thermal sources may be fossil fuels, bio fuels, nuclear power or solar energy.

TPV systems are categorized based on these different thermal sources. If an emitter and a filter is added to a conventional PV system then it’s called a solar TPV system (STPV) which uses the sun as a thermal source [1, 12]. It may come to mind that a STPV system has no advantage over a conventional solar PV system. What can be achieved by implementing an emitter and filter? The answer is by adding a selective emitter plus filter, the solar spectrum, which is a graybody emitter at about 6000 K, can be shifted to match the bandgap of the PV cells.
Some TPV systems are designed to use radioisotope decay (RTPV) [1, 12]. These are useful in space applications like deep space missions where the sun’s energy is not strong enough to power a conventional PV system. The RTPV systems use thermoelectric energy converters (RTG).

So TPV systems are able to provide more efficiency than the thermoelectric systems as explained and they are being replaced gradually.

Another TPV system which is considers the most common one, is using fossil fuel thermal sources like butane or propane to generate electricity.

Among all TPV systems, combustion driven TPV systems have many applications in industry. These applications include natural gas-fired appliances (furnaces and hot water tanks) for electricity co-generation. In these kinds of applications, the efficiency of the TPV system is not vital because the waste heat for conversion is fully utilized.

Commercial and military applications are also provided by TPV systems due to their portability, low maintenance nature and low noise. These are especially important in military missions to keep the mission safe and undetected. The commercial usage example for combustion driven TPVs are as a power supply for hybrid electric vehicles. The other advantage of TPV systems are their environment-friendly nature; they produce no pollutants. Besides, if they use a thermal source that is a combustion driven, there is not much pollution production. The reason is using the atmospheric pressure burning in these systems, the combustion temperature is controlled and the toxic nitrous oxides production (NOX) is very limited.

So, a clean TPV system power generator is much desired to replace diesel generators in remote, backup or marine power generation. This is even more important in locations that are not suitable for PV setup and battery storage.

There are other applications for TPV systems like power generation for vehicles and ships, and utilization of waste heat in industrial factories and nuclear plants.

Thermal sources option for TPV systems consist of combustion of hydrocarbons such as gasoline or diesel fuels; propane or butane burners; highly focused sunlight; radioactive decay of radioisotopes such as plutonium-238; and heat exchangers coupled to nuclear reactors, furnaces, exhaust systems, fossil fuel-fired boilers, space heaters, or internal combustion engines.
An example of an interesting commercial application is autonomous oil or gas fired residential heating systems equipped with TPV systems that convert waste heat to electricity to power circuits, relays, fans and so on that are able to work during electricity outages [13].

In general, there are lots of interest in both scaling up TPV systems to use in power plants, submarines, nuclear reactors and buildings as well as energy recovery for paper and glass making companies, and to miniaturize TPV systems for small electronics power supply applications.

Mostly in military applications, small scale TPV systems are desirable to consider as a replacement for batteries of small communication devices, spying creatures, laptops, and portable lighting.

Other advantages of TPV systems are being modular, safe, pollution free, and low maintenance [14]. In some conditions, fuel-powered TPV systems can complement solar power systems for better reliability and load management.

However, although unlimited applications for TPV systems are apparent, widespread adoption depends on their cost. At this stage of research and development, it is not easy to promise a cost-effective application for TPV systems.

Despite all these interesting applications, TPV systems are relatively unknown and not widely commercialized. So far as the author is aware, only one company (JX Crystals) is actually manufacturing complete systems.

### 1.4 Thermophotovoltaic (TPV) Cells Basic Operation

The TPV cell performance can be described like conventional solar cells using an open-circuit voltage, $V_{oc}$, short-circuit current density, $J_{sc}$, and fill factor $FF$ [1, 12, 46].

$V_{oc}$ is the voltage produced by the TPV cell under illumination with no electrical load ($R_L = \infty$) and $J_{sc}$ is the current produced per unit area of the cell, under the same illumination when the load is short-circuited ($R_L = 0$).

$FF$ measures the ratio of the maximum power operating point ($J_{max}$-$V_{max}$ product) to the product of $J_{sc}V_{oc}$.

So, the efficiency is the output power density divided by the input power density:
\[ \eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{V_{\text{max}}I_{\text{max}}}{P_{\text{in}}} = \frac{FFV_{\Omega SC}}{P_{\text{in}}} \]

where \( P_{\text{in}} \) is the power density per unit area of the radiation incident on the TPV cell.

\( P_{\text{in}} \) (incident power density) is calculated by integrating the spectral density of the incident radiation over all wavelengths. The spectral power density is defined as \( P_E(E) \) [power/unit area/photon energy] in terms of the photon energy \( E \), or as \( P_\lambda(\lambda) \) [power/unit area/photon wavelength] in terms of photon wavelength \( \lambda \), equivalently. The photon energy and wavelength are related by \( E = \frac{hc}{\lambda} \).

So \( P_{\text{in}} \) is:

\[
P_{\text{in}} = \int_{0}^{\infty} P_E(E)dE = \int_{0}^{\infty} P_\lambda(\lambda)d\lambda
\]

or

\[
P_{\text{in}} = \int_{0}^{\infty} \frac{hc}{\lambda} \phi(\lambda)d\lambda
\]

Here \( \phi(\lambda) \) is the spectral photon flux [photons/unit area/unit time/photon wavelength].

The short current density is defined by:

\[
J_{\text{sc}} = \int_{E_G}^{\infty} P_E(E)SR_E(E)dE = \int_{0}^{\frac{hc}{E_G}} P_\lambda(\lambda)SR_\lambda(\lambda)d\lambda
\]

where \( SR_E(E) \) is the spectral response as a function of photon energy \( E \) (or photon wavelength \( \lambda \)). Also, \( J_{\text{sc}} \) can be calculated from the photon flux density \( \phi(\lambda) \) of the incident radiation and the external quantum efficiency \( QE_{\text{ext}}(\lambda) \) [dimensionless], as below:

\[
J_{\text{sc}} = q \int_{0}^{\frac{hc}{E_G}} \phi(\lambda) QE_{\text{ext}}(\lambda)d\lambda
\]

where \( q \) is the electric charge.

The definition for external quantum efficiency is the probability that an incident photon of wavelength \( \lambda \) will generate a charge carrier that contributes to the short-circuit current of
the TPV cell. The external quantum efficiency is a factor that indicates the reflection and absorption of incident photons, generation of minority carriers, and collection of minority carriers by the p-n junction. In conclusion, the external quantum efficiency considers three different loss mechanisms:

1- The loss due to reflection of incident photons from the front surface of the cell.
2- The loss resulting from sub-bandgap and low-energy photons that are not absorbed.
3- The loss due to photogenerated minority carriers that recombine before they are collected by the p-n junction.

Figure 1.2. Measured external quantum efficiency spectrum of several types of TPV cells [12].

Figure 1.2 displays external quantum efficiencies measured for several types of TPV cells. These TPV cells are covering a bandgap range of 0.35 to 0.7 eV.

The devices include TPV cells that were made as diffused junctions in different semiconductors like monocrystalline and polycrystalline GaSb and Ge wafers. They are also made out of diffused junctions in wafers cut from polycrystalline InGaSb ingots and epitaxial junctions in GaInAsSb heterostructures made on single-crystal GaSb substrate wafers. The last devices are made from diffused junctions in InAsSbP epitaxial layers grown on monocrystalline InAs substrate wafers. An antireflection coating was applied
only to the GaSb TPV cell. Shadowing losses caused by the contact grid were in the 15-20% range. [12]

These data indicate that the current TPV cell materials cover a wide spectral range. So, it is obvious that a cell type selection is based on spectral response consideration.

It seems that for the attractive TPV technologies like GaSb, InGaAsSb, and InGaAs, external quantum efficiencies of 50 to 80% are not impossible over a wide spectral range [12]. In this regard, since the front contact metallization grid obscures 10 to 20% of the front surface, this imposes a limit on the external quantum efficiency. A perfect anti-reflection coating and no minority carrier recombination losses don’t prevent this loss.

The diode equation has an open-circuit voltage $V_{oc}$ that is related to the reverse-saturation current $J_0$ of the p-n junction and the short circuit current $J_{sc}$ as follows:

$$J = J_0 \left[ \exp \left( \frac{qV}{nkT_c} \right) - 1 \right] - J_{sc}$$

$n$: diode ideality factor
$k$: Boltzmann’s constant
$T_c$: TPV cell temperature
$J_0$: TPV cell dark current

By rearranging the above equation and solving for $V_{oc}$ when $J = 0$ we have:

$$V_{oc} = \frac{n k T_c}{q} \ln \left[ 1 + \frac{J_{sc}}{J_0} \right]$$

Using modeling softwares, a generalized formula for $J_0$ is suggested for solar cells [15-17]. This is helpful to predict performance, determine the best bandgap for a particular situation, and assess the potential of various TPV materials:

$$J_0 = \beta(E_g) \cdot T_c^3 \exp \left( -\frac{E_g}{kT_c} \right)$$

The constant $\beta(E_g)$ is calculated as:

$$\beta(E_g) = C = 17.9 \quad (mA/cm^2/K^3) \quad [16]$$
or as:

\[
\beta(E_g) = C = 3.165 \times 10^{-4} \cdot \exp(2.19 \cdot E_g (ev)) \quad (Acm^{-2}K^{-3}) \quad [17]
\]

using different references.

Figure 1.3 demonstrates the experimental \( J_0 \) values for low-bandgap semiconductor p-n junctions. As shown in Figure 1.3, increasing the minority carrier lifetime decreases the dark saturation current. There is a well-known theoretical limit to minority carrier lifetime. This limit is due to radiative recombination phenomena and depends on whether photon recycling effects are operative or not. This can be enhanced by a backside reflector or other designs. The backside reflector accommodates photon recycling by providing the possibility of reabsorption of photons produced by radiative recombination of minority carriers. Then the re-absorbed photon generates a minority carrier. However, photons that pass through the absorbing layer reflect back to the thermal source and assist to maintain its temperature. Photon recycling is capable of increasing the effective minority carrier lifetime twice or more [18, 19].

![Figure 1.3](image_url)

*Figure 1.3. Dark current density \( J_0 \) as a function of bandgap \( E_g \) for PV and TPV devices. Experimental and theoretical modeling predictions are presented [12].*
It is very useful to compare the predicted theoretical values of $J_0$ as a function of bandgap with the experimental values. The reason is that the open circuit voltage is largely determined by saturated dark current $J_0$. As discussed briefly before, most of the modeling results point out that TPV systems with high efficiencies are approachable using low bandgap TPV cells. These bandgaps are less than 0.5 eV, which is achievable using InGaAsSb and InGaAs materials for TPV cells. Furthermore, micro-gap TPV cells that are within a very small gap (a fraction of a wavelength) to the emitter and tandem TPV cells will benefit from lower bandgap TPV cells rather than those of current interest with larger bandgaps. For example, the InAsSbP alloy system is a good candidate for TPV cells with bandgaps in the 0.3 to 0.5 eV range as Figure 1.2 shows. This will extend the spectral response out to the wavelength of about 3.5 μm. But, the drawback is making low bandgap TPV cells may result in severe Auger recombination effects as Figure 1.3 displays. Therefore, there should be a compromise between using low bandgap materials and dark current generation and to what extent the trend indicated in Figure 1.3 can be extrapolated to low-bandgap ($< 0.5$ eV) devices, remains to be seen in the future.

Moreover, the low-bandgap materials such as InGaAsP compared to InGaAs and InGaAsSb are not well studied and developed. Also, other problems with using these low bandgap semiconductors are the hardship of doping the material due to electrically-active defects and intrinsic doping effects.

The cell efficiency, as explained earlier depends on $J_{SC}$, $V_{OC}$, and the fill factor $FF$. There is no simple analytical formula to estimate the fill-factor. One helpful approximation is [12, 48]:

$$FF = \frac{\nu - \ln(\nu + 0.72)}{\nu + 1}$$

where $\nu$ is defined as:

$$\nu = \frac{qV_{oc}}{kT_c}$$

and $T_c$ is the cell temperature. The fill factor is dependent on the leakage current, diode ideality factor $n$, and shunt and series resistances. For good TPV cell qualities, fill-factors should be in the range of 60–70%.
These fill factors are lower than what is expected for solar cells. This is because of several factors as listed below:

1- relative non-ideality and leaky junction behavior of low-bandgap diodes
2- high current levels in TPV devices which increase series resistance effects

### 1.5 TPV System Thermodynamic Limits

A broad-spectrum incident solar radiation which includes visible, infrared, and ultraviolet components, illuminates on solar cells. This incident radiation can be approximated as a blackbody emitter at 6000 K. This incident radiation has a total intensity of 100 mW/cm². There are different loss mechanisms happening in solar cells. Some of them are listed below with possible solutions:

1- Front surface reflection that causes a certain fraction of the incident radiation to be wasted. The solution is to use antireflection coatings and surface texturing to reduce total reflection losses.

2- Shading effects of the metal grids on the front surface of the solar cell. This reduces the incident light absorption and typically causes an additional 5% loss. There is no solution for this loss in PV systems but fortunately there is a way of reducing it in TPV systems, which will be discussed in this section.

3- Low energy photons that do not contribute to the photovoltaic effect. The reason is that they cannot be absorbed since the energies are less than the semiconductor bandgap energy. The solution is to use filters to prevent these photons into the system.

4- Photons with energies larger than bandgaps increase thermalization.

The formula for the fraction of incident power with sub-bandgap energy photons that do not contribute to the electricity generation for a radiating emitter with temperature $T_E$ is given by [12]:

$$F_{\text{sub-}E_g \text{ loss}} = \frac{\int_0^{E_g} \left\{(E^3 / \left[ \exp \left( \frac{E}{kT_E} \right) - 1 \right]\right\} dE}{\int_0^{\infty} \left\{(E^3 / \left[ \exp \left( \frac{E}{kT_E} \right) - 1 \right]\right\} dE}$$

Nevertheless, those photons with energies larger than the bandgap will be absorbed and generate minority carriers. These minority carriers thermalize from upper states of
conduction and valence bands to energies within ~$kT_c$ of the conduction and valence band edges. So, some part of the incident power will be lost due to thermalization of photo-excited carriers. This lost fraction is given by:

$$F_{>E_g \text{ thermalization loss}} = \int_{E_G}^{\infty} \frac{E^2 (E - E_G)}{\exp\left(\frac{E}{kT_E}\right) - 1} dE$$

To make an efficient TPV or PV cell, the material bandgap should be selected in a way that minimizes the sum of these two losses. These two loss mechanisms, which include not absorbing sub-bandgap energy photons and thermalization of minority carriers that are generated with higher than bandgap energy photons, are unavoidable in a conventional solar cell. But the very interesting fact is that these losses can be compensated or minimized in a TPV system design. The reason is that a TPV system presents a different case than a PV system with respect to energy flows.

In TPV cells:

1- Principally, light reflected from the front surface can be returned to the emitter. Thus, reflection is not necessarily a loss to the system efficiency.

2- The sub-bandgap radiation can also be returned to the emitter. This is not possible with solar cells. The efficient recovery of sub-bandgap radiation requires that parasitic (e.g., free-carrier) optical absorption losses be avoided.

Because of the limits listed above the single-junction solar cells have efficiency limits in the range of 30-35%. Furthermore, in the PV system, the photogenerated minority carriers need to diffuse or drift to the p-n junction in order to get collected and produce current. After these minority carriers pass the p-n junction then they will be converted to majority carriers that generate the photocurrent of the solar cell. These mechanisms introduce additional losses due to surface and bulk minority carrier recombination, as well as series and shunt resistance.

So, in comparison to PV systems in which reflection is an unavoidable loss, in TPV systems, reflection is not necessarily considered a loss and it can be compensated in the
overall system efficiency. Moreover, if we use an antireflection coating that is capable of reflecting higher than bandgap energy photons, the losses attributed to thermalization of photo-generated minority carriers can be reduced. Also, if a TPV system contains a selective filter or a reflector on the backside of the TPV cell and a reflector between the emitter and TPV cell, then the selective filter and reflector will redirect most of the high energy photons back to the heater and compensate for this loss as well as helping with maintaining the heater at a desired temperature. The other advantage of using a backside reflector is to redirect sub-bandgap photons to the emitter. Alternatively, it is possible to redirect the sub-bandgap photons to the emitter by using a reflector between the emitter and a cell that has a high reflectivity for low energy photons. The act of returning the photons to the emitter by using an extra element in a TPV system is called photon recuperation. These elements consist of selective filters, backside and frontside reflectors, and reflective cell coatings. These methods provide more possible efficiency enhancements for TPV systems rather than conventional PV systems. So, the design and optimization of TPV cells should be well investigated to fully utilize photon recuperation effects. TPV device performance limits are formulated using a system with blackbody emitters. The TPV efficiency $\eta$ is calculated as below [21]:

$$\eta = \overline{QE} \cdot FF \cdot \left( \frac{q_{\text{Voc}}}{E_G} \right) F_0$$

$\overline{QE}$: external quantum efficiency

FF: fill factor

$\left( \frac{q_{\text{Voc}}}{E_G} \right)$: voltage factor

$F_0$: photon over-excitation factor

The voltage factor is considered as a measure of the degree to that the device exploits the potential energy barrier of the p-n junction. This depends on the bandgap of the semiconductor to generate a working external cell voltage. The photon over-excitation factor quantifies the thermalization losses that are produced by photons with energies above the bandgap. If we assume perfect photon recuperation of sub-bandgap photons for TPV systems, then the photon over-excitation factor is defined as [12]:
\[ F_0 = \frac{E_G \int_{E_G}^{\infty} E^2 \left[ \exp \left( \frac{E}{kT_E} \right) - 1 \right]^{-1}}{\int_{E_G}^{\infty} E^3 \left[ \exp \left( \frac{E}{kT_E} \right) - 1 \right]^{-1}} \]

If we don’t account for the recuperation of sub-bandgap photons, a more general factor \( F_0' \) can be used to estimate the TPV efficiency as:

\[ F_0' = \frac{E_G \int_{E_G}^{\infty} E^2 \left[ \exp \left( \frac{E}{kT_E} \right) - 1 \right]^{-1}}{\int_{0}^{\infty} E \left[ \exp \left( \frac{E}{kT_E} \right) - 1 \right]^{-1}} \]

The formulas listed above don’t count for some unavoidable additional losses inherent in PV and TPV devices and are highly idealized. One fundamental limit that a TPV system contains is the presence of radiative recombination in such a system. This radiative recombination current density is given by [22]

\[ J_{rad} = \frac{q(n^2 + 1)}{4\pi^2c^2} \int_{E_G}^{\infty} \omega^2 \exp \left( \frac{\hbar \omega}{kT_c} \right) - 1 \right]^{-1} d\omega \]

\[ \approx \frac{q(n^2 + 1)}{4\pi^2c^2\hbar^3} \left[ E_G^2kT_c - 2(kT_c)^3 \left( \frac{E_G}{kT_c} - 1 \right) \right] \exp \left( -\frac{E_G}{kT_c} \right) \]

\[ \approx \frac{q(n^2 + 1)E_G^2kT_c}{4\pi^2c^2\hbar^3} \exp \left( -\frac{E_G}{kT_c} \right) \]

Here symbols have their usual meanings, \( n \) is the refractive index of the semiconductor and \( T_c \) is the cell temperature. In the same way, the short-circuit current of a TPV cell illuminated by an emitter with temperature \( T_E \) is given as [22]:

\[ J_{sc} = \frac{q(n^2 + 1)}{4\pi^2c^2\hbar^3}T_E \exp \left( -\frac{E_G}{k_BT_c} \right) \]

Combining these two equations together provides a radiative limit for the “voltage factor” as below [22]:

\[ voltage \ factor \equiv \frac{V_{oc}}{E_G} = 1 - \frac{T_c}{T_E} + \frac{kT_c}{E_G} \ln \left( \frac{T_E}{T_c} \right) \]

For example, the voltage factor is about 0.88 for InGaAsSb TPV cells with \( E_G \approx 0.5 \) eV, placed in a system with a radiator temperature of 1500 K, and with the TPV cell temperature kept at 300 K. This corresponds to an open circuit voltage of about 440 mV.
This result does not match with the best-demonstrated InGaAsSb TPV cells open-circuit voltages of 300–350 mV. So, there are other unknown factors reducing the open-circuit voltage of TPV cells. This situation is for TPV cells with a bandgap range of 0.5–0.7 eV. This case is worse for TPV cells with bandgaps < 0.5 eV where the theoretical voltage factor is even smaller than the experimental one. This latter phenomenon is because of the Auger recombination in low bandgap materials. In conclusion, because the fill factor and the quantum efficiency of a TPV system are already close to their theoretical limits, it is more advantageous to enhance the voltage factor to improve the efficiency. One of the main goals of modeling TPV systems, independent of extrinsic materials properties, is to calculate the optimum emitter bandgap for a specific temperature or spectrum. Modeling is also utilized to predict the performance potential as a function of radiation characteristics and bandgaps for TPV cells [23-29].

