Metal Contacts on GaSb Substrates and GaInAsSb Epilayers for Infrared Detector Applications

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ABSTRACT

Any electronic device requires ohmic contacts for interconnection with the outside. In this case, a manufacturing process of ohmic contacts on GaSb substrates and GaInAsSb epilayers was tested as part of the manufacture of an infrared detector for monitoring environmental aromatic pollutants.

The process includes seven steps: cleaning, surface passivation, thermal annealing premetallization, photolithography, metallization, lift-off and thermal annealing after metallization. In order to validate the process and to know the effects of each step, a series of tests were carried out using GaSb substrates. Those tests show mainly the effects of the passivation and the thermal annealing on contact parameters. In GaInAsSb epilayers, the cleaning procedure and the metal layers deposited were changed taking into account the previous results and the composition of the epilayers.

Through the complete process and depositing Pd/In/Pd/Au-Ge/Pd/Au on GaSb, ohmic contacts with a linear current-voltage characteristic have been obtained. Moreover, Schottky barriers have been the result of applying the process on GaInAsSb epilayers. Thus, taking into account the effects of the carrier concentration in the height and width of the barrier, tests on GaInAsSb epilayers doped in the range of $5 \times 10^{15} - 8 \times 10^{17} \text{ cm}^{-3}$ have been carried out. I-V measurements show the domain of the field emission mechanism on the thermionic emission mechanism as the doping density increases.
RESUMEN

Todo dispositivo electrónico requiere contactos óhmicos para interconectarse con el exterior. En este caso, un proceso de fabricación de contactos óhmicos (sobre sustratos de GaSb y películas cuaternarias de GaInAsSb) ha sido probado como parte de la fabricación de un detector infrarrojo para el monitoreo de contaminantes ambientales de tipo aromático.

El proceso contempla siete pasos: limpieza, pasivación de la superficie, recocido térmico antes de la metalización, fotolitografía, metalización, lift-off y recocado térmico después de la metalización. Para validar el proceso y conocer los efectos de cada paso se llevaron a cabo una serie de pruebas empleando sustratos de GaSb. Estas pruebas revelan principalmente los efectos de la pasivación y los recocidos térmicos sobre los parámetros de contacto. En las películas de GaInAsSb, el procedimiento de limpieza y las capas de los metales depositados fue modificado teniendo en cuenta los resultados preliminares y su composición.

Con el proceso completo y depositando Pd/In/Pd/Au-Ge/Pd/Au sobre GaSb, se obtuvieron contactos óhmicos con una característica corriente-voltaje lineal. Por otra parte, barreras Schottky han sido el resultado de aplicar el proceso a muestras de GaInAsSb. Por ende, teniendo en cuenta los efectos de la concentración de portadores en el alto y ancho de la barrera, se llevaron a cabo pruebas sobre películas de GaInAsSb dopadas en el rango de $5.0 \times 10^{15} - 8.0 \times 10^{17} \ cm^{-3}$. Las mediciones I-V revelan el dominio del mecanismo de conducción de efecto de campo sobre el mecanismo de conducción de emisión termoiónico a medida que la concentración de portadores aumenta.
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INTRODUCTION

From technological standpoint, both new requirements and new opportunities appear every day. Taking into account it, man explores his environment and adapts it to his needs. From this process, III-V semiconductor compounds have emerged as an option to advance technologically. The gallium antimonide (GaSb) is one of them and as well as other materials has properties which are interesting in several applications. Furthermore, the GaSb serves as a substrate because several ternary and quaternary compounds match with its lattice parameter. There are a large number of devices that can be made based on those compounds and also, many applications in which are required them. In terms of applications, III-V compounds-based devices fit nonsilica fibers, which would improve optical communications; operating in infrared, some sensors may be useful in military and civilian area. At device level, devices with higher frequencies of operation and better optical and transport properties can be obtained. To achieve those profits, man must set a route which from microelectronic technology involves a series of stages. One of them is to grow and master whatever the growth technique of these materials. Other stages include characterization of the material, device fabrication and characterization. To characterize the device is necessary to provide it with metal contacts. This research focuses on the manufacturing and characterization of metal contacts on GaSb substrates and GaInAsSb epilayers grown by liquid phase epitaxy on GaSb substrates. Within the technological process, this research is a step towards the satisfaction of a need, monitoring environmental pollution.

A year ago, the stage of obtaining these materials was completed and there were still some aspects of characterization to end, but it was not an obstacle to start the device fabrication process. Given the importance of the metal contacts and their
repercussion on some parameters of device design, manufacture of the metal contacts began by means of this research. Now, some results have been obtained and this thesis not only presents these results but also the research process undertaken to reach them.