1.6 TPV Device Model

To model TPV device performance, an approach is to use closed form solutions of the one-dimensional minority carrier transport equations. This includes taking into account bulk and surface recombination of minority carriers in quasi-neutral regions, optical generation, and the space-charge region of the p-n junction. These closed-form solutions of the one-dimensional minority carrier transport equation can be programmed on a computer to simulate the spectral response and the current voltage characteristics of the TPV cell. These models provide a variety of useful information and let us optimize the device structure like epitaxial layer thicknesses, doping levels and alloy compositions. Also, they analyze the sensitivity of the device to different variations like material properties changes.

As a result, the simulated results like spectral response, I-V curves and quantum efficiencies can be compared with the measured ones to estimate the amount of losses that are not considered in a theoretical model. This also estimates minority carrier recombination lifetimes. These comparisons give solar cells, detectors, and TPV devices the great change to perform as diagnostic tools to evaluate material quality. Although 2-D and 3-D simulations provide a more accurate model, the one-dimensional closed-form
solutions are very useful. These 1-D models provide an excellent and approximately accurate insight into the basics of TPV device workings.

Among all the factors that impact TPV device performance, it is the most sensitive to minority carrier recombination lifetimes. This factor can change so much, sometimes by several orders of magnitude depending on doping concentration, bandgap narrowing effects, defects, other impurities and contaminants, electric fields, and the stress in the constituent semiconductors.

Nevertheless, there are some factors that TPV device performance is less sensitive to. These factors are optical absorption, mobility, bandgap narrowing effects on carrier concentration, and resistivity.

In conclusion it is very useful to have these insights and then start a TPV system simulation. For example, a simulation can be designed that studies device performance as a function of minority carrier lifetime. By adjusting this parameter the best optimization of the TPV system is approachable. But there are some limits to the minority carrier lifetime that should be taken into account in the simulation. These limits are due to Auger and radiative recombination. As a result, there are some limits to the corresponding maximum open circuit voltage attainable for such lifetimes. This is where simulated TPV performance is higher than the real one.

Figure 1.4 demonstrates a double heterostructure that consists of a p-n junction that is sandwiched between two cladding layers with wide bandgaps. The backside cladding layer, that is called a buffer, is utilized to realize a back surface field (BSF) effect creation. This happens by means of a combination of doping strategies or confinement due to a minority carrier band-offset or both. The band offsets are created by the discontinuity in bandgaps between the lower-bandgap base and higher-bandgap buffer layer. There is no need for a separate buffer layer if the substrate bandgap and/or doping is higher than the base layer bandgap and/or doping. However, having an epitaxial buffer layer is advantageous anyway. The reason is that the buffer layer blocks the defects from the growth interface and improves material quality.
The emitter and base are the active layers of the TPV cell. This means that the radiation absorption and minority carrier generation is happening in these layers. In Figure 1.4, the emitter and base doping types are not mentioned by the source since both p-on-n and n-on-p configurations are very common. There is a window layer in the design that should have the same doping type as the emitter and the buffer layer that should have the same doping type as the base.

If the radiation spectrum is given and fixed, then the bandgaps of emitter and base are the main elements that determine the short-circuit current and open-circuit voltage of the TPV cell.

The window layer has a wide bandgap of about 0.7 to 1.0 eV to keep transparent for the desired wavelengths. It is advantageous to dope the window layer in order to reduce the emitter sheet resistance and solar cell series resistance, however excessive doping results in undesirable free-carrier absorption.

Figure 1.4. Device geometry for TPV cell model. This model is showing the various layers of the double heterostructure like window HW, emitter HE, base HB and buffer HBF layer as grown epitaxially on a substrate. Also, the metallurgical junction and quasi-neutral regions (HE' and HB') are shown that result from the space-charge region (SCR) of width W formed around the p-n junction [12].
1.6.1 MINORITY CARRIER RECOMBINATION AND LIMITS TO OPEN-CIRCUIT VOLTAGE

The minority carrier recombination rate $R$ in each layer of the device like emitter, base, space-charge region, and window is characterized by minority carrier lifetime $\tau_{\text{eff}}$ as below [12]:

$$ R = \frac{\Delta u}{\tau_{\text{eff}}} $$

$R$: minority carrier recombination rate

$\tau_{\text{eff}}$: minority carrier lifetime

$\Delta u$: excess minority carrier concentration

This formula is only valid when the low minority carrier injection conditions apply. For example, it is when the minority carrier concentration is smaller than the doping level.

The effective minority carrier lifetime is defined for a layer of thickness $d$ by considering radiative recombination ($\tau_{\text{rad}}$), Auger recombination ($\tau_{\text{Aug}}$), Shockley-Read-Hall (SRH) type defect-mediated recombination via midgap states ($\tau_{\text{SRH}}$), and surface recombination at both bounding interfaces of the layer as characterized by surface recombination velocities $S_1$ and $S_2$. The equation for the effective minority carrier lifetime is as below:

$$ \frac{1}{\tau_{\text{eff}}} = \frac{1}{M \cdot \tau_{\text{rad}}} + \frac{1}{\tau_{\text{Aug}}} + \frac{1}{\tau_{\text{SRH}}} + \frac{S_1}{d} + \frac{S_2}{d} $$

where $M$ is a photon-recycling factor. This factor accounts for the regeneration of minority carriers due to photon absorption of radiatively recombined minority carriers.

The factor $M$ ranges anywhere from 1 to $\sim 10$. This depends on the absorption properties of the layer, the optical properties of the interfaces and the thickness of the layer [18, 19, 22, 30]. For example, photon-recycling effects will be enhanced by scattering or reflective interfaces. In contrast, transmissive or optically-absorbing interfaces will foil photon recycling.

The radiative recombination rate formula is:
\[ R_{rad} = Bnp \]

B is the proportionality constant that is called the bimolecular recombination coefficient. The radiative lifetime \( \tau_{rad} \), for low-level injection is related to the doping concentration \( N \) by the formula:

\[ \frac{1}{\tau_{rad}} = BN \]

From literature search [18] a formula that is found for B is:

\[ B = 0.58 \times 10^{-12} \sqrt{\varepsilon} \left( \frac{1}{m_p + m_n} \right)^3 \left( 1 + \frac{1}{m_p} + \frac{1}{m_n} \right) \left( \frac{300}{T} \right)^{3/2} E_G^2 \]

Approximating this equation gives us [31]:

\[ B = 3 \times 10^{-13} \left( \frac{300K}{T} \right)^{3/2} \left( \frac{E_G}{1.5 \text{ eV}} \right)^2 \]

As Figure 1.5 displays some B values for various bandgaps semiconductors [12].

![Figure 1.5. Experimental and theoretical values of the radiative coefficient (bimolecular recombination coefficient) B for direct bandgap III-V compounds at T = 300 K [12, 32].](image)
The Auger recombination rate formula is:

$$R_{Auger} = C_n n^2 p + C_p p^2 n$$

which at high injection becomes:

$$R_{Auger} = C_n n^3 + C_p p^3 = C n^3 = C p^3$$

At low injection levels, an Auger lifetime is:

$$\frac{1}{\tau_{Auger}} = C N^2$$

Figure 1.6 shows some C values for various bandgap semiconductors.

Figure 1.6. Experimental and theoretical values of Auger coefficients C for direct bandgap III-V compounds at T = 300 K [12, 32].

The defect concentrations are essentially effective to change the lifetime by the Shockley-Read-Hall (SRH) process and surface recombination effects. These defects produce
midgap energy states that contribute to SRH recombination and increase it. Therefore, it is not feasible to derive useful correlations as a function of bandgap analogous to those shown in Figure 1.5 and Figure 1.6. In high quality, well-passivated TPV devices, the effective lifetime is mostly dominated by radiative and Auger recombination. SRH and surface recombination have negligible effect in this situation. A variety of studies have been done to understand minority carrier recombination properties in III-V compound alloys used for TPV cells, especially InGaAsSb. These are available in references [33-41].

To forecast and compare the performance of TPV materials, finding the optimum bandgap and understanding all the loss mechanisms are very useful to explore the limitations on dark current \( J_0 \) and open circuit voltage \( V_{OC} \) in detail.

As discussed before, the dark current is derived as [21]:

\[
J_0 = \frac{q(n^2 + 1)E_G^2}{4\pi^2\hbar^3 c^2} \exp \left( \frac{-E_G}{kT} \right) \exp \left( \frac{qV}{kT} \right)
\]

This equation displays the minimum dark current and specifies an absolute upper limit to TPV cell open-circuit voltage. This is derived for a cell that is placed on an optically absorbing substrate. If a TPV cell contains a perfect back reflector and using benefits of photon recycling, the term \( (n^2 + 1) \) should be replaced by 1. This is leading to more than ten times reduction in dark current. These two cases serve as a lower theoretical limit to \( J_0 \), and an upper limit to \( V_{OC} \), as a function of the TPV bandgap. So, the dark current is estimated more accurately by considering all the various recombination mechanisms in real devices. Below the calculation of the dark current as a sum of recombination over a cell thickness \( H \) is shown:

\[
J_0(V) = \int_0^H R(V) \, dx
\]

where

\[
R(V) = R_{rad} + R_{Auger} + R_{SRH} + R_{surfaces}
\]

The open-circuit voltage \( V_{oc} \) will be calculated by solving this equation:

\[
J_0(V_{oc}) = J_{sc}
\]
Using the charge neutrality condition and carrier densities relationships in a device with external applied voltage $V$ leads to:

$$n \times p = n_i^2 \exp \left( \frac{qV}{kT} \right)$$

So, expressions for the dark current for each recombination mechanism, under either high or low injection can be calculated.

Table 1.1 summarizes various dark current and open-circuit voltage limitations for different recombination mechanisms. These could be under high or low level injection. For more details and derivation of the formulas in Table 1 refer to reference [12]. The symbols are as defined in the context and $H$ is the thickness of the solar cell. The open-circuit voltage is limited by the recombination mechanisms that give the lowest value of $V_{oc}$.

*Table 1.1. Formulas indicating recombination limitations on open-circuit voltage and diode dark current [12].*
1.7 Survey of TPV Materials

There are different materials that have potential for TPV applications. This section will discuss these materials and their pros and cons.

1.7.1 Black Body Radiation

To understand how to select suitable semiconductor material for PV and TPV cells, the black body radiation concept is essential. Many common light sources like the sun or incandescent light bulbs can be modelled as a blackbody radiator. The definition of a blackbody emitter is an object that absorbs all the incident radiation on its surface and emits based on its temperature. Blackbody emitters will appear black because of the complete absorption of all the incident wavelengths if they don’t emit in the visible range. This is the reason that the blackbody emitter name is given to them. The blackbody sources that are interesting for photovoltaic applications emit light in the visible range, but the ones that are interesting for Thermophotovoltaic applications emit radiation in the IR and near-IR range of the spectrum. The following equation demonstrates the spectral irradiance from a blackbody. This is given by Planck’s radiation law [46]:

\[
F(\lambda) = \frac{2\pi he^2}{\lambda^5 \left( \exp \left( \frac{hc}{k\lambda T} \right) - 1 \right)}
\]

where:

\(\lambda\) is the wavelength of light;

\(T\) is the temperature of the blackbody (K);

\(F\) is the spectral irradiance in \(\text{Wm}^2\mu\text{m}^{-1}\); and

\(h, c\) and \(k\) are constants.

Taking care with the units is essential to getting the correct results. Using SI units are the most common way of solving this equation, so that \(c\) is in m/s, \(h\) is in joule.seconds, \(T\) is in Kelvin, \(k\) is in joule/Kelvin, and \(\lambda\) is in meters. These units lead to spectral irradiance units of \(\text{Wm}^3\). If the results are divided by \(10^6\) then will lead to the conventional units of spectral irradiance in \(\text{Wm}^2\mu\text{m}^{-1}\). The spectral irradiance \(F(\lambda)\) changes with wavelength.
The following formula shows the total power density of a blackbody. This is calculated by integrating the spectral irradiance over all wavelengths:

\[ H = \sigma T^4 \]

Here the notation \( \sigma \) is Stefan-Boltzmann constant and \( T \) is blackbody temperature in Kelvin.

The most important parameter of a blackbody radiator is its wavelength where the spectral irradiance is maximum. This wavelength is where that the emitted power is the most.

The spectral irradiance peak wavelength is calculated by differentiating the spectral irradiance and solving the derivative when it equals to 0. The resultant formula is named as Wien's Law and it is shown in the following equation [46]:

\[ \lambda_p(\mu m) = \frac{2898}{T} \]

Here \( \lambda_p \) is the peak wavelength and \( T \) is the blackbody temperature in Kelvin.

This equation indicates as the blackbody temperature changes, the spectral distribution and power of the emitted light will change. For example, a blackbody emitter like a human body or turned off light bulb at room temperature, will emit low power radiation with a peak at greater than 1 \( \mu m \) wavelength. This is out of the visual range of the human eye. But, a heated blackbody at 3000 K emits radiation with a peak in the red part of the spectrum. The reason is that the emitted light spectrum will shift to higher energies in the visible spectrum. By increasing the filament temperature to 6000 K, the radiation will be emitted at visible spectrum from red to violet wavelengths. This makes the light appear as a white color. Figure 1.7 demonstrates the blackbody spectral irradiance at three different temperatures as discussed. The blackbody at room temperature 300K has no emitted power in the visible and near infrared part of the spectrum as displayed in the plot. Large variation is observed in the emitted power and the range of emitted power wavelengths. The next page log graph displays these variations more clearly in the emitted blackbody spectrum as a function of temperature [46].
1.7.2 TPV Semiconductor Materials

PV and TPV cells are more efficient when the incident photons have the same energy as their semiconductor bandgaps. It is desirable to match the wavelength for maximum emissive power, \( \lambda_{\text{max}} \), to the bandgap energy, \( E_g \), of these PV and TPV cells. There is an equation that relates any bandgap to the emitter’s temperature as stated:

\[
E_g = \frac{\hbar c_0}{\lambda_{\text{max}}} = 4.28 \times 10^{-4} T \quad \text{eV}
\]

Generally emitters with temperature ranges from 900 to 1700°C are desirable due to the difficulty for getting higher temperatures and low spectrum intensity of lower temperatures.

So if the black body is operating at the maximum desirable temperature of 1700 K (1427 °C), then \( E_g = 0.73 \) eV in order for the maximum emissive power to occur at the photon energy \( E_g \). This 0.73 eV bandgap is typical used as the maximum possible bandgap for a material in TPV cells application and is close to that of GaSb.

---

*Figure 1.7. Spectral intensity of a black body emitted light on a log-log scale. The emission is very low at room temperature and centered around 10 \( \mu \text{m} \) [46].*
The most widely used PV cells are silicon ($E_g = 1.2 \text{ eV}$) and gallium arsenide ($E_g = 1.42 \text{ eV}$) which obviously do not meet the requirement of $E_g \leq 0.73 \text{ eV}$.

Looking at Figure 1.8, materials that match the radiation emitted by a 900-1427 °C black body are the low bandgap materials ($E_g \leq 0.73 \text{ eV}$) like Ge, GaSb, InGaAs/InP, the quaternary InGaAsSb/GaSb and InGaAsP/InP.

Figure 1.8. Semiconductor bandgaps versus lattice constant [47-48].

Figure 1.9 shows the black body spectrum for Ge, GaSb and InGaAsSb/GaSb, their bandgaps and corresponding peak energies. Germanium cells with the bandgap of 0.67 eV provide much better spectral response matched with lots of thermal sources compared to silicon TPV cells. Despite this fact, Ge is not a practical good TPV material. The reason is the electron effective mass of Ge is high, which leads to a high conduction band density of states and consequent high intrinsic carrier concentration density. This is why Ge diodes demonstrate high reverse-saturation current (dark current) and consequently low open circuit voltages compared to III-V compounds with a similar bandgap. Also, the Ge cell surface is very hard to passivate.
**InGaAsSb/GaSb**
- Wavelength of peak: 2.36909 μm
- Peak energy: 0.525 eV

**Ge**
- Wavelength of peak: 1.84201 μm
- Peak energy: 0.67 eV
The next candidate to use in TPV cells is GaSb which has a bandgap close to Ge. Unlike Ge cells, GaSb TPV cells performs much better with significantly lower dark current. GaSb TPV cells are typically fabricated using Zn diffusion into a GaSb wafer to build a p-n junction [42]. This method is also used to form p-n junctions in InGaSb, InAsSbP and InGaAsSb. The resulting profile creates a built-in electric field effect. This effect improves carrier collection and decreases the dark current [42]. The problem is a formation of a dead layer on the surface after diffusion which is heavily Zn-doped. This layer should be removed by post-diffusion anodic oxidation of the front surface. This method also should passivate the front surface to minimize the minority carrier surface recombination and form a dielectric film that acts as an encapsulating layer and antireflection coating. If the top dead layer has not been removed the device performance degrades dramatically due to the bandgap narrowing and increased minority carrier recombination by surface defects [58]. Another innovative way of making GaSb TPV cells which has remained unexplored up to date is using ion implantation to make GaSb diodes. This method has a lot of advantages over diffusion techniques like material design turnaround time is rapid, it is a low
temperature process that allows accurate control of the dopant profile with good reproducibility and no dead layer formation on the surface. This innovative technique will be discussed in detail in chapter 3.

The last method of making a TPV diode is using epitaxial growth to make the p-n junctions. This will be discussed in chapter 2.

The next material suitable for TPV application is quaternary InGaAsSb/GaSb. This material has the ability to be grown lattice-matched to the GaSb substrate at the bandgaps of interest. This diminishes all the defects associated with lattice mismatch growth. Furthermore, there is no need for a graded metamorphic buffer layer and there is better absorption of long wavelengths and efficient transport of photo generated electrons due to the long electron minority carrier diffusion length (29 μm) [40].

The next material candidate to make TPV cells is InGaAs grown lattice-mismatched on an InP substrate. This material is easier to grow than quaternary materials but because of the high lattice mismatch between the grown epitaxial layer and the substrate, it has a bad effect on long term reliability of TPV cells. Also, generally semiconductors with band gaps less than 0.6 eV suffer from compressive strain and defects in this particular InGaAs/InP material system. For TPV cells made of this ternary semiconductor material, processing a back surface field is essential.

The last candidate, which is InGaAsP/InP material, is not very favorable. The reason is this quaternary low bandgap material has a high dark saturation current due to high Auger recombination rate. Because of all the reasons above, GaSb and InGaAsSb grown lattice-matched on GaSb substrates have demonstrated the highest performance for TPV application.

Table 1.2 summarizes all the possible materials for TPV application with their corresponding advantages and disadvantages.
Table 1.2. Semiconductor materials for TPV application, advantages and disadvantages

<table>
<thead>
<tr>
<th>S.C.</th>
<th>Bandgap</th>
<th>Emitter Temp.</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>0.66 eV</td>
<td>1300ºC</td>
<td>Availability, Cheaper than GaSb and InP</td>
<td>High intrinsic carrier concentration and consequent low photo-voltages, poor performance due to the extremely high effective electron mass, Difficult surface passivation</td>
</tr>
<tr>
<td>GaSb</td>
<td>0.72 eV</td>
<td>1420ºC</td>
<td>Longer diffusion lengths, simpler device structure, inexpensive since no epitaxy is required, Auger recombination evidently does not severely limit the performance of GaSb - based TPV devices and high performance can be achieved in relatively simple device structures</td>
<td>Long band gap, higher temperature emitter needed &gt;1400ºC</td>
</tr>
<tr>
<td>InGaAs/InP</td>
<td>0.74 eV</td>
<td>900-1600ºC</td>
<td>Easier to grow (ternary versus quaternary), long-term infrastructure development for optoelectronic applications and its demonstrated mass-reproducibility</td>
<td>High lattice mismatch bad effect on long term performance of TPV cells, band gap less than 0.6 eV suffers from compressive strain and defects, back surface field is essential</td>
</tr>
<tr>
<td>InGaAsSb/GaSb</td>
<td>0.5 to 0.6 eV</td>
<td>900-1100ºC</td>
<td>Better absorption of long wavelengths, possibility of bandgap engineering, the ability to lattice match epitaxial layers to the substrate at the bandgaps of interest, avoid defect generation or the need for graded buffer layer, efficient transport of photo generated electrons in p-InGaAsSb (long electron minority carrier diffusion length (29 μm))</td>
<td>Phase segregation, expensive and not commercially viable, shallow n-type ohmic contacts have not yet been developed for Sb-based devices</td>
</tr>
<tr>
<td>InGaAsP/InP</td>
<td>0.3–0.55 eV</td>
<td>700-950ºC</td>
<td>Lower temperature emitter needed</td>
<td>High dark current due to high Auger recombination rate</td>
</tr>
</tbody>
</table>
1.8 Motivation for Investigating InGaAsSb/GaSb TPV Cells (MAST Project)

As discussed in the previous section, due to a bandgap of 0.726 eV, GaSb is an excellent candidate to use in multijunction solar cells as well as TPV cells. The GaSb lattice parameter is matched with various ternary and quaternary III-V compounds covering bandgaps from 0.3 eV to 1.58 eV. GaSb-based binary and ternary alloys are also very important for applications in laser diodes with low threshold currents and photodetectors with high quantum efficiencies. Furthermore, another low bandgap material is the quaternary InGaAsSb grown on GaSb. This has the advantage of being lattice matched to GaSb wafers, thus offering the possibility of a low concentration of crystalline defects with consequently good carrier lifetimes. Modules incorporating these TPV cells have demonstrated greater than 19% power conversion efficiency from a 950°C blackbody source [43-45]. So, this thesis is focused on improving GaSb and InGaAsSb/GaSb TPV cells using different approaches, for a project founded by the Army MAST program.

The MAST (Micro Autonomous System Technologies) project is defined to provide electricity for robot crawlers and flyers of less than 100 grams. An army on the go needs a lot of electricity to operate variety of devices like radios and computers and to power autonomous vehicles. To provide this power, batteries are not a very ideal power source. The reason is they are heavy, bulky and they can pack just limited energy into a given amount of material. Furthermore, because of their heavy weight and slow speed performance, they will slow the soldiers down during the mission. One of the most important research centers that has worked to improve energy sources and provide a lightweight source of portable power is MIT Lincoln Lab. They have done much research on this subject and this project is continuing their findings and developing the device they have explored to provide a lightweight portable energy source.

The device that MIT Lincoln Lab researchers built is a sandwich of TPV cells and a micro-burner. This is a square with a size of 2-cm × 2-cm and approximately 1 cm thick as shown in Figure 1.12. This device generally consists of a burner, filters, cooling system and TPV cells [43].
The burner is a catalytic combustor that has two pipes. These pipes are designed to lead the fuel (in this case butane) in and the waste product out. The inside of the burner is lined with alumina and coated with platinum nanoparticles. This burner ignites by passing oxygen and hydrogen through it. Then platinum’s role is to catalyze this reaction and heat the device [43]. On both side of the burner is a filter to reflect unwanted heat that doesn’t have the desired wavelength and permit only wavelengths of about 2 μm to emit on the TPV cells. This cell, which is responsible for producing electricity, is shielded by filters and vacuum, so its temperature is always kept at 60°C [43].

The reason to choose butane as a burner fuel is that butane provides an energy density of about 13,000 watt-hours per kilogram. Even a device that is using five percent of that energy would generate 650 W-hr/kg. This is even more than triple of the best battery energy density of 200 W-hr/kg. So, even considering 5% efficiency, then 300 ml of butane will provide enough energy for 50 hours talking time with a BlackBerry. This is ten times longer than the time that high-performance lithium-ion battery lasts [43].

This butane burner needs to be combined with a TPV cell that has a bandgap matched with the burner temperature. To do this, high efficiency TPV cells and filters are needed to convert infrared radiation at longer wavelengths to electricity. Lincoln Lab developed TPV cells that were made from the compound semiconductor gallium indium arsenide antimonide (GaInAsSb). This material could be grown in the right bandgap matched with burner temperature using Metal Organic Chemical Vapor Deposition (MOCVD). But. The problem was this is a very difficult material to work with. The reason is growing quaternary material has four elements involved and it’s hard to produce a uniform alloy. How efficient this device needs to be, to become competitive with existing micro-power technology efficiency needs future considerations!

The emitter radiations needs to be engineered carefully. This is because the TPV cell just uses higher than bandgap photons, and the rest will contribute in unwanted processes that lower the efficiency.
Figure 1.10. Illustration of the emission of a blackbody source at 1200 K. The shaded region corresponds to high-energy photons that can be converted into electricity [43].

Figure 1.11. Using photonic crystal to narrow the blackbody radiation and filter unwanted low energy photons [44].
Figure 1.10 demonstrates the blackbody radiation source at 1200 K. Here, the input heat is used to warm a thermal emitter and this radiates on a photovoltaic diode. The photons with energies larger than semiconductor bandgap will convert into electricity that is represented by the shaded region in the figure [43].

Figure 1.11 indicates the importance of utilizing a filter in the system to reflect low energy photons back to the thermal emitter in order to help maintain its temperature.

Figure 1.12 shows the general schematic of MIT TPV design. As mentioned briefly, this design consists of a MEMS microreactor with integrated 1D photonic crystal, four 0.54 eV InGaAsSb cells, and a maximum power point tracker. A silicon/silicon dioxide stack is deposited on the microreactor. This enhances above-bandgap thermal emission and suppresses below-bandgap emission. The maximum power point tracker is used to step up the voltage from InGaAsSb array to 3.6 volts. This also provides on-the-fly impedance matching between the cells and the load in order to ensure the cells are operating at their maximum power point [44].
The microreactor burns hydrocarbon gaseous fuels like butane and propane in oxygen and reaches approximately 950 °C. If the propane used in this design has high energy density of 12000 Wh/kg, then the efficiency of 2.2% translates to 264 Wh/kg usable specific energy that is approximately three times the energy density of typical lithium batteries, neglecting the generator weight [43].

The TPV cells are four GaInAsSb cells, were grown by metal-organic vapor phase epitaxy (MOCVD). With \( x = 0.15 \) and \( y = 0.12 \), the material has a bandgap of 0.54 eV.

This innovative device is ideal for autonomous systems. This is because of the light weight and long lifetime of these energy sources. Using these sources the flyers could fly longer and carry more power with less weight and crawlers could move faster and farther.

As mentioned before, the goal of this project is to improve the efficiency of these TPV cells. MIT Lincoln lab has achieved an efficiency of about 0.5% to 2.2% as reported [43]. They have used MOCVD to grow the GaInAsSb TPV cells. This method has the disadvantage of difficult composition control, which may be responsible for the TPV cells relatively low efficiency.

In this project, we have pursued fabrication and design methods that will allow us to scale GaSb-based diode technology to 10-mm x 10-mm area dimensions and improve their efficiencies at the same time. TPV yield is a serious issue for this size device. Typical focal plane array technology, which uses similar antimonide materials technology, is based on devices with length scales at least 100 times smaller. As a result, the functional TPV cells using epitaxial GaSb, epitaxial GaInAsSb, and implanted GaSb with areas up to 1 square cm is realized. These are the first devices of their kind since MIT-Lincoln Labs TPVs from nearly a decade ago that were fabricated using Metal-Organic Chemical Vapor Deposition (MOCVD).

Non-epitaxial TPV cells are realized using beryllium ion implantation into an n-type GaSb substrate. Also, the ion-implanted approach is intended to maximize shunt resistance compared to the epitaxial technique. Furthermore, an innovative rapid thermal annealing (RTA) process was developed to activate the Be dopant in the n-type GaSb substrate to form a \( pn \) junction.
For epitaxial cells, we have identified and eliminated killer shunt defects that were limiting the yield of TPVs on GaSb to less than 100-µm X 100-µm diode area.

To improve the fabricated TPV cells efficiency, in-depth characterization and analysis of ohmic contact technology to GaSb is done. So, we developed and characterized state-of-the-art ohmic contact process technology to minimize series resistance of the TPV cells.
CHAPTER 2

EPITAXIALLY GROWN TPV CELLS
Thermophotovoltaics (TPVs) are expected to have significant applications in efficiently converting thermal energy to electrical energy as explained in Chapter 1. The scenarios for such conversions include heat from engines, small nuclear sources and even portable fuel-based sources. The applications for such TPVs will be to enable access to power in situations where traditional sources to power do not exist. Furthermore, TPVs can also help to achieve higher efficiencies in the operation of equipment where the wasted heat is converted back to electrical energy.

Group-III antimonide semiconductors have been previously identified [35, 43, 44, 45] as the material with the preferred range of energy bandgaps for conversion of thermal black body radiation to power. The antimonide-based TPV cells can benefit from the introduction of technologies that have revolutionized solar cells and the use of novel growth technologies that allow for the realization of high quality, low bandgap crystals. In this chapter, we will discuss epitaxial approaches to make high quality TPV cells. We shall also describe some of the challenges in the realization of such devices and technologies developed to overcome them.

2.1. TECHNICAL DISCUSSION

2.1.1 FACILITY

The samples for this study are grown using either a Vacuum Generators V80 machine or a Veeco GEN 10 automated elemental source MBE reactor. The GEN 10 is the first reactor of its kind for III-V semiconductors and has demonstrated the ability grow with extreme growth stability and areal compositional uniformity.
2.1.2 CURRENT EPITAXIAL STRUCTURES

In our experiments, we have successfully grown bulk InGaAsSb by MBE for the 5-micron base layer of a TPV as shown in Figure 2.2. High-resolution x-ray diffraction (HRXRD) and photoluminescence (PL) measurements have clearly demonstrated that we have control of the target composition of $\text{In}_{0.18}\text{Ga}_{0.82}\text{As}_{0.16}\text{Sb}_{0.84}$ and energy bandgap of about 0.51-0.54 eV. Digital alloy technique would address the need to use even lower bandgap energies for which group V phase segregation is a common problem. The detail of this growth method is found elsewhere [50]. Figure 2.5 shows an example of a digital alloying technique with clear interfaces that are a hallmark of accurate compositional control grown in CHTM. Figure 2.3 shows symmetrical (004) omega-2theta x-ray diffraction (XRD) spectrum for the quaternary bulk alloy described above. The 0\textsuperscript{th} order peak of the GaInAsSb has a full-width at half maximum (FWHM) $\sim 39.6$ arcseconds, which is only 36\% larger than the FWHM value for the GaSb substrate peak. The narrow FWHM indicates good crystalline quality. The epi-to-substrate peak separation is -81.6 arcseconds, indicating near lattice match to the GaSb substrate.
**Figure 2.2** The baseline TPV structure that uses a 5-micron GaInAsSb bulk alloy in the p-type base layer.

![Diagram of TPV structure](image)

**Figure 2.3** XRD $\omega$-2$\theta$ (004) scan of Ga$_{0.18}$In$_{0.82}$As$_{0.16}$Sb$_{0.84}$ bulk alloy showing the FWHM of the 0$^{th}$ order peak (higher peak) to be ~1.36 times that of the substrate (lower peak). This result indicates good crystalline quality.

Figure 2.4 shows data for the photoluminescence of the alloy. The peak at 2450 nm corresponds to a bandgap of about 0.51 eV which is within the tolerance of the TPV design.
Figure 2.4. The photoluminescence intensity of the GaInAsSb bulk alloy that is used in the base layer of the TPV device. The peak wavelength of emission corresponds to a bandgap of 0.51 eV which is within the target bandgap range.

Figure 2.5. An example of a AlGaInAsSb digital alloy layer is shown in this TEM image, showing excellent interface control.

The strength of the PL signal from this quaternary layer was also substantial, indicating a good carrier lifetime that is not dominated by defect recombination. This PL measurement is an important qualitative measure of the material and serves as a way of screening the wafer growth before device processing.
2.2 CHARACTERIZATION METHODS

2.2.1 CRYOGENIC HALL APPARATUS FOR MEASURING FREE-CARRIER MOBILITY AND CONCENTRATION

The primary method of testing the doping concentration and mobility of the antimonide layers is the Hall Effect technique. Low-temperature Hall measurements are particularly advantageous. The old setup was unable to accommodate this type of measurement. Therefore, the sample board was modified with a new clip-based sample holder to ensure a limited thermal history of each sample. Indium dots were annealed to the surface of the Hall samples and measured using the Van der Pauw method. A short annealing time was performed so that only the top epitaxial layer was measured. Figure 2.6 shows a geometrical diagram of a Hall sample and the I-V curves for six arbitrary antimonide samples.

![Figure 2.6](image)

*Figure 2.6. Hall sample geometrical diagram & I-V curves of Indium Ohmic contacts on six different antimonide Hall samples showing ohmic behavior.*

The curves show a strong linear appearance and are considered Ohmic. The new sample holder was tested to ensure consistency with our previous measurements. A sample consisting of the structure SI-GaAs/p-GaSb with a thickness of 1000 nanometers was compared. The intended doping concentration of the sample was p-3e17 (cm⁻³). Table 2.1 shows the results of the Hall Effect measurements using the new sample holder and the old sample holder.
Table 2.1. Hall Effect measurements for SI-GaAs/p-GaSb 1000nm using new and old sample holder

<table>
<thead>
<tr>
<th>Sample Holder</th>
<th>Hall Carrier Concentration (cm(^{-3}))</th>
<th>Hall Mobility (\mu) (cm(^2)/V-s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>New Sample Holder</td>
<td>p-2.40e17</td>
<td>612.78</td>
</tr>
<tr>
<td>Old Sample Holder</td>
<td>p-2.205e17</td>
<td>615.15</td>
</tr>
</tbody>
</table>

The data from the new sample holder was very similar to the data obtained from the old sample holder. The percent errors in Hall carrier concentration and Hall mobility were 8.84% and 0.35% respectively. Therefore, the data from the new sample holder was deemed reliable and may be used during cryogenic Hall measurements. Many other comparison tests were conducted and similar results were found.

2.2.2 SECONDARY ION MASS SPECTROSCOPY (SIMS) ANALYSIS

SIMS analysis is used to compare the doping values with the Hall measurements. SIMS analysis is expected to show the total implemented doping and the Hall measurement is likely to measure the activated doping. So, it is expected to have a lower values for Hall measurements than SIMS analysis due to partial activation of doping. Therefore, the doping concentration of two Te doped GaSb samples and two Be doped GaSb samples were analyzed and compared using both Hall and SIMS measurement techniques. The SIMS analyses were done by Evans Analytical Group, East Windsor, NJ. The data show distinct differences between the Hall measurements and the SIMS measurements. The differences are most prominent for the GaSb:Te samples. One representative SIMS data for a GaSb:Te sample is shown in Figure 2.7. The results are consistent with our expectations, since we didn’t expect complete activation for the incorporated Te dopant. Figure 2.8 and Figure 2.9 show the carrier concentration versus inverse cell temperature for Te doped GaSb and for different sample runs R12-65 and R12-52 respectively. R12-65 is a stepped n(Th)-doped GaSb sample. The intended doping and thicknesses are as follows: 5e18 (170 nm)/3e18 (170 nm)/1e18 (220 nm)/5e17 (250 nm).
Figure 2.7. SIMS data for R12-65, a stepped n (Te)-doped GaSb. The intended doping surface first is as follows: 5e18 (170nm)/ 3e18 (170nm)/ 1e18 (220nm)/ 5e17 (250nm)/ unintentionally p-doped 5e16 (300nm) GaSb/ Interface between the top MBE layers and the bottom bulk GaSb material. This interface apparently contains both Te and Be, although Be was not used in the MBE machine during growth. The possible reasons for their existence is still unknown.

Figure 2.8. Te doped GaSb carrier concentration vs inverse cell temperature.
Figure 2.9. Te doped GaSb carrier concentration vs inverse cell temperature.

A 300 nm unintentionally p-doped GaSb layer with a doping concentration of 5e16 cm\(^{-3}\) is an interface between the top MBE layers and the bottom bulk GaSb material. R12-52 is also a graded (Te)-doped GaSb grown on SI-GaAs. The structure is 1e19 (250 nm)/ 5e18 (250 nm)/ 1e18 (250 nm)/ 5e17 (250 nm)/ smoothing layer of GaSb/ IMF/ SI-GaAs.

Figure 2.10 and Figure 2.11 show the carrier concentration vs inverse cell temperature for Be doped GaSb for different sample runs R12-63 and R12-64 respectively. Sample R12-63 is a stepped p(Be)-doped GaSb. The intended doping are as follows: 5e16, 1e17, 3e17 and 1e18 cm\(^{-3}\) with a total thickness of 1.3 \(\mu\)m. Sample R12-64 is also a graded p(Be)-doped GaSb on GaSb with the intended doping of 5e16, 1e17, 3e17, 1e18 and 2e18 cm\(^{-3}\) and the overall thickness of 1.3 \(\mu\)m. The GaSb:Be samples SIMS data are nonsensical when compared to Hall measurements. They show the Hall measured data are higher than the actual incorporated Be atoms. Part of this discrepancy is due to the 5e16 cm\(^{-3}\) residual hole concentrations in the undoped MBE GaSb caused primarily by grown-in point defects. But this doesn’t account for the entire difference. We suspect other causes including possible calibration errors in SIMS data collection. The standard deviation for the measured incorporation of Be atoms is large therefore we do not trust the SIMS data for Be incorporation.
2.3 DIFFICULTIES FOR EPITAXIAL GROWTH OF TPV STRUCTURES

While attempting to make large area MBE epitaxial p-n diodes for photovoltaic testing we found them to be mostly leaky or shorted due to the existence of variety of defects. We conducted investigations to study and identify the effect of these defects on the electrical behavior of the TPV.
diode. Typically the TPV size is expected to be 10-mm x 10-mm, and therefore it is necessary for the epitaxial p-n diodes to be defect-free over larger areas. So it is essential for us to determine the areal density and nature of the defects that cause leakage paths or shunt paths to form in parallel with the diodes.

2.3.1 **CORRELATION BETWEEN DEFECTS AND DIODE CHARACTERISTICS FOR GaSb pn DIODES**

In order to study the effect of defects on electrical properties of TPV diodes, an experiment is designed using epitaxially grown GaSb pn structures. These diodes were grown using V-80 MBE reactor consisting of a 300 nm p-doped GaSb layer and a 600 nm n-doped GaSb layer grown monolithically on an undoped GaSb substrate with a p-type background doping of ~ 1x10^{17}cm^{-3} and a crystal orientation of (100).

First, a 10-cm x 10-cm grown piece was metallized on both sides. A correspondent J-V curve was also measured. According to the results, no diode behavior was detected. Instead, a resistor J-V curve was observed. In order to find out if there was a doping issue or defect problem, a mask has been used with square-shaped contact pads as small as 100-µm x 100-µm. All the contact pads have been isolated by etching to the substrate and n-type metallized. These contact pads are defined using conventional UV lithography. Immediately after the lithography and prior to loading into the metal evaporator, the native oxide was removed by dipping the sample into a solution of HCL: H_2O (1:3) for 60s. The metals were deposited in an e-beam evaporation system at a base pressure of 2x10^{-7} mbar. The contacts on n-GaSb consist of: n-GaSb// Pd 87Å/Ge 560Å/ Au 233Å/ Pt 476Å/ Au 2000Å. The p-contacts are evaporated on the backside of the substrate and consist of p-GaSb// Ti 500Å/ Pt 500Å/ Au 3000Å. Finally the contacts were annealed by rapid thermal annealing (RTA) at 300°C for 45s in an N_2 ambient. In the next step J-V curves were measured for squares scattered periodically on ¼ of a 2 inch grown wafer. The schematic setup for J-V measurements and wafer mapping is shown in Figure 2.12.

To investigate the defects density and their relation with shorting the p-n diodes, Normarski pictures of fabricated squares were taken before the metallization. Every Normarski image of a specific square was compared to a correspondent J-V curve of the same square after metallization. As a result of these comparisons, we found 2 major types of defects named defect A and defect B.
shown in Figure 2.13. Defect A looks like a surface defect called “Orange Peel”. Defect B is more likely Ga spitting or substrate originated defects that will be explained later.

Figure 2.12. Schematic setup for measuring J-V curves and wafer mapping. The ovals shown on the Normarski micrograph for 100x100 micron diodes indicate location of extended defects.

Figure 2.13. (a) Defect A (b) Defect B (Ga Spitting defect or Substrate Originated defect)
Figure 2.14. (a) Good diode (b) Leaky diode (c) Very leaky diode ~ resistor.

The results were characterized as good, leaky and very leaky diodes as they are shown in Figure 2.14. It can be inferred that J-V characteristics are defect location dependent. Defect A doesn’t seem to affect pn diode behavior, but we have seen that the number of defect B correlates well with leaky J-V characteristics. Below are the plots that show the correlation between the number of defects and current at certain voltages (0.5 V, 1.5 V, and -3 V).

Figure 2.15. Number of defects versus forward current density at V= 0.5 V.

Ignoring the outliers, Figure 2.15 shows that the forward current has a significant positive correlation with the number of defects. In other words, increasing the defect numbers is responsible for more leakage and J-V curve transition from diode to resistor. As seen in Figure 2.16, it is
obvious the same positive correlation exists which indicates that as defect numbers increase, so does the current.

![Graph: Number of Defects versus Current at V= 1.5 volts]

**Figure 2.16. Number of defects versus forward current density at V= 1.5 V**

![Graph: Number of Defects versus Current at V= -3 volts]

**Figure 2.17. Number of defects versus reverse current density at V= -3V.**

The reverse current coresspondent to V= – 3 V is related to the leakage and shunt resistance. For a good diode it is very small, but as it increases it shows a leaky diode with reduced shunt
resistance. Figure 2.17 indicates that the defect number increases while the corresponding reverse current increases. The presence of defects degrades the electrical performance of the diode; the more defects, the higher the leakage current. For more than 8 defects per mesa the electrical device characteristic becomes purely resistive.

Because we encountered unexpected yields, we determined the potential cause to be one or more of the following:

1- Defects due to polishing
2- Bad boule quality (perhaps antimony clusters)
3- In situ oxide desorption before MBE growth

To investigate whether boule quality was acceptable or not, we replicated the same procedure with different wafers from different boules. The performed results showed improvement in quality indicating less defect density and better diode quality with smaller amount of leakage current for 100-µm x 100-µm diodes. The same plots generated for the new growth on different wafers are presented in Figure 2.18, Figure 2.19 and Figure 2.20, below.

![Figure 2.18. Number of defects versus current density at V= 0.5 V from quality boule.](image-url)
2.3.2 SHORTING DEFECTS

As explained before, the first processed large scale TPV devices grown at UNM were resistors instead of diodes. With decreasing the TPV cells’ sizes to 100-μm x 100-μm, the leaky diodes were resultant. The killer defects were responsible for unsuccessful diode fabrication called defect B. These defects observed on the GaSb diode structures can be broadly classified into faceted
defects that have geometric profiles and irregular defects that don’t exhibit any crystallographic orientation based on various used microscopy techniques. We named the first one as Ga spitting defect and the second one as substrate originating defect. Figure 2.21 shows Scanning Electron Microscopy (SEM) images, illustrating these two types of defects. The insets in Figure 2.21 show the appearance of the respective defects under optical Nomarski microscopy (phase contrast imaging). The defect in Figure 2.21 (a) is highly crystallographic with a rectangular profile. Also, there is a central circular core that is a prominent feature in the SEM images but is not visible in optical Nomarski microscopy, as it is less than a micron in diameter. In all the rectangular faceted defects identified and subsequently investigated with SEM, this circular core is present without exception. In comparison, the defect shown in Figure 2.21 (b) has a very different, irregular morphology, as shown by SEM. Plan-view EDS analysis of the core of such irregular defects shows the composition to be amorphous or poly-crystalline GaSb. We have, through cross-section FIB/TEM studies, traced the source of these defects to pre-growth surface contaminants including oxide from local failures in thermal desorption, stray particulates, and polishing remnants. This is determined by the presence of an oxide, silicate or carbonaceous composition at the substrate/epi interface of these irregular defects as one example is shown in Figure 2.22. In the GaSb based homoepitaxial diodes grown for this study, the dominant defects on the post epitaxial surface are the faceted rectangular defects shown in Figure 2.21 (a) that we named as Ga Spitting defect.

![Figure 2.21. SEM images of visible defects on the GaSb epitaxial surface, (a) highly-faceted defect. (b) Irregular defect. The insets show 50x magnification Nomarski micrographs.](image-url)
Figure 2.22. a) Nomarski image of the surface of epitaxial GaSb grown on a GaSb substrate, b) Cross-sectional, transmission electron microscopy of an embedded foreign object.

Figure 2.23. SEM images of faceted defects: (a) early stage of defect with large gallium core. (b) late stage rectangular faceted decoration around small gallium core. (c) EDS area scan in the area enclosed by the red line in (a) confirming a gallium core. (d) EDS area scan in the area enclosed in the red line in (b) confirming gallium antimonide.
Multiple examples of these defects have been observed with varying core sizes and depths. Figure 2.23 shows the defect at different stages of its formation, with Figure 2.23 (a) showing the early stage, and Figure 2.23 (b) showing the late stage, as confirmed in the following. An SEM investigation shows that the defect in Figure 2.23 (a) features a large central gallium droplet (confirmed by plan-view EDS), while there is a circular void in the center of the defect shown in Figure 2.23 (b), Figure 2.23 (c), (d) shows the results of the EDS area scan for Figure 2.23 (a), (b) respectively. A high-resolution crystallographic and compositional analysis of the defect shown in Figure 2.21 (a) and Figure 2.23 (b) is presented in Figure 2.24. The defect is identified with SEM and a lamella for cross-section study is prepared by FIB. The cross-section of the defect is studied using TEM and EDS.

The X-TEM image is shown in Figure 2.24 (a). The line EDS analysis across the lighter colored region at the core of the pyramidal shape (Figure 2.24 (b)) shows the presence of the gallium core within the GaSb epi-layer. This confirms that the defects shown in Figure 2.23 are indeed the same in different stages of formation.

Figure 2.24. XTEM and EDS analysis of the highly-faceted defect: (a) XTEM showing EDS line scan of gallium core. (b) EDS line scan confirming gallium core.
A mechanism for the formation of these rectangular defects is presented in Figure 2.25. The starting point for these defects is a gallium droplet ejected from the effusion cell as shown in the illustration in Figure 2.25 (a). As the epitaxial process proceeds, the gallium droplet acts as a metal mask and prevents growth in that area. The Ga droplet also partially dissolves the GaSb underneath. Similar phenomena were observed in M. DeJarld et al. [51] and C. Somaschini et al. [52] with Ga droplets grown on AlGaAs and GaAs, as well as in J. Lee et al. [53] and Cohen et al. [54] with In droplets grown on GaAs. The epitaxy proceeds around the defect as shown in Figure 2.25 (b). After sufficient growth around the droplet, the structure turns into a distinctly faceted pyramidal shape with the droplet at the center of the structure. At this point, the droplet feeds the epitaxy as a secondary source of gallium and this additional growth creates a characteristic decorative feature around the gallium droplet as shown in Figure 2.25 (c). The masking effect of the gallium droplet creates a vertical shaft, with sidewalls that are comprised of the \{110\} family of planes. The gallium from the droplet migrates up the \{110\} facets till it combines with the Sb at the surface to form the pyramidal shape. The pyramidal shape itself has specific facets with the high index facets on the inside of the pyramid and the low index facets on the outside. The gallium droplet is a group III source for the growth of the pyramidal defect. The defect growth ceases when the gallium droplet depth is beyond the surface diffusion length of the gallium ad-atoms. At this point the defect growth mechanism is shut off and a small gallium core remains at the original droplet’s location. It should be noted that there are significant striations or step-like patterns in the outer facet of the pyramid as can be seen in Figure 2.25 (b). This is due to the gallium droplet becoming smaller as it feeds the epitaxial growth and the diameter of the droplet-based mask keeps reducing and the central columnar void defined by the \{110\} planes reduces in diameter.
Figure 2.24 (a) shows that the platinum deposited on the sample during TEM lamella preparation using the FIB is able to migrate all the way down the shaft of the defect to the core. Thus if a $pn$ junction is fabricated from this material, and the gallium core is located below the $pn$ junction, the metal contact would bypass the $pn$ junction and lead to a leakage current. We hypothesize that the gallium droplet deposition occurs with a uniform temporal distribution throughout the growth process and only those defects that are grown prior to the $pn$ junction will short the diodes.

2.4 Solutions

2.4.1 Substrate Vendor and MBE Reactor Comparison

As it is shown by XEM images and EDS analysis, one of the shorting defects is generating from an impurity in the GaSb substrate. This impurity can be a particle remained in the substrate from polishing. So, the substrate quality is very important. Also, we understood that the quality of epitaxial layers grown by V80 is different from the quality of epitaxial layers grown by Gen 10. Therefore, we decided to perform a substrate vendor manufacturability study as well as MBE machines comparisons. In order to perform these comparisons, 2 µm of epitaxial GaSb layer was grown on GaSb substrates using two different MBE reactors. These wafers were bought from two different vendors available at the time, Wafertech and Galaxy.

Figure 2.26 demonstrates Nomarski images taken from these samples. It is inferred from Figure 2.26 that the Wafertech wafers generally show smoother surface after growth with less defects. Also, Gen 10 MBE machine is appeared to have a better growth quality.
Figure 2.26. Nomarski images of epitaxial GaSb grown on GaSb substrate bought from different vendors and using different MBE machines.

### 2.4.2 Use of Epitaxial Vendor’s Production MBE Machines

Due to the defects problem and yield improvement issues of CHTM grown TPV diodes, we decided to use another vendor MBE machines. Therefore, IntelliEpi Inc. of Richardson, TX were contracted to grow the TPV structure shown above. IntelliEpi was selected because of their vertical integration. They grow bulk GaSb, slice wafers from their own boules and polish them in-house. They then can grow on these wafers in their production MBE. It is believed that this process control will reduce the possibility of defective substrates (a problem encountered with Galaxy, Inc. and WaferTech, Inc.) that is frequently encountered in the GaSb industry. Also it is expected that the Ga spitting defects present in the UNM MBE research-grade machine will be eliminated in the IntelliEpi production reactor. They supposed to grow both GaSb binary and GaInAsSb quaternary
materials in their production MBE chambers. Figure 2.27 shows the diode structures that were grown. The first time, delivered antimonide samples from IntelliEpi were shown surface defects similar to the defects observed in samples from other vendors. The main differences were that the IntelliEpi wafers had a lower density of gallium spitting and oval defects as expected, but a high density of defects that have been identified coming from slurry remnants during the polishing process. These defects can be observed in Figure 2.28.

IntelliEpi was still trying to deliver usable TPV samples. The second time that these structure were grown and delivered, epitaxial layer quality inspection was performed. Investigation of the surface morphology by Nomarski microscopy showed similar defects as CHTM grown diodes again. However the defect density is significantly less this time, at an average of 300–400 defects per cm². 2-mm x 2-mm diodes were successfully realized in both the binary and quaternary designs grown by IntelliEpi. This material is now the baseline for the future work that will focus on scaling the
devices to 10-mm x 10-mm and to study high-yield epitaxial designs that are less sensitive to the epitaxial defects common to GaSb growth by MBE. Lastly, we are pursuing a completely non-epitaxial, ion-implanted TPV approach in GaSb that will be described in chapter 3.

2.4.3 NEW MASK DESIGNS

Due to the killer defects limiting large area diode yield in GaSb $pn$ junctions, new masks have been designed to cover a variety of different sizes.

**Small area diodes mask set designs:** These masks are made to process full 2-inch and 3-inch wafers including cells from 500 µm to 2000 µm. The existing solar cell mask has a minimum cell size of 2000 µm and the detector mask, which was used to process diodes, has different features from 20 µm to 400 µm. Therefore, the sizing scales between 400 µm to 2000 µm were missing and the new masks will fill this gap and most likely enable us to increase diode areas. Figure 2.29 shows the unit cell and mask layout for 2-inch wafers. As it can be seen, different sized cells have been placed in a 1-cm × 1-cm area and Transmission Line Model (TLM) patterns are located between rows to measure the specific contact resistance and sheet resistivity of each cell.

Figure 2.30 indicates the unit cell and mask layout for 3-inch wafers. The unit cell includes different rows with dimensions ranging from 500 µm to 2000 µm from right to left in an approximately 2-cm × 2-cm area with TLM patterns along different rows. Using these newly designed masks, we will improve diode area yields methodically and be able to find the critical device dimension that killer defects are shorting.
Process mask set design for large area diodes:

In order to process large area TPV cells, new mask sets were designed, ordered and received. These mask layouts contain 10-mm ×10-mm and 5-mm ×5-mm cells. Figure 2.31 shows a schematic top view of all the mask layers in one image. They consist of the metallization, mesa and Si$_3$N$_4$ etch masks. The mask set is intended for processing of up to 3-inch wafer.
2.5 CONCLUSIONS AND DISCUSSIONS

Surface defects on GaSb based diodes have been investigated. The source of these defects has been identified as gallium droplets, ejected from the Knudsen cell during the epitaxy. The gallium droplet is a second gallium source for epitaxial growth, and this leads to the formation of a highly faceted defect in the epitaxial layer. This process eventually leaves behind a small core of gallium at the center of the defect with a \{110\} enclosed void connecting the surface of the defect to the core. The presence of these defects shows a strong correlation to the leakage current in the GaSb diodes due to top contact metal migration into the void. The mechanism for the formation of the defects is presented along with cross-sectioned SEM, TEM, and EDS of the defects. The second defect formation that is substrate-originated is discussed in detail. The effect of these defects on the electrical characteristics of \textit{pn} diodes is investigated.

2.6 FUTURE WORK

A knowledge of the nature and origination points for the extended defects would allow us to design special epitaxial growth techniques to either eliminate or reduce the number of these extended defects. Possible candidates are

\textit{Figure 2.31. Mask design for 10×10 mm and 5×5 mm TPV cells.}
(i) A thin strting layer of AlSb grown at a lower temperture that could bury the defect and would stop its propagation into the subequent epitaxial layer

(ii) AlSb/GaSb or AlGaSb/GaSb superlattices over bulk-grown GaSb substrates, that would simultaneously bury extended defects, deflect substrate dislocations and act as a diffusion barrier for point defects coming out of the Czochralski (bulk) grown GaSb substrates.
CHAPTER 3

ION IMPLANTED GaSb TPV
**ION IMPLANTED GaSb TPV**

GaSb has found application in a variety of optoelectronic devices such as lasers [55, 56], detectors [57, 58] and photovoltaics [59, 60] in the mid-wave and long-wave infrared spectral range. In the case of a GaSb-based photovoltaic for which scaling of a *pn* junction area to values on the order of at least a square centimeter is critical, the simultaneous introduction of selective doping while minimizing defects can be challenging. Whereas selective doping is routinely realized using epitaxial and non-epitaxial techniques in GaAs and InP, the versatility of options for selective doping in GaSb is limited due to lower quality substrates, *n*-type dopant activation issues and processing limitations [61-64]. For instance, molecular beam epitaxy (MBE) for the growth of GaSb *pn* diodes faces the issue of shunt defect formation which can limit the diode area [65, 66]. In contrast, diffusion and ion-implantation, [67, 68] which enable selective doping without the need for epitaxy, do not have the shunt defect problem and are generally simpler and less expensive approaches to implement. Diffusion in GaSb is not straightforward on account of the Sb evaporating from the GaSb surface at the temperatures required for optimal introduction of the dopant [69]. This leaves ion implantation as a possibility for selective doping of GaSb.

The ion implantation of semiconductors is an effective method to achieve localized doping profiles. However, the use of ion implantation in III-V semiconductors and especially in GaSb introduces undesirable damage to the crystalline structure [70-72]. The damage in GaSb is difficult to eliminate on account of the low incongruent evaporation temperature of 370 °C and a low melting point of 710 °C which leads to significant wafer degradation through Sb loss at the temperatures needed for defect elimination. To date only a few reports on device-quality, ion-implanted GaSb have been published, and in these publications, there is a limited discussion of thermal activation methods, their effect on the device surface quality, and the resultant crystalline damage [73-77].

In this study, Be ion implantation is performed to define p-type regions in an *n*-type GaSb substrate with an *n*-doping of < 2×10$^{17}$ cm$^{-3}$. We perform simulations using TRIM software to determine dose and energy required for the intended doping concentrations and junction depths [78]. These simulations are critical to avoid the amorphization of the GaSb at the near-surface region due to the high energy and the dosage of the ion implantation [79, 80]. The electrical activation of the Be ions is accomplished using an RTA process with the intent of both activating the dopant as well as
removing the damage caused to the crystalline structure by the implantation. The low melting temperature of GaSb leads to issues with the annealing process since a significant loss of the more volatile lattice constituent, in this case antimony, occurs at the surface. This leads to concentrations of vacancies resulting in the aggregation of group III on the surface. A protective encapsulant is a typical solution to this issue and we have made use of a deposited Si$_3$N$_4$ capping film to protect the underlying GaSb surface. After the samples were annealed, the implant activation was measured by processing a basic diode structure using the ion-implanted GaSb samples followed by the electrical characterization of the resulting diodes. Defect formation on the GaSb surface after RTA due to the high temperature exposure is studied using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS). A study of GaSb implant induced damage recovery after RTA is performed using XTEM.

3.1 Simulations to Calculate Ion Implant Energy and Dose

For the implant species, the p-type dopant Be for n-GaSb substrates and n-type dopant Te for p-GaSb substrates were chosen to fabricate pn junctions. The reason for choosing Be is its small atomic size, which introduces less damage into the GaSb crystal structure during implantation. Simulations were performed to determine the required dose and energy for the designed doping and junction depth as shown in Figure 3.1 and Figure 3.2 using TRIM software [78]. Both the Be and Te implants were performed with a 7º tilt to avoid channeling.

**Be Implant**: The simulations were designed to have two sequential Be implantation processes performed on the same n-GaSb substrate. The first implantation is for the ohmic contact that is designed to have a high p-doping (1×10$^{19}$ cm$^{-3}$) at the surface for low resistance, unalloyed p-ohmic contacts. The ion dose and energy calculated for the ohmic contact implantation was 1×10$^{14}$ cm$^{-2}$ and 10 keV, respectively. The second implantation process is required for the emitter section, which is designed to be thicker than the first layer in order to realize the pn junction deeper into the sample. Considering these parameters, the simulated dose for the desired doping was calculated as 5.7×10$^{13}$ cm$^{-2}$ with an energy of 60 keV. The p-doping at the pn junction is expected to be about 2×10$^{18}$ cm$^{-3}$ at a depth of 200 nm. These simulations are demonstrated in Figure 3.1.

**Te implant**: for the ohmic contact section, the simulated dose and energy for the intended doping of $N_d = 3×10^{18}$ atoms/cm$^3$ are 1.5×10$^{13}$ ions/cm$^2$ and 100 keV, respectively. For the emitter section, a dose of 1.4×10$^{13}$ ions/cm$^2$ of Te at 180 keV should obtain a peak 5×10$^{17}$ cm$^{-3}$ electron
concentration at a depth of 56 nm assuming 50% activation. The shallow junction depth of 56 nm was limited by the maximum ion implantation energy for Te available from the vendor. The result of this simulation is shown in Figure 3.2.

Figure 3.1. Be Implant into n-GaSb simulations for pn diode formation a) Ohmic contact section with the intended doping of $N_a = 1 \times 10^{19}$ atoms/cm$^3$ and the calculated dose of $1 \times 10^{14}$ ions/cm$^2$. b) emitter section with the intended doping of $N_a = 2 \times 10^{18}$ atoms/cm$^3$ and the calculated dose of $5.7 \times 10^{13}$ ions/cm$^2$. 
Figure 3.2. Te Implant into p-GaSb Simulations for pn diode formation a) Ohmic contact section with the intended doping of \( N_d = 3 \times 10^{18} \) atoms/cm\(^3\) and the calculated dose of \( 1.5 \times 10^{13} \) ions/cm\(^2\). b) Emitter section with the intended doping of \( N_d = 1 \times 10^{18} \) atoms/cm\(^3\) and the calculated dose of \( 1.4 \times 10^{13} \) ions/cm\(^2\).

3.2 **RAPID THERMAL ANNEALING (RTA) PROCEDURE AND DAMAGE RECOVERY**

The implanted GaSb wafers were subjected to annealing, processing and subsequent analysis. Rapid thermal annealing was implemented in order to activate the implanted doping and remove the damage caused to the crystalline structure. The low melting temperature of GaSb at 712°C and the Sb out-diffusion temperature of 370°C can lead to issues with the annealing process since a
significant loss of the more volatile lattice constituent, in this case antimony, occurs at the surface. This leads to concentrations of vacancies resulting in the aggregation of group III on the surface. So RTA anneal requires precautions to be taken to ensure the safety of the material during the heating process. So, two different protection methods were tested. The first approach, called the “face-to-face method”, used two other GaSb wafers and sandwiched the implanted one between these two. The results for this method were not promising and near-surface melting happened even for temperatures as low as 550 °C. The second method used a Si$_3$N$_4$ protection layer on the implanted GaSb wafer to preserve the surface of the GaSb by blocking the out-diffusion of Sb. Si$_3$N$_4$ was deposited on the GaSb using Plasma Enhanced Chemical Vapor Deposition (PECVD). In contrast to the ‘face to face’ protection method which exhibited evident of melting, the Be implanted GaSb wafers annealed using a Si$_3$N$_4$ capping layer did not show melting or any other anomalous behavior. Prior published results indicate an optimal RTA process temperature range of 600 °C to 630 °C to activate the ion-implanted doping and simultaneous removal of crystal damage [81-83]. The optimal RTA duration for GaSb at these temperatures is typically between 5 to 30 s [81-83]. Several recipes for the rapid thermal annealing process were attempted. A final process temperature and duration was chosen to be 600 °C for 10 s. Several time and temperature recipes for the RTA were tried. Among these, the best results were found for annealing at 600 °C for 10 sec. The rapid thermal annealing temperature profile is presented in Table 3.1.

*Table 3.1. Rapid thermal annealing temperature sequence for recipe with a nominal peak temperature of 600 °C for 10 sec. Maximum set point temperature (606 °C) was chosen due to ~6 °C undershoot.*

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After annealing at 600 °C for 10 s, the annealed sample showed many defects on the surface as well as on the edges. Figure 3.3 shows an implanted sample after the RTA process with these defects on the surface and edges, identified as defects 1 and 2, respectively, on the photograph. SEM images and EDX scans were used to study the defect shapes and compositions to identify their formation mechanism. Figure 3.4 shows SEM images of these defects along with the EDX scans. As can be seen from the figure, both defects have a droplet in the center, which is high in Ga and low in Sb content. The reason for these defects is the high process temperature used, which is very close to GaSb’s melting point resulting in Sb out-diffusion and Ga agglomeration on the surface. It is postulated that the Sb out-diffusion is due to a porous Si₃N₄ capping layer.

An SEM image of the Si₃N₄ capping film was taken to investigate the film quality and the resulting micrograph is shown in Figure 3.5. The Si₃N₄ surface has a high density of pinholes with diameters about a few nanometers. It can be concluded that the Sb out-diffusion and the Ga clustering after annealing are due to the presence of these pinholes in the Si₃N₄ capping layer. Initially the Si₃N₄ film was chosen to be 850 Å thick as an arbitrary starting point.
Figure 3.4. a) SEM image and EDX scan of defect No. 1. The EDX scan demonstrates this defect is a Ga droplet b) SEM image and EDX scan of defect 2. EDX scan shows Ga clustered at the center with low Sb content. Both defects formed due to Sb out-diffusion and Ga clustering during the high temperature annealing process.
This led to pinhole formation, and as a result, degradation of the GaSb surface, making it unsuitable for use in devices. In order to prevent the formation of pinholes, a new recipe for Si$_3$N$_4$ deposition was created and a double-sided, front and back deposition of Si$_3$N$_4$ was also tested. In the new recipe the content of N$_2$ was increased to provide more nitrogen ions and thus facilitate a more stoichiometric Si$_3$N$_4$ formation. The increase in the nitrogen improved the capping layer quality but did not completely eliminate the pinholes. An additional step of increasing the thickness of the Si$_3$N$_4$ capping film by 3 times (~2600 Å) was added to further reduce pinholes.

Using this Si$_3$N$_4$ deposition process, we have determined that the surface morphology is acceptable unless the annealing temperature exceeds 650 °C or if the annealing time exceeds 60 s for temperature > 600 °C. Through an iterative process we have established that an annealing temperature of 600 °C for 10 s is optimal. Figures 3.3a and 3.3b show the surface comparison before and after the Si$_3$N$_4$ optimization.
3.3 **Microscopy Analysis of Crystalline Structure Damage Recovery**

There are different microscopy techniques that are used to compare the crystalline structure quality before and after the RTA process at 600°C for 10s.

### 3.3.1 Cross Sectional Transmission Microscopy (XTEM) and Fast Fourier Transform Imaging (FFT)

The process of ion implantation produces a large density of vacancies, dislocation loops, microtwins, and in the case of GaSb, amorphization of the material [80-85]. For implant doses below the amorphization threshold, rapid thermal annealing produces good recovery of the lattice, with backscattering yields similar to unimplanted material [80-85]. Figure 3.6 displays XTEM images before and after performing RTA. The crystalline structure improvement is seen from these low-resolution images by comparing the micrographs. The dark spots in the crystalline structure are attributed to damage caused by the ion implantation process.

Figure 3.7 shows the Fast Fourier Transform of the crystalline structure and verifies crystalline formation after rapid thermal annealing.

Figure 3.8 demonstrates an XTEM image of the Be-implanted GaSb surface and an EDS Scan of the layer that is formed on the surface of implanted GaSb. It is observed that a very thin, Ga-rich layer of about 20 nm forms on the implanted GaSb after RTA process. The reason is the tendency of Sb to outdiffuse at 600 °C even with using a Si₃N₄ capping layer as explained before. This thin layer doesn’t affect the diode performance due to the ohmic contact penetration through this thin layer.

The oxygen content in the layer close to the surface is due to SiO₂ deposition on the GaSb surface prior to taking the XTEM image. This oxide layer is used as a capping layer to protect the GaSb surface during Focused Ion Beam milling (FIB) that is used to make the XTEM sample.
Figure 3.6. XTEM image of Be implanted n-GaSb a) before annealing b) after annealing at 600 °C for 10 sec.

Figure 3.7. XTEM and FFT images of Be implanted GaSb after annealing to show crystallinity.
Figure 3.8. XTEM image and EDS scan of Be implanted n-GaSb wafer after annealing at 600°C for 10 s, showing a Ga-rich surface of 20 nm thick.
3.3.2 **ATOMIC FORCE MICROSCOPY (AFM)**

AFM images of the implanted surface are shown in Figure 3.9. These images are for the Be-implanted GaSb wafers before anneal and after anneal at 600 °C for 10 s.

It is obvious from the figure that the surface is much rougher before anneal in comparison to the same surface after anneal. The RMS for the GaSb surface before anneal is 14.93 nm and for the GaSb surface after anneal is 1.98 nm. This indicates the sample surface is much smoother and better surface quality is achieved after annealing at 600 ºC for 10 s.

It can be concluded that not only annealing made improvements to the crystalline structure deep into the material, but also the surface morphology was refined. This is very useful to fabricate high quality devices specially the ones that are thin and sensitive to surface defects.

![AFM images](image)

*Figure 3.9. AFM images of Be implanted n-GaSb wafer a) before anneal and b) after anneal at 600°C for 10 s, showing smoother surface morphology.*

3.3.3 **SECONDARY ION MASS SPECTROSCOPY (SIMS)**

Figure 3.10 displays Secondary Ion Mass Spectroscopy (SIMS) results for Be implanted n-GaSb substrate before and after annealing. Near the surface of the structure the Ga/Sb ratio is not the expected 1:1. This is due to SIMS measurement artifacts at the start of the analysis. The SIMS profiles of the implanted dopants after annealing doesn’t show significant migration of Be into the GaSb or towards the surface. This is unlike using other dopants like Mg and Si implant in GaSb where there is a large migration of these dopants deep into the GaSb substrate [69, 72].
Figure 3.10. SIMS atomic profiles for a) Ga and Sb contents and b) Be content of GaSb samples implanted with Be (doses of $5.7 \times 10^{13}$ & $1 \times 10^{14}$ ions/cm$^2$ and energies of 10 & 60 keV, respectively) before and after annealing at 600°C for 10s. Plot b indicates that there is no appreciable diffusion of Be during the RTA.

3.3.4 X-RAY DIFFRACTION SPECTROSCOPY (XRD)

X-ray diffraction spectra for the [004] plane have been measured and plotted on ion-implanted GaSb substrates. The objective is to investigate how implantation changes the crystalline structure of GaSb and how annealing heals the damage introduced to the crystalline structure after implantation. The implantation damage created in the host material can only be removed via subsequent annealing procedures as mentioned before. All the annealing procedures have been
performed at 600 ºC for 10 s for these sets of data. Figure 3.11 shows XRD spectra for Te-implanted GaSb before and after implantation compared to a GaSb substrate with no implantation. 

![XRD spectrum for [004] plane comparing GaSb substrate with T-implanted GaSb before and after annealing.](image)

**Table 3.2. Full width half maximum (FWHM) for the different peaks of Figure 3.11.**

<table>
<thead>
<tr>
<th>Material</th>
<th>FWHM (arcsecs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaSb Substrate</td>
<td>15.84</td>
</tr>
<tr>
<td>Te implanted GaSb</td>
<td>15.48</td>
</tr>
<tr>
<td>Te implanted GaSb after RTA process</td>
<td>16.20</td>
</tr>
</tbody>
</table>

No significant change has been observed, so further study is required to determine if XRD characterization is compatible with the shallow implantation depths of a Te implant. Figure 3.12 presents XRD spectra for Be-implanted GaSb before and after annealing compared with an un-implanted GaSb substrate. It can be seen that a new peak appears at smaller angles in the X-ray
diffraction (XRD) spectrum of the Be-implanted GaSb before annealing. A similar phenomenon was observed in GaN implanted with Mg and Be and ion-implanted GaAs cases as well [86]. This new peak is postulated to be an expansion of the GaSb zinc-blende lattice driven by the introduced impurities and displaced host atoms onto interstitial sites or by the incorporation of larger atoms on substitutional sites, and not a phase change in the GaSb. As observed in Figure 3.12, annealing Be-implanted GaSb at 600°C for 10s has repaired the lattice structure and not only eliminated the extra peak but also decreased the FWHM of the GaSb substrate peak from 28.44 arcsec to 16.92 arcsec, which is about the same as the un-implanted substrate.

![XRD spectrum for [004] plane comparing GaSb substrate with Be implanted GaSb before and after annealing.](image)

**Figure 3.12. XRD spectrum for [004] plane comparing GaSb substrate with Be implanted GaSb before and after annealing.**

**Table 3.3 full width half maximum for different peaks of Figure 3.12.**

<table>
<thead>
<tr>
<th>Material</th>
<th>FWHM (arcsecs)</th>
</tr>
</thead>
<tbody>
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<td>GaSb Substrate</td>
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</tr>
<tr>
<td>Be implanted GaSb</td>
<td>28.44</td>
</tr>
<tr>
<td>2nd peak: 79.56</td>
<td></td>
</tr>
<tr>
<td>Be implanted GaSb after RTA process</td>
<td>16.92</td>
</tr>
</tbody>
</table>
As was shown in the XRD analysis, the Te implant p-GaSb didn’t show promising results but to the contrary, Be implanted n-GaSb demonstrated significant damage recovery. So, we performed more detailed analysis on different RTA process temperatures to optimize the dopant activation and crystalline damage recovery. Selected annealing temperatures were varied from 580 °C, 600 °C, 625 °C, 650 °C and 680 °C. The anneal time was kept at the same value of 10 s for all the temperatures.

In the next page X-ray diffraction (XRD) spectra for the [004] plane is presented for these different annealing temperatures. The objective is to investigate how different annealing temperatures heal the damage introduced into the crystalline structure during implantation. The implantation damage created in the host material can only be removed via subsequent annealing procedures. Figure 3.13 shows XRD spectra for Be-implanted n-GaSb annealed for different temperatures in comparison with n-GaSb substrate before implantation and after implantation but no anneal.

It is seen that a new peak and wide broadening appears at smaller angles in the X-ray diffraction (XRD) spectrum of the Be-implanted n-GaSb before annealing. This new peak is postulated to be an expansion of the GaSb zinc-blende lattice driven by the introduced impurities and displaced host atoms onto interstitial sites or by the incorporation of larger atoms on substitutional sites, and not a phase change in the GaSb. As shown in Figure 3.13, annealing Be implanted n-GaSb at temperatures of 600°C and 625°C for 10s achieves the most repair for the lattice structure. This procedure not only eliminates the extra peak but also decreases the FWHM of the n-GaSb substrate peak from 28.44 arcsec in the un-annealed one to 13.68 and 15.48 arcsec in the annealed samples at 600°C and 625°C, respectively. In conclusion, we expect the best temperature for annealing to be somewhere between 600°C and 625°C. Also, XRD results follow the same trend as the electrical characteristics and samples annealed at 600°C and 625°C have shown the best recovery.
Figure 3.13. XRD spectrum for [004] plane comparing GaSb substrate with Be-implanted GaSb before and after annealing at different temperatures.

Table 3.4. Full width half maximum for Different peaks of Figure 3.13

<table>
<thead>
<tr>
<th>Material</th>
<th>FWHM (arcsecs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaSb Substrate</td>
<td>14.76</td>
</tr>
<tr>
<td>Be implanted GaSb</td>
<td>28.44</td>
</tr>
<tr>
<td>Be implanted GaSb after annealing at 580°C</td>
<td>18.36</td>
</tr>
<tr>
<td>Be implanted GaSb after annealing at 600°C</td>
<td>13.68</td>
</tr>
<tr>
<td>Be implanted GaSb after annealing at 625°C</td>
<td>15.48</td>
</tr>
<tr>
<td>Be implanted GaSb after annealing at 650°C</td>
<td>16.2</td>
</tr>
<tr>
<td>Be implanted GaSb after annealing at 680°C</td>
<td>16.92</td>
</tr>
</tbody>
</table>
3.4 **ELECTRICAL CHARACTERIZATION**

3.4.1 **CURRENT DENSITY – VOLTAGE (J-V) CURVE**

After annealing the samples the implant activation was measured by processing a basic GaSb diode structure. The result for Be doped n-type substrates is a 300 µm x 300 µm diode that showed an excellent current-voltage (J-V) characteristic. A turn-on voltage of 0.4 V was achieved, with a series resistance of about 1 Ω, and a very large shunt resistance of 25,000 Ω. The J-V curve is displayed in Figure 3.6. This is in significant contrast to the un-annealed J-V curves, which did not exhibit diode like properties.

The Te-doped p-type substrates exhibited typical resistor characteristics with R ~ 2 Ω. Therefore implant activation for Te cannot specifically be considered a success. This confirms the XRD results that a significant change of spectra before and after anneal weren’t observed. These results are shown in Figure 3.14.

![J-V Curve Graph](image)

*Figure 3.14. a) Beryllium implant into n-GaSb substrate. Diode I-V characteristics with \( V_{\text{turn on}} = 0.4 \) V, \( R_{\text{series}} \sim 1 \) Ω, \( R_{\text{shunt}} \) = very large. b) Tellurium implant into p-GaSb substrate. Resistor characteristics with \( R \sim 2 \) Ω.*

After encountering difficulty with shunt defects in diodes fabricated on epitaxial material, ion implantation of beryllium into n-GaSb substrate was one of the alternate paths we selected to make large area GaSb diodes. A key process step in this design approach is to optimize the anneal process needed to activate the beryllium (Be). At a constant anneal time of 10s, different annealing temperature were tried to find the optimum temperature needed to anneal the ion implantation damage out from the crystalline structure and facilitate its recovery. These annealing temperatures
ranged from 580ºC to 680ºC. In addition new masks were developed to study the change in diode characteristics and yield as function of diode area. These masks were made to process full 2-inch and 3-inch wafers including cells from 500 µm to 2000 µm.

Figure 3.15 shows the current density (J) – voltage (V) curves for diodes fabricated on wafers annealed at the different temperatures. As shown, the series resistance is increasing as the annealing temperature increases. Also, the absolute value of the breakdown voltage for n-GaSb annealed at 580ºC is much lower in comparison to the others. In general, from the J-V curves in Figure 3.16, it can be concluded that the lower annealing temperatures in the range create better electrical characteristics. 600ºC is optimal in terms of giving both a good breakdown voltage and an acceptable series resistance.

Figure 3.15. Current density (J (A/cm²)) versus voltage (V) for different annealing temperatures.

3.4.2 IDEALITY FACTOR AND DARK SATURATION CURRENT MEASUREMENTS

To perform more investigations regarding the electrical characteristics of Be-implanted n-GaSb and its variations with different annealing temperatures, ideality factors and reverse saturation currents were calculated from J-V curves taken in the dark. As displayed in Figure 3.16, the lowest dark saturation currents (I₀) and reasonable ideality factors (n) belong to Be-implanted n-GaSb annealed at 600ºC and 625ºC. These results are compatible with inferences made from Figure 3.15.
Figure 3.16. ideality factor versus voltage for Be implanted n-GaSb annealing at a) 580°C, b) 600°C, c) 625°C, d) 650°C and e) 680°C.

3.4.3 SERIES RESISTANCE AND SHUNT RESISTANCE AS A FUNCTION OF DIODE AREA FOR THE BE-IMPLANTED GaSb, EPITAXIAL GaSb, AND EPITAXIAL GaInAsSb DIODES

Series resistance in a photovoltaic cell has three common causes: 1) the movement of current through the emitter and base of the solar cell (spreading resistance), 2) the contact resistance of the metallization to the underlying semiconductor, and 3) the resistance of the top and rear metal
layers. The main impact of series resistance is to reduce the fill factor and efficiency of the PV, although excessively high values may also reduce the short-circuit current. A common way to estimate the series resistance of a PV cell is to find the slope of the IV curve at the open-circuit voltage point. In the case of this project, since the experiments were conducted under non-illuminated (dark) conditions, the linear part of the IV curve was used at relatively high forward voltage.

From all the causes that are listed above to contribute in increasing $R_s$, the contact resistance between the metal contact and the semiconductor has the most influence in a properly designed cell. The chances of this are considerably reduced by fabricating low resistance ohmic contacts. Hence, this is the reason for my work to develop state-of-the-art ohmic contacts on antimonide semiconductors used in GaSb-based TPVs that is explained in chapter 4.

As Figure 3.17 (a), (c) and (e) demonstrate, the series resistance decreases as the TPV cell size increases, which is what we expect. The major reason is that the ohmic contact resistance is decreasing with larger contact size. As the contact area increases, the metal-semiconductor interface increases, which reduces the resistance. It is noticed that the series resistance in the Be-implanted device is generally higher than the epitaxial GaSb and GaInAsSb devices. The origin of this is most likely that the doping-thickness product in the emitter of the Be-implanted GaSb is not quite high enough. Thus, in the implanted case, a spreading resistance through the emitter is observed. However, as anticipated, the benefit of the implanted approach is the improved (increased) shunt resistance, which can be observed in comparing the plots in Figure 3.17 (b), (d) and (f).

Shunt resistance, $R_{SH}$, which is typically due to growth defects in the GaSb epitaxy, can cause power losses in solar cells by providing an alternate current path for the light-generated current. Very low values of $R_{SH}$ will produce a significant reduction in the open-circuit voltage, $V_{oc}$. To estimate the shunt resistance for the epitaxial and implanted TPV cells, the slope of the IV curve at the short-circuit current point is used.

As Figure 3.17(d) and (f) show, the shunt resistance generally decreases as the TPV cell size increases for epitaxial InGaAsSb and implanted TPVs as expected. However, this trend does not occur in the epitaxial GaSb case. This leads us to believe that current flow in the contacts may be restricted to around the contact metallization in the dark conditions used for the measurement.
Figure 3.17. Shunt and series resistance variation with TPV diode area a) series resistance b) shunt resistance vs. area for the epitaxial GaSb TPV; c) series resistance and d) shunt resistance vs. area for epitaxial InGaAsSb TPV; and e) series resistance and f) shunt resistance vs. area for the implanted GaSb TPV.
3.4.4 LARGE AREA DIODES CHARACTERIZATION

After 2-mm x 2-mm diodes successfully were made, we tried to fabricate devices with up to 100 times greater area which are necessary for the MAST project described in Chapter 2. For this purpose a new mask with 5-mm x 5-mm and 10-mm x 10-mm area diodes was designed and ordered. The IntelliEpi-grown TPV wafers and Be-implanted GaSb wafer were processed using the new mask and the resultant 10-mm x 10-mm diodes were electrically characterized. Figure 3.18 demonstrates the finished TPV cells with antireflection coating and an IV curve under dark condition showing an excellent diode behavior.

![IV Curve](image)

**Figure 3.18.** a) Picture of processed large area TPV cells with anti-reflection coating b) Dark I-V plot for large area TPV cell.

Figure 3.19 demonstrates the quantum efficiency curves comparison for different UNM fabricated cells using epitaxial and non-epitaxial approaches and Figure 3.20 shows different correspondent JV curves under illumination. The current density axis is inverted to show the photogenerated current as a positive value since the cell is generating power. The quantum efficiency (Q.E.) is defined as the ratio of the number of collected carriers by TPV or solar cell to the number of incident photons of a given energy. The quantum efficiency plot is typically given as a function of energy or wavelength. If all the incident photons of a particular wavelength are absorbed and all the resultant minority carriers are collected, then the quantum efficiency at that wavelength is unity. The quantum efficiency for the photons with the energy of below the bandgap is zero because they are not capable of generating minority carriers. Different minority carrier recombination processes can lower the quantum efficiency like surface recombination due to the
presence of dangling bonds and different bulk recombination mechanisms like SRH and Auger. Figure 3.19 shows that as expected the Be implanted GaSb cell has a higher QE in comparison with the epitaxial GaSb cell. The reason is that Be implanted GaSb contains less defects than epitaxial GaSb that leads to less bulk recombination in the semiconductor and larger quantum efficiency. Also, it can be seen that depositing anti-reflection coating on the surface make a huge improvement in the quantum efficiency. This is mostly due to the surface passivation effect of ARC and prevention of surface recombination.

![Quantum Efficiency Comparison for Different UNM Fabricated TPV Cells](image)

*Figure 3.19. Quantum efficiencies comparison between different UNM fabricated cells with epitaxial and non-epitaxial approaches.*
Figure 3.20. J-V plot for different UNM fabricated TPV cells under illumination.

3.5 **FUTURE WORK**

It will be helpful to try different Be implant dose and energy to achieve an optimal doping concentration, decreasing series resistances and increasing shunt resistances. Also, implementing the Back Surface Field in the implanted GaSb will keep minority carriers away from high recombination rear contact and increase the efficiency.

To activate Te implantation in p-GaSb and damage removal, it will be useful to try the lower Te implant dose to avoid an extreme damage to the crystal structure.
CHAPTER 4

OHMIC CONTACT STUDY
For the photovoltaic and thermophotovoltaic devices, the particular issue with antimonide alloys is the creation of low resistance top contacts to n-type GaSb. In photovoltaic and thermophotovoltaic cells, an n-on-p semiconductor structural design is desirable due to the long minority carrier diffusion length in p-type semiconductors. The electron mobility in p-GaSb is approximately 3 times larger than for holes, making it a good choice for bottom cell designs [87]. In order to connect the active region of semiconductor devices such as solar cells or TPV cells to the external circuit, contacts with low electrical resistances (ohmic contacts) are required so that the loss of power outside of the absorption region is minimized and the net efficiency is maximized. So, all PV and TPV devices require ultra-low semiconductor–metal contact resistances (ohmic contacts) so that the loss of power to the outside of the absorption region is minimized and the net efficiency is maximized. These contacts should have optimized resistance, thermal stability, lateral uniformity and good adhesion to the semiconductor surface. Making a low resistance ohmic contact to n-GaSb is not trivial due to the complexity of growing a highly n-type GaSb material, difficulties in oxide removal and a relatively undeveloped process technology [88].

To date, ohmic contacts to n-GaSb are mainly Au-based [87-95] and Pd-based [96-99]. The first attempts at making ohmic contacts to n-GaSb were modeled on the same contact scheme used for n-GaAs [100]. This typically consists of a Ni/Ge/Au metallization sequence which has achieved a minimum contact resistance ($\rho_c$) of about 0.4 $\Omega$-cm [101-102]. However, the result is poor due to an unoptimized temperature window for annealing, a lack of a diffusion barrier in the metal sequence, partial oxide removal and poor vacuum conditions for metal evaporation. There is a report of Te/Au (60/340 nm) metallization that yields a specific contact resistance of $1\times10^{-6}$ $\Omega$-cm$^2$ when annealed at 380 °C for 1 h and then 450 °C for 2 s [95]. These contacts diffuse deeply into the semiconductor due to the lack of a diffusion barrier and are not suitable for thin layer multi-junction devices. Palladium-based contacts that do not include indium provide specific contact resistances as low as $4.9\times10^{-6}$ $\Omega$-cm$^2$ [96]. Palladium is known to disperse the native oxide on GaAs [103], and is likely to do the same on GaSb. Prior research involved combining Pd with Ge, S, or Te in an attempt to create a heavily-doped layer in the semiconductor just beneath the contact [96-100]. Fabricating Pd based-contacts is more difficult due to the high evaporation temperature of Pd over Ni. Recently In-based ohmic contacts to GaSb have been developed [104-
that have demonstrated the lowest specific contact resistance of $1.4 \times 10^{-6} \ \Omega \cdot \text{cm}^2$ using a Pd/Ge/Pd/In/Pd metallization on n-GaSb alloyed at 350 °C for 60 s [104]. Although, these contacts demonstrate a very good thermal stability, still they are based on a Pd interfacial layer to make low resistance ohmic contacts.

In this work we describe an approach to fabricating low resistance ohmic contacts to n-GaSb using two different metallization schemes. One metallization scheme is Nickel based and the second one is Molybdenum/Palladium based.

In the Ni based metallization, the choice of Ni as the semiconductor/metal interfacial layer is because of its ability to allow the formation of intermetallic compounds easily with III-V semiconductors and its good adhesion properties. Also, Ni reacts at a lower temperature than Pd and so it is likely that it would penetrate surface oxides more easily than Pd.

We selected Germanium as the second layer, as it will form a shallow diffusion through the Ni layer creating an n$^+$-GaSb top layer allowing for tunneling as the dominant current transport mechanism. The choice of Au as the next layer is due to the fact that using Ge and Au metallization together facilitates a solid phase reaction between the alloyed contacts and the semiconductor. The Pt layer on top of the Ni/Ge/Au serves as a diffusion barrier for the thick top Au layer. The upper most Gold layer acts as the final layer for bonding and probing.

In the case of Mo/Pd based metallization, all the layers are similar to the nickel based metallization except using Mo/Pd layer instead of Nickel. Molybdenum/Palladium (90/10 ratio) is used as a diffusion barrier in this metallization scheme. The reasons for selecting Mo as the diffusion barrier material are as follows. First, Mo is a refractory metal and has low atomic diffusion and then has good diffusion barrier properties. Second, compared with other refractory metals such as Pt, Ni, Cr, W, its work function is smaller [107-108]. This is important because for the metal with high work function, contact barrier height increases and it is disadvantageous to the formation of Ohmic contacts [109]. In addition, Mo is relatively cheap and easy to implement in industrial production and has potential commercial value.

The successful realization of this approach will allow us to fabricate ohmic contacts to n-GaSb with reduced processing complexity while maintaining very low resistance in the contact and semiconductor boundary. In this thesis, different doping concentrations and thicknesses of n-GaSb
have been investigated to understand the tunneling transport mechanism between the metal contacts and the semiconductor. To achieve low contact resistance, annealing is performed which causes interdiffusion between the metals and semiconductor. This provides contact stability and uniformity. Different contact metallization and process windows for annealing time and temperature have been studied to minimize ohmic contact resistances and to achieve optimal penetration depth of Au in GaSb for low resistances. The electrical properties of ohmic contacts are defined by specific transfer resistance and specific contact resistance. Specific contact resistances should be smaller than $10^{-4} \, \Omega$-$cm^{-2}$ to be considered as ohmic, but, values in the $10^{-6}$ to $10^{-7}$ range are preferable [110].

Furthermore, the fabrication, electrical characterization and microstructure analysis of the metal-semiconductor interfaces created during ohmic contact formation are discussed. The characterization techniques include four point probe measurement, Hall measurement, cross-sectional Transmission Electron Microscopy (XTEM) and Energy Dispersive Spectroscopy (EDS). Specific transfer resistances down to 0.1 $\Omega$-mm and specific contact resistances of $1 \times 10^{-6}$ $\Omega$-$cm^{-2}$ is observed for the Ni based metallization. For the Mo/Pd based metallization, the specific transfer resistances down to 0.39 $\Omega$-mm and specific contact resistances of $3 \times 10^{-6}$ $\Omega$-$cm^{-2}$ is obtained.

### 4.1 INTERFACIAL MISFIT DISLOCATION TECHNIQUE (IMF)

The samples for ohmic contact study were made by growing GaSb epitaxial layer on semi-insulating GaAs. Epitaxial GaSb grown on substantially cheaper GaAs substrates would not only reduce cost, but also provide high efficiencies by combining its wide infrared absorption spectral range with the high absorption in the visible spectrum from GaAs. Also, using a semi insulating substrate is assisting Hall measurement for the current confinement inside the epitaxial GaSb layer and not measuring the substrate parameters.

However, the lattice constant of GaSb is 7.8% larger than that of GaAs causing high dislocation densities at the interface. To overcome this lattice mismatch, techniques such as continuously-graded metamorphic buffers or thick strain-relaxing buffer layers of GaSb on GaAs substrates have been attempted. These techniques are successful at reducing threading dislocations. However, they give rise to other difficulties, such as poor thermal conductivity and high recombination in the
thick metamorphic layers. Metamorphic layers have very low carrier lifetimes and can be difficult to dope with n- or p-type dopants for appropriate carrier densities required in multijunction solar cells.

The 90° Interfacial Misfit Dislocation (IMF) technique is used to reduce the thick metamorphic layer to a single monolayer interface. Nearly all the strain associated with the GaSb-GaAs lattice mismatch is relaxed resulting in lower defect density which increases the lifetime of the device [111-114]. The IMF technique thereby offers a new method for multijunction GaSb/GaAs solar cells with reduced cost and potentially increased solar-to-electrical power conversion efficiency. However, the IMF layer must not be penetrated in the fabrication of the ohmic contacts; otherwise shunt paths will short the device.

4.2 OHMIC CONTACT CURRENT TRANSPORT MECHANISMS

Ohmic contacts work by the following mechanisms, as shown in Figure 4.1:

a) Tunneling through very narrow Schottky barriers,
b) High electric field thermionic emission through metallic and intermetallic sharp points created by non-uniform alloying processes, and
c) Successive reductions in effective barriers due to the formation of epitaxial or intermetallic compounds of intermediate bandgaps. Alloyed ohmic contacts to n-GaSb were found by other researchers to occur at narrow temperature ranges at around 300 C due to the production of epitaxial intermetallics at the interfaces [110].

Figure 4.1. Simplified energy band diagram of metal-semiconductor interface showing three different ohmic transport mechanisms.
4.3 EXPERIMENTAL PROCEDURE

Layers of n-GaSb:Te were epitaxially grown on semi-insulating GaAs substrates using molecular beam epitaxy (MBE) in an Oxford Instruments VG V80 reactor with a valved cracker cell for arsenic and a standard cracker cell for antimony. A 100-nm GaAs smoothing layer was grown on the SI-GaAs substrate after desorption of the native oxide. The GaAs was grown at substrate temperature of 580 ºC. An interfacial misfit dislocation array (IMF) was grown at the interface between GaAs and GaSb to mitigate the lattice mismatch problem. The IMF is a single monolayer of GaSb grown at ~600-610 ºC for less than one minute. The higher temperature allows the IMF array to nucleate. After recognizing the IMF 2x8 RHEED pattern, the substrate temperature is brought down to regular GaSb growth temperatures of 490-510 ºC. The n-doping source was tellurium, evaporated from a standard conical effusion cell, with Ga$_2$Te$_2$.

Te doping of the epilayers is determined by the base temperature of the GaTe effusion cell.

Table 4.1 shows the MBE grown layers tested for different GaTe (n-doping) cell temperatures during GaSb growth. Higher GaTe cell temperatures produced higher electron concentrations with successive lowering of Hall mobility, and this indicated that the residual 1e4 cm$^{-2}$ dislocation densities in the n-GaSb materials after IMF growth were not detrimental to either electron density or their transport. The doping and the thickness combinations of the samples were designed to achieve an approximate sheet resistivity of 100 Ω/□. Electron mobility measured by the Hall Effect increases as the doping concentration decreases, as expected. Hall measurements also show that the doping activation is slightly lower than intended. This is because the doping integrates into interstitial positions in the host semiconductor lattice structure rather than substitutions in Ga sites or Sb sites in the crystal. Moreover, since the Hall measurement was performed using n-GaSb grown on SI-GaAs, these structures provide accurate results due to current confinement in the n-GaSb material. This is due to the high resistance of semi-insulating GaAs which avoids current leakage through the substrate.
Table 4.1. Carrier density, Hall mobility and sheet resistivity of n-GaSb grown on IMF layer

<table>
<thead>
<tr>
<th>MBE Runs</th>
<th>Layer Structure: Te Cell Temperatures (plus GaSb-specific carrier concentrations) &amp; Thicknesses</th>
<th>GaTe cell temperature (°C)</th>
<th>Hall carrier conc. (cm$^3$)</th>
<th>Hall Mobility $\mu$ (cm$^2$/V-s)</th>
<th>Sheet Resistivity Without B-field (Ω/square)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R12-53</td>
<td>SI-GaAs/IMF/n-GaSb 1e19(Te:503C) 300nm</td>
<td>503</td>
<td>n-9.69e17</td>
<td>1203.84</td>
<td>179</td>
</tr>
<tr>
<td>Sample 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R12-54</td>
<td>SI-GaAs/IMF/n-GaSb 5e18(Te:484C) 500nm</td>
<td>484</td>
<td>n-6.95e17</td>
<td>1908.86</td>
<td>94</td>
</tr>
<tr>
<td>Sample 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R12-55</td>
<td>SI-GaAs/IMF/n-GaSb 1e18(Te:444C) 1000nm</td>
<td>444</td>
<td>n-2.16e17</td>
<td>3648.26</td>
<td>79</td>
</tr>
<tr>
<td>Sample 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R12-56</td>
<td>SI-GaAs/IMF/n-GaSb 5e17(Te:428C) 1000nm</td>
<td>428</td>
<td>n-9.25e16</td>
<td>4562.04</td>
<td>148</td>
</tr>
<tr>
<td>Sample 4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The transmission line method (TLM) was used to determine the contact resistivity. TLM patterns were defined using conventional UV lithography including edge bead removal, which is essential for high quality patterns. Reactive Ion Etching (RIE) has been used to etch the rectangular mesas to locate TLM patterns. The heights of the mesas were set to be more than 1 µm in order to penetrate the GaAs substrate and isolate the GaSb mesa completely on four sides. Surface preparation prior to evaporating metal contacts was found to be very critical for achieving low contact resistivity. Immediately after the lithography for metallization and prior to loading into the metal evaporator, native oxide was removed using HCL: H$_2$O (1:3) for 60s. Metals were deposited in an e-beam evaporation system at a starting pressure of 2x10$^{-7}$ Torr. Ge, Au and Pd have been evaporated thermally from a graphite boat, and Pt was evaporated from a tungsten boat.

For ohmic contacts, the following metallizations were chosen:
An acetone/N2 spray gun was used for the lift-off procedure after metal deposition. Next, a soak in acetone followed by ultrasonic treatment if needed was performed.

As the last step of processing, rapid thermal annealing (RTA) was applied with N2 as a cooling gas for different annealing times and temperatures. The annealing profile was found to be very critical. The as-deposited contacts are not always ohmic because the Fermi level is pinned in the bandgap [109]. Therefore, the annealing profile as showed in Figure 4.2 has been used. The annealing program details are shown in Table 4.2. For this experiment, annealing temperatures were changed from 260ºC to 320ºC with 20ºC increments. The annealing time was changed from 40s to 60s with 5s steps to assess the best specific contact resistance for each metallization and annealing temperature.

Table 4.2 Modified annealing program table for 300ºC temperature & 45s annealing time

<table>
<thead>
<tr>
<th>Step</th>
<th>Ramp Idle Hold Stop</th>
<th>Time (s)</th>
<th>Temp (deg C)</th>
<th>Gas 1 N2 (SLM)</th>
<th>Gas 2 Forming H2/N2 (SCCM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Idle</td>
<td>30</td>
<td>250</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Ramp</td>
<td>15</td>
<td>250</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Ramp</td>
<td>15</td>
<td>300</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>Hold</td>
<td>45</td>
<td>300</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>Ramp</td>
<td>10</td>
<td>250</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>Idle</td>
<td>240</td>
<td>250</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>Stop</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
The TLM metal pads have the dimension of 50 X 100 μm with an interspacing between contacts from 10, 20, 30 to 70 μm. Also, they have been processed on top of 110-μm wide mesas to ensure current confinement. Four point probe measurements were applied to obtain the contact resistances to exclude probe resistances. This method applies a current through two outer probes and measures the voltage across two inner probes. This technique is used to measure the resistances between two adjacent metal pads for the different gap spacings. The resistances were measured between the voltages of -0.1 V to 0.1 V and the current between -100 mA to 100 mA. The selected voltage and current ranges are within the desired working range of solar cell and thermal photovoltaic applications. The resistances are plotted as a function of the pads interspacing. Specific contact resistances were calculated using the formula:

$$\rho_c = R_{sh}L_T^2$$

Where $\rho_c$ is the specific contact resistance (Ω-cm$^2$), $R_{sh}$ is the sheet resistivity (Ω/□) and $L_T$ is the transfer length (μm). $L_T$ and $R_{sh}$ were computed by extrapolating the resistances versus interspacing plots as shown in Figure 4.3. Different measurements on different TLM patterns were made to prove consistency and reproducibility on each sample for each annealing temperature and time.

**Figure 4.2.** Actual annealing temperature profile taken from RTA for T=300 ºC & t=45s.

**Figure 4.3.** a) Resistance versus distance plot for $\rho_c$ & $\rho_t$ calculations b) TLM pattern.
4.4 RESULTS

Specific contact resistances and specific transfer resistances for samples R12-53 to R12-56 under different annealing temperatures were measured for various metallization schemes. These recipes should have shallow diffusion through Molybdenum/Palladium or Nickel.

4.4.1 N-GaSb// (Mo/Pd) 87Å /Ge 560Å /Au 233Å /Pt 476Å /Au 2000Å

The $\rho_c$ and $\rho_t$ values for GaSb// (Mo/Pd) 87Å /Ge 560Å /Au 233Å /Pt 476Å /Au 2000Å Au metallization are summarized in Table 4.3. Lower specific contact resistances are expected for R12-53 due to higher doping concentration based on Hall measurement. However, the measured data doesn’t follow this trend and R12-54 shows lower $\rho_c$ and a better ohmic property. Excluding R12-53, measured $\rho_c$ values for R12-54 to R12-56 follow the expected trend and decrease as the doping concentration increases. After analyzing measurements for different temperatures and times, the optimum value for GaSb// (Mo/Pd) 87Å /Ge 560Å /Au 233Å /Pt 476Å /Au 2000Å metallization is found to be 290ºC at 45s for R12-53 and R12-54. For R12-55 and R12-56 (with lower doping concentrations) the optimum values of temperature and time are 300ºC and 45s. Surface degradation was observed for annealing temperatures above 300ºC. The specific contact resistance as low as $3e-6 \Omega \cdot \text{cm}^2$ is reported for this metallization design and is considered excellent for ohmic contacts to n-type GaSb.

Table 4.3. Specific contact and transfer resistances for GaSb// (Mo/Pd) 87Å /Ge 560Å /Au 233Å /Pt 476Å /Au 2000Å metallization.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T=260^\circ$C</th>
<th>$T=280^\circ$C</th>
<th>$T=290^\circ$C</th>
<th>$T=300^\circ$C</th>
<th>$T=310^\circ$C</th>
<th>$T=320^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\rho_c$ ((\Omega \cdot \text{cm}^2))</td>
<td>$\rho_t$ ((\Omega \cdot \text{mm}))</td>
<td>$\rho_c$ ((\Omega \cdot \text{cm}^2))</td>
<td>$\rho_t$ ((\Omega \cdot \text{mm}))</td>
<td>$\rho_c$ ((\Omega \cdot \text{cm}^2))</td>
<td>$\rho_t$ ((\Omega \cdot \text{mm}))</td>
</tr>
<tr>
<td>R12-53</td>
<td>Not ohmic</td>
<td>9.8e-6</td>
<td>0.65</td>
<td>5.3e-6</td>
<td>0.59</td>
<td>1.31e-5</td>
</tr>
<tr>
<td>R12-54</td>
<td>Not ohmic</td>
<td>1.1e-4</td>
<td>1.3</td>
<td>3.1e-6</td>
<td>0.39</td>
<td>1.5e-5</td>
</tr>
<tr>
<td>R12-55</td>
<td>Not ohmic</td>
<td>Not ohmic</td>
<td>Not ohmic</td>
<td>2.4e-3</td>
<td>1.27</td>
<td>1.61e-4</td>
</tr>
<tr>
<td>R12-56</td>
<td>Not ohmic</td>
<td>Not ohmic</td>
<td>Not ohmic</td>
<td>5.7e-3</td>
<td>2.72</td>
<td>2.6e-3</td>
</tr>
</tbody>
</table>
Figure 4.4. Plot of measured resistances as a function of contact separation to calculate $\rho_c$ and $\rho_t$ for GaSb/(Mo/Pd) 87Å /Ge 560Å /Au 233Å /Pt 476Å /Au 2000Å metallization & 45s annealing time.

Figure 4.5. Plot of measured specific contact resistances as a function of temperature for GaSb/(Mo/Pd) 87Å /Ge 560Å /Au 233Å /Pt 476Å /Au 2000Å metallization and 45s annealing time.
The measured specific contact and transfer resistances values for GaSb//Ni 87Å/Ge 560Å/Au 233Å/Pt 476Å/Au 2000Å metallization are reported in Table 4.4. As in the case of the GaSb//Mo/Pd 87Å/Ge 560Å/Au 233Å/Pt 476Å/Au 2000Å contact described before, R12-53 here shows higher contact resistance in spite of being made on n-GaSb of the highest electron concentration among the four samples. But, for R12-54 to R12-56 specific contact resistances decrease as the doping concentration gets higher, as expected. This was attributed to the difficulty of removing residual oxides from the GaSb surface. In particular, an excellent $\rho_c$ value of 1.1e-6 $\Omega$-cm$^2$ is achieved. It is clear that GaSb//Ni 87Å/Ge 560Å/Au 233Å/Pt 476Å/Au 2000Å metallization exhibited better ohmic characteristic than the Mo-Pd based metallization. Minimal surface morphology change was observed with changing annealing temperatures. In Figure 4.7, the specific contact resistance is plotted versus annealing temperature for the different trials. The annealing temperature was found to be very sensitive in forming ohmic contacts. As Figure 4.7 shows, increasing or decreasing the anneal temperature from the optimal value of 290ºC by as little as 10 degrees changes the contact resistances by as much as a factor of 100.

**Table 4.4. Specific contact and transfer resistances for GaSb//Ni 87Å/Ge 560Å/Au 233Å/Pt 476Å/Au 2000Å metallization.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>T=260ºC</th>
<th>T=280ºC</th>
<th>T=290ºC</th>
<th>T=300ºC</th>
<th>T=310ºC</th>
<th>T=320ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\rho_c$ (Ω-cm$^2$)</td>
<td>$\rho_t$ (Ω-mm)</td>
<td>$\rho_c$ (Ω-cm$^2$)</td>
<td>$\rho_t$ (Ω-mm)</td>
<td>$\rho_c$ (Ω-cm$^2$)</td>
<td>$\rho_t$ (Ω-mm)</td>
</tr>
<tr>
<td>R12-53</td>
<td>Not ohmic</td>
<td>NA</td>
<td>4.1e-2</td>
<td>2.89</td>
<td>1.2e-6</td>
<td>0.176</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R12-54</td>
<td>Not ohmic</td>
<td>NA</td>
<td>2.7e-6</td>
<td>0.28</td>
<td>1.1e-6</td>
<td>0.121</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R12-55</td>
<td>Not ohmic</td>
<td>NA</td>
<td>3e-6</td>
<td>0.32</td>
<td>1.7e-6</td>
<td>0.182</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R12-56</td>
<td>Not ohmic</td>
<td>NA</td>
<td>Not ohmic</td>
<td>NA</td>
<td>1.12e-2</td>
<td>12.6</td>
</tr>
</tbody>
</table>

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Figure 4.6. Plot of measured resistances as a function of contact separation to calculate $\rho_c$ and $\rho_t$ for GaSb//Ni 87Å /Ge 560Å /Au 233Å /Pt 476Å /Au 2000Å metallization & 45s annealing time.

Figure 4.7. Plot of measured specific contact resistances as a function of temperature for GaSb//Ni 87Å /Ge 560Å /Au 233Å /Pt 476Å /Au 2000Å metallization & 45s annealing time.
4.4.3 GaSb//Ge 560Å/Au 233Å/(Mo/Pd) 87Å/Pt 476Å/Au 2000Å

The specific and transfer contact resistances are reported in Table 4.5. It is observed that sample R12-54 has the smallest $\rho_c$ for GaSb//Ge 560Å/Au 233Å/(Mo/Pd) 87Å/Pt 476Å/Au 2000Å metallization after annealing for 280ºC. Samples R12-54 to R12-55 have a similar trend of decreasing $\rho_c$ and $\rho_t$ as the annealing temperature increases. Sample R12-53 showed exceptionally higher $\rho_c$ and $\rho_t$ than R12-54. Figure 4.9 indicates measured specific contact resistance changes as a function of different temperatures. The worst surface morphology was found for this metallization due to surface degradation after annealing for 300ºC.

Table 4.5. Specific contact and transfer resistances for GaSb//Ge 560Å/Au 233Å/(Mo/Pd) 87Å/Pt 476Å/Au 2000Å metallization.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T=260ºC</th>
<th>T=280ºC</th>
<th>T=290ºC</th>
<th>T=300ºC</th>
<th>T=310ºC</th>
<th>T=320ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\rho_c$</td>
<td>$\rho_t$</td>
<td>$\rho_c$</td>
<td>$\rho_t$</td>
<td>$\rho_c$</td>
<td>$\rho_t$</td>
</tr>
<tr>
<td></td>
<td>(Ω-cm²)</td>
<td>(Ω-mm)</td>
<td>(Ω-cm²)</td>
<td>(Ω-mm)</td>
<td>(Ω-cm²)</td>
<td>(Ω-mm)</td>
</tr>
<tr>
<td>R12-53</td>
<td>Not ohmic</td>
<td>NA</td>
<td>1.07e-4</td>
<td>1.46</td>
<td>1.5e-4</td>
<td>1.83</td>
</tr>
<tr>
<td>R12-54</td>
<td>Not ohmic</td>
<td>NA</td>
<td>1.04e-4</td>
<td>1.02</td>
<td>1.4e-4</td>
<td>1.16</td>
</tr>
<tr>
<td>R12-55</td>
<td>Not ohmic</td>
<td>NA</td>
<td>3.4e-4</td>
<td>1.68</td>
<td>3.5e-4</td>
<td>1.71</td>
</tr>
<tr>
<td>R12-56</td>
<td>Not ohmic</td>
<td>NA</td>
<td>1.6e-3</td>
<td>5.27</td>
<td>2.4e-3</td>
<td>6.06</td>
</tr>
</tbody>
</table>
Figure 4.8. Plot of measured resistances as a function of contact separation to calculate $\rho_c$ and $\rho_t$ for GaSb/Ge 560Å /Au 233Å /(Mo/Pd) 87Å /Pt 476Å /Au 2000Å metallization & 45s annealing time.

Figure 4.9. Plot of measured specific contact resistances as a function of temperature for GaSb/Ge 560Å /Au 233Å /Pd 87Å /Pt 476Å /Au 2000Å metallization & 45s annealing time.
4.4.4 GaSb// Ge 560Å /Au 233Å /Ni 87Å /Pt 476Å /Au 2000Å

Table 4.6 shows the ρ_c and ρ_t values for GaSb// Ge 560Å /Au 233Å /Ni 87Å /Pt 476Å /Au 2000Å metallization. It is seen that similar trends exist here with R12-53 as an exception. The ohmic resistances for R12-54 to R12-56 decrease as the doping concentrations increase as expected. This is not a good metallization considering the lowest specific contact resistance was found to be only 5e-5 Ω-cm^2 leading to poor current transport. Also, the optimum temperature for annealing increased for GaSb// Ge 560Å /Au 233Å /Ni 87Å /Pt 476Å /Au 2000Å metallization to 300ºC for all samples. This metallization wasn’t too sensitive to the temperature change. For instance, the ρ_c values for R12-53 and R12-54 approximately didn’t change as the temperature increased from 290ºC to 300ºC in contrast to the two previous metallization schemes. Moreover, sample R12-56 is not considered ohmic since the specific contact resistances are too high. Surface morphology with high uniformity was observed similar to GaSb// Ni 87Å /Ge 560Å /Au 233Å /Pt 476Å /Au 2000Å metallization.

Table 4.6. Specific contact and transfer resistances for for GaSb// Ge 560Å /Au 233Å /Ni 87Å /Pt 476Å /Au 2000Å metallization.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T=260ºC</th>
<th>T=280ºC</th>
<th>T=290ºC</th>
<th>T=300ºC</th>
<th>T=310ºC</th>
<th>T=320ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ρ_c (Ω-cm^2)</td>
<td>ρ_t (Ω-mm)</td>
<td>ρ_c (Ω-cm^2)</td>
<td>ρ_t (Ω-mm)</td>
<td>ρ_c (Ω-cm^2)</td>
<td>ρ_t (Ω-mm)</td>
</tr>
<tr>
<td>R12-53</td>
<td>Not ohmic</td>
<td>NA</td>
<td>1.1e-4</td>
<td>1.82</td>
<td>1.05e-4</td>
<td>1.74</td>
</tr>
<tr>
<td>R12-54</td>
<td>Not ohmic</td>
<td>NA</td>
<td>5.08e-5</td>
<td>1.04</td>
<td>5e-5</td>
<td>1.06</td>
</tr>
<tr>
<td>R12-55</td>
<td>Not ohmic</td>
<td>NA</td>
<td>1.2e-3</td>
<td>3.14</td>
<td>1.7e-3</td>
<td>4.81</td>
</tr>
<tr>
<td>R12-56</td>
<td>Not ohmic</td>
<td>NA</td>
<td>Not ohmic</td>
<td>NA</td>
<td>8.7e-3</td>
<td>10.4</td>
</tr>
</tbody>
</table>
Figure 4.10. Plot of measured resistances as a function of contact separation to calculate $\rho_c$ and $\rho_t$ for GaSb/Ge 560Å /Au 233Å /Ni 87Å /Pt 476Å /Au 2000Å metallization & 45s annealing time.

Figure 4.11. Plot of measured specific contact resistances as a function of temperature for GaSb/Ge 560Å /Au 233Å /Ni 87Å /Pt 476Å /Au 2000Å metallization & 45s annealing time.
4.5 Microstructural Analysis of Low-Resistance Ohmic Contacts to n-GaSb

4.5.1 (Pd+Mo)-Based Contacts

In Figure 4.12, an XTEM image of the metal-semiconductor interface after annealing at 290°C for 45s is displayed. The metal/semiconductor interface is not so rough with shallow gold spikes penetration about 50 nm or less. Rarely, it’s seen that a large metallic spike runs into the GaSb, approximately 1 per 6 micron, as it’s estimated from several XTEM image analysis. Two EDS line scans were done, one in an area of no metal penetration and one in an area of shallow metal penetration less than 50 nm. Figure 4.13 demonstrates the elements in the various compositional regions formed after annealing for 290°C at 45 s. Analysis showed Pd/Mo metallization performed nicely as a diffusion barrier and caused to a minimal gold penetration.

Figure 4.12. XTEM image of GaSb//Mo (plus 10% Pd) 87Å /Ge 560Å /Au 233Å /Pt 476Å /Au 2000Å contact annealed at 290°C for 45 s with low magnification to show semiconductor metal interaction and different sized divots formation after annealing.
Figure 4.13. XTEM image and EDS line scans of GaSb//Mo (plus 10\% Pd) 87Å/Ge 560Å/Au 233Å/Pt 476Å/Au 2000Å contact annealed at 290°C for 45 s showing semiconductor metal intermixing at smooth interface.

Figure 4.14 displays widespread intermixing regions present under the Pd/Mo layer. This is mainly Au that has formed a Ga/Au compound in the deep region of the spike. The data shows that some Au remains in the original Ge/Au layer and some starts to diffuse through the metal layers into the semiconductor. The different EDS line scans show that the bright regions penetrating into GaSb are mainly Au. It can be concluded, that the larger metal–semiconductor inter-diffusion areas are the main reason for the lower specific contact resistivity of the contacts on n-GaSb. The microstructure analysis confirms and clarifies the electrical results: samples 1 and 2 annealed at 290 °C show the best interface structure and inter-diffusion behavior as derived from the contact resistances. Despite other’s work [91-96], the EDS analysis does not show significant Ge diffusion into GaSb directly below the Mo/Pd metallization layer. The reason may be the use of Secondary Ion Mass Spectrometry (SIMS) and Secondary Neutral Mass Spectrometry (SNMS) analysis methods in these studies which averages the content of materials over the specific region instead of doing an accurate spatial analysis.
4.5.2 Nickel-based Contacts

In Figure 4.15 (a) we show a schematic of the metal layers used for Ni metallization. Figure 4.15 (b) shows a cross-section transmission electron microscopy (X-TEM) image of a processed structure as-deposited.

Figure 4.16 shows an XTEM image with EDS line scans of the “as deposited” contact on GaSb. Ga rich GaSb formation close to the surface is possibly due to the Sb out-diffusion during MBE growth or high temperature processing steps. This Figure indicates that metal layers are generally
well defined with as-expected compositions and no visible metal penetration into the semiconductor. However, the existence of a Au-Ge intermixed layer is revealed using EDS analysis. It appears that room temperature or the energy of evaporated metals is sufficient to cause this inter-diffusion process or it is an artifact of the deposition process. The melting point of Ge is significantly lower than the other metals used so a float layer is a possibility. Also, there is a thin interfacial layer (4.9 nm) at the GaSb surface which contains Ga, Sb, and Ni. Some Ge appears to have migrated to the first Au/Pt interface. The Ge reported at the second Pt/Au interface appears to be erroneous and is due to Pt/Au/Ge peak overlaps.

Figure 4.16. XTEM image and EDS line scans of the as-deposited contact for GaSb// Ni 87Å /Ge 560Å /Au 233Å /Pt 476Å /Au 2000Å  metallization. The metal layers are well defined with as-expected compositions and no visible metal penetration into the semiconductor.

In Figure 4.17, an XTEM image of the metal-semiconductor interface after annealing at 290ºC for 45s is presented. The metal/semiconductor interface is much rougher and metallic spikes can be seen running into the GaSb. Two EDS line scans were done, one in an area of shallow metal penetration and one in an area of deep metal penetration. Figure 4.18 identifies the elements in the various compositional regions formed after annealing. Analysis shows widespread intermixing regions present under the Ni layer. This is mainly Au that has formed a Ga/Au compound in the deep region of the spike. The data shows that very little Au remains in the original Ge/Au layer and that Sb starts to out-diffuse through the metal layers. The different EDS line scans show that the bright regions penetrating into GaSb are mainly Au and the larger spike (Line Scan 2) shows more Au content than expected. It can be concluded that an increased presence of spikes, or larger
metal–semiconductor inter-diffusion areas, is the main mechanism for achieving lower specific contact resistivity of contacts on n-GaSb.

Furthermore, the microstructure analysis confirms and clarifies the electrical results: Samples 1 and 2 annealed at 290 °C show the rugged interface and localized spiking consistent with low ohmic contact resistance. Despite other’s work [96-99], the EDS analysis does not show significant Ge diffusion into GaSb directly below the Ni metallization layer. The reason may be the use of Secondary Ion Mass Spectrometry (SIMS) and Secondary Neutral Mass Spectrometry (SNMS) analysis methods in these studies which averages the content of materials over the specific region instead of doing an accurate spatial analysis.

![Figure 4.17. XTEM image and EDS line scans of the GaSb//Ni 87Å /Ge 560Å /Au 233Å /Pt 476Å /Au 2000Å contact annealed at 290°C for 45s. The rugged metal/semiconductor interface and localized metallic spikes are responsible for low resistance ohmic contacts.](image)

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4.6 DISCUSSION AND CONCLUSION

Alloyed ohmic contacts on n-GaSb were studied within small (10 °C) incremental temperatures around 300 °C, a temperature reported to be optimal by others’ work [96-99]. Our work shows that in all cases, the temperature windows for making ohmic contacts were very narrow, of ~10 °C. But, unlike others’ work [96-99], a temperature of 290 °C and not 300 °C, produced the lowest resistance ohmic contacts on n-GaSb. The metals Ni and Pd are traditionally chosen as parts of alloyed n-ohmic contacts because of their abilities to make intermetallic compounds easily with III-V compound semiconductors. Prior work by others [96-99] identified Pd to be preferable over Ni even though intermetallics form at lower temperature for Ni than for Pd. This work shows that it is Ni, and not Pd, that produces lower resistance alloyed ohmics to form on n-GaSb more easily. It should be pointed out, however, that metals that react easily also tend to migrate easily both inwards (lattice diffusion into the crystal) and laterally (grain boundary diffusion into the interconnect and pad metallizations connected to the alloyed region). Therefore, how Ni would stand up against Pd in long-term thermal stability is not presently known.

We found that GaSb// (Mo/Pd) 87Å /Ge 560Å /Au 233Å /Pt 476Å /Au 2000Å and GaSb// Ni 87Å /Ge 560Å /Au 233Å /Pt 476Å /Au 2000Å metallization schemes lead to a remarkable improvement in the ohmic contact resistance in comparison with GaSb// Ge 560Å /Au 233Å /(Mo/Pd) 87Å /Pt 476Å /Au 2000Å and GaSb// Ge 560Å /Au 233Å /Ni 87Å /Pt 476Å /Au 2000Å metallization

Figure 4.18. XTEM image of the GaSb// Ni 87Å /Ge 560Å /Au 233Å /Pt 476Å /Au 2000Å contact annealed at 290°C for 45s.
For a fair number of cases, ohmic contacts were found to be relatively higher than expected and these are attributed to the difficulty of removing residual oxides from GaSb surfaces. Therefore, the two latter metallization schemes require further experimentation in order to eliminate any possibility of surface oxides hindering the formation of high quality ohmic contacts.

The lowest recorded specific contact resistances for ohmic contacts were $3.1 \times 10^{-6} \ \Omega \cdot \text{cm}^2$ for GaSb/(Mo/Pd) and $1.1 \times 10^{-6} \ \Omega \cdot \text{cm}^2$ for GaSb/Ni, both significant improvements over $\sim 5 \times 10^{-6} \ \Omega \cdot \text{cm}^2$ reported elsewhere [96-99]. These two results are new, and the lowest reported to date, in the technology of ohmic contacts to n-GaSb.

For R12-54 to R12-55 the value of $\rho_c$ decreased as the carrier concentration increased as should be expected for tunneling and for Schottky barrier lowering due to image forces. However the lowest $\rho_c$ value was expected for R12-53 due to its highest doping concentration, which we didn’t observe. While the reason for this discrepancy is unclear, the higher ohmic resistance behavior was found to be the same for all four metallization schemes. Therefore, this is not attributed to systematic or chance-based coincidences of bad experimental results due to residual surface oxides on GaSb. The causes for this unexpected result require further attention.

It can be concluded from XTEM images that our state-of-the-art ohmic contacts are made by larger metal-semiconductor interfaces formed by gold spikes penetrating into GaSb, despite conclusions by others that emphasized the importance of electron tunneling due to an n$^+$-GaSb layer formed by Germanium diffusion into GaSb. Au spikes into the semiconductor increases the metal-semiconductor interface and facilitates tunneling-based current transport. It is also possible that the reaction of Au with Ga, makes open sites in the GaSb crystalline structure close to the surface which can be filled by Ge doping migration to these free sites. This phenomenon makes an n$^+$ layer close to the semiconductor metal interface and improves tunneling as a current transport mechanism resulting in low resistance ohmic contacts.

Although, for the case of Mo/Pd metallization, it is found to be shallow with minimal spiking, this makes it suitable to use in thin semiconductor devices. Also, XTEM images show that large spikes are very rare, approximately 1 per every 6 microns and small gold spikes about 50 nm long or less formed in faceted shapes, which increases the metal/semiconductor interface.
4.7 FUTURE WORK

The thermal stability of Ni-based contacts in comparison with Pd-based contacts needs further studies and experiments.

The inconsistency in some results requires further attention like the unexpected higher $\rho_c$ value for sample R12-53.

This work is presented changing different metallization layers but not the thickness of each metallization layer. Another study with examining different thicknesses mostly for diffusion barrier layer will be informative and useful.
### APPENDIX

<table>
<thead>
<tr>
<th>Step</th>
<th>Process for GaSb-based TPV Device</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Wafer Clean Prep: Solvent Clean/DI Water rinse</td>
</tr>
<tr>
<td>2</td>
<td>Soak wafer in the following solvent for a few minutes each: Acetone/ Methanol/ IPA</td>
</tr>
<tr>
<td>3</td>
<td>Rinse with DI water for several seconds and N₂ dry.</td>
</tr>
<tr>
<td>4</td>
<td>Remove native oxide: 1 HCL: 3 H₂O for 30 sec. (Don’t Use Pre-mix bottle)</td>
</tr>
<tr>
<td>5</td>
<td>Top n-contact Photolith Patterning (n-metal evap): Mask#1</td>
</tr>
<tr>
<td>6</td>
<td>Dehydration Bake: 150 ºC / 10 min.</td>
</tr>
<tr>
<td>7</td>
<td>Spin HMDS: 4000 rpm / 30 sec.</td>
</tr>
<tr>
<td>8</td>
<td>Bake 150 ºC / 3 min.</td>
</tr>
<tr>
<td>9</td>
<td>Spin AZ-5214E_IR. Spin 4000 rpm / 30 sec.</td>
</tr>
<tr>
<td>10</td>
<td>Soft Bake 90 ºC / 2 min.</td>
</tr>
<tr>
<td>11</td>
<td>Pattern Expose SC mask#1: for 2 sec (wavelength = 405 nm / right aligner, Power 275mW) Note: Align SC contact pattern to the wafer major flat/sample edge</td>
</tr>
<tr>
<td>12</td>
<td>Post Expose Bake: 112 ºC / 60sec.</td>
</tr>
<tr>
<td>13</td>
<td>Flood Exposure: 30 sec (wavelength = 405 nm / right aligner)</td>
</tr>
<tr>
<td>14</td>
<td>Developer 1:4 AZ400K:DI Water (60 ml AZ400k: 240 ml DI Water).</td>
</tr>
<tr>
<td>15</td>
<td>Develop time: ~ 20 sec. Take wafer out of Developer as soon as resist has cleared.</td>
</tr>
<tr>
<td>16</td>
<td>Rinse in DI water for several sec and then N₂ dry.</td>
</tr>
<tr>
<td>17</td>
<td>Inspect to ensure complete pattern definition</td>
</tr>
<tr>
<td>18</td>
<td>O₂ Plasma Descum: O₂ pressure: RF Power: Time:</td>
</tr>
</tbody>
</table>

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<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td><strong>20</strong></td>
<td>Conditioning run:</td>
<td>100 mTorr</td>
<td>50 Watts</td>
</tr>
<tr>
<td><strong>21</strong></td>
<td>Actual run:</td>
<td>100 mTorr</td>
<td>50 Watts</td>
</tr>
<tr>
<td><strong>22</strong></td>
<td>Measure photoresist height / O₂ descum</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>23</strong></td>
<td>Remove Native Oxide before Evap.</td>
<td></td>
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<tr>
<td><strong>24</strong></td>
<td>Dip in 1 HCL: 3 DI Water for 30 sec</td>
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<tr>
<td><strong>25</strong></td>
<td>Load immediately into the metal evaporation chamber.</td>
<td></td>
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</tr>
<tr>
<td><strong>26</strong></td>
<td>Metal Evaporation: front Side (n-doped) Ohmic contact</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>27</strong></td>
<td>Pump down to 1x10⁻⁶ torr and Deposit at 1-2 Å/sec</td>
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</tr>
<tr>
<td><strong>28</strong></td>
<td>Deposit:</td>
<td></td>
<td></td>
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<tr>
<td><strong>29</strong></td>
<td>Pd (87 Å)/ Ge (560 Å)/ Au (233 Å)/ Pt (476)/ Au (2000)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>30</strong></td>
<td>or Ni (87 Å)/ Ge (560 Å)/ Au (233 Å)/ Pt (476)/ Au (2000)</td>
<td></td>
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</tr>
<tr>
<td><strong>31</strong></td>
<td>Top Side n-Ohmic Metal Lift-Off:</td>
<td></td>
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</tr>
<tr>
<td><strong>32</strong></td>
<td>Use acetone spray gun / Soak in acetone</td>
<td></td>
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</tr>
<tr>
<td><strong>33</strong></td>
<td>Rinse with methanol and IPA/ N₂ blow dry</td>
<td></td>
<td></td>
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<tr>
<td><strong>34</strong></td>
<td>Metal Evaporation: Back Side (p-doped) Ohmic contact</td>
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<tr>
<td><strong>35</strong></td>
<td>Deposit:</td>
<td></td>
<td></td>
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<tr>
<td><strong>36</strong></td>
<td>Ti (500 Å) / Pt (500 Å) / Au (3000 Å)</td>
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</tr>
<tr>
<td><strong>37</strong></td>
<td>Lift off/ wafer annealing 290 °C for 45 S</td>
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<tr>
<td><strong>38</strong></td>
<td>Isolation Mesa Photolith Patterning : Mask#3 mesa</td>
<td></td>
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</tr>
<tr>
<td><strong>39</strong></td>
<td>Litho/ O₂ descum</td>
<td></td>
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<tr>
<td>Step</td>
<td>Description</td>
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<tr>
<td>40</td>
<td>Batch Process: &quot;Zia_InP&quot; (calculate the target etch depth based on the epi structure and calculated the ICP etch time) ~ 0.3μm/min</td>
<td></td>
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</tr>
<tr>
<td>41</td>
<td>Chlorine removal</td>
<td></td>
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<tr>
<td>42</td>
<td>Soak wafer in DI water for minutes to remove Chlorine residue from ICP etch.</td>
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<tr>
<td>43</td>
<td>N₂ blow dry.</td>
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<tr>
<td>44</td>
<td>O₂ Plasma Photoresist removal</td>
<td></td>
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<tr>
<td>45</td>
<td>Acetone spray using spray gun to remove any photoresist left behind.</td>
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<tr>
<td>46</td>
<td>Si₃N₄ ARC/passivation layer deposition (~1000 Å)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>PECVD Si₃N₄ deposition</td>
<td></td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>Gas Follow Rates: NH₃=50 sccm, SiH₄-Ar=30 sccm, N₂= 15 sccm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>49</td>
<td>Substrate Temp : 300°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>Deposit Time: ~7 min</td>
<td></td>
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<tr>
<td>51</td>
<td>Film color after deposition:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>Si₃N₄ VIA (Prob Pads Opening): Mask#2</td>
<td></td>
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</tr>
<tr>
<td>53</td>
<td>litho</td>
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<tr>
<td>54</td>
<td>O₂ Plasma Descum</td>
<td></td>
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</tr>
</tbody>
</table>
| 55   | Si₃N₄ etch :  CF₄:  45 sccm; O₂: 255 sccm;  RF Power: 200W  
<p>|      | Time: 3min |
| 56   | Conditioning run: CF₄:  45 sccm; O₂: 255 sccm;  10 min |
| 57   | Actual run: CF₄:  45 sccm; O₂: 255 sccm;  3 min |
| 58   | O₂ Plasma Descum |
| 59   | Soak the wafer in Acetone for 15 minutes. |</p>
<table>
<thead>
<tr>
<th>60</th>
<th>Acetone spray to remove any photoresist left behind.</th>
</tr>
</thead>
<tbody>
<tr>
<td>61</td>
<td>Rinse with methanol / IPA then N₂ dry</td>
</tr>
</tbody>
</table>
References:


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