Theoretical aspects related to both metal-semiconductor contacts and with the manufacturing process have been reviewed in the literature [1-9]. This review has been compacted in the first chapter addressing the main issues. In this regard, the first chapter is the helm that has guided this research. Therefore, the reader should pay particular attention to the definitions, the effects of non-idealities, the mathematical developments and the processes and their relevance to the objectives.

Once the theoretical aspects were understood, a manufacturing process of metal contacts was proposed and put under test. The process steps translated into a series of procedures are set out in the second chapter. In the second chapter are included the samples used, the tools, the particular process of each sample, the procedures and parameters as well as some additional experiments performed in support of evaluating the effects of some parameters on the results. At the end of the second chapter, the reader should be clear about the overall process and the modifications made to it sample to sample.

Doping density, one of the main parameters of the epilayers will be presented to the third chapter. Thus, only culminating the third chapter, the reader will have the tools to interpret the results that are presented there. This is because the electrical measurements to characterize the metal contacts have also been used to characterize the epilayers. Finally, in the last chapter, an analysis of the results is done and accordingly the main conclusions of this research are put on paper.
OBJETIVES

General objective

To establish a process to manufacture metal contacts on GaSb substrates and GaInAsSb epilayers grown on GaSb substrates by liquid phase epitaxy.

Specific objectives

- To review the main theoretical aspects related to the fabrication and characterization of metal-semiconductor contacts.
- To study and to implement a surface passivation process.
- To characterized the metal contacts through the contact resistance and specific contact resistivity.
- To classify the metal contacts obtained and to explain their electrical behavior.
Chapter 1

THEORETICAL FUNDAMENTALS

This chapter contains the collection of the theoretical basis which guided the development of this research. Their presentation has been organized into seven sections, as follows. First, exposition of the physical models that represent the metal-semiconductor contacts; second, the main parameters used to describe any contact; third, surface passivation as a method for the reduction of surface energy states; fourth, some methods used to evaporate metals in microelectronics; fifth, theoretical fundamentals involved in rapid thermal processes; sixth, a review of measurement techniques for characterization of contacts; and finally, a summary of some properties of gallium antimonide (GaSb) and gallium indium arsenide antimony (Ga$_x$In$_{1-x}$As$_y$Sb$_{1-y}$). Although the main aim is to obtain ohmic contacts on GaSb and Ga$_x$In$_{1-x}$As$_y$Sb$_{1-y}$, the properties of those materials have been left for last; it is recommended that the reader has it in mind.

1.1 Metal-semiconductor contacts

All electronic devices need a metal-semiconductor contact in order to interconnect with others. Therefore, it is important to understand the main physical aspects related with the junction metal-semiconductor. In this research, the semiconductor is a III-V compound. Despite the relevance of those compounds for this research, first general concepts that occur in any metal-semiconductor contact will be presented. Initially, the surfaces are considered ideal and the characteristics of
contact are entirely dependent on the work functions of metal and semiconductor. Later, the analysis will include non-ideal surfaces.

1.1.1 Ideal contacts

The metal-semiconductor contacts are usually represented by energy diagrams. To make an energy diagram is necessary to know the work functions of the materials. In a metal-semiconductor contact, according to the difference between work functions, the interface is an electron accumulation region, an electron depletion region or neutral region. If the work function of metal \((\phi_m)\) is greater than the work function of semiconductor \((\phi_s)\), the contact is a Schottky contact; otherwise, there is an ohmic contact. In a Schottky contact, electrons flow in one direction easier than any other. While in an ohmic contact the electron flow resistance is very low and it is the same in both directions.

1.1.2 Schottky contact

If the semiconductor is n-type, when the metal and the semiconductor are joined, three events occur simultaneously:

- Electrons in the semiconductor flow to the metal.
- That originates a space charge region.
- And finally, it creates an electric field that opposes to the flow of electrons.

The electron transfer occurs at the interface until the Fermi level of the semiconductor equals the Fermi level of metal. The final result is shown in Figure 1. As can be seen, the band bending forms the Schottky barrier \((\phi_B)\) [7]:

\[
\phi_B = \phi_m - \chi
\]  

(1)
where $\chi$ is the electron affinity of the semiconductor. When the applied potential in the metal is greater than in the semiconductor, the potential barrier is reduced and the electrons can flow easily. On the other hand, when the metal-semiconductor contact is polarized with a lower potential in the metal, the barrier potential increases and the electron flow resistance becomes larger.

![Figure 1. Schottky contact, n-type semiconductor.](image)

If the semiconductor is p-type, similar processes occur. In that case:

- Electrons in the metal flow to the semiconductor.
- That originates a space charge region.
- And finally, it creates an electric field that opposes the flow of electrons.

Metal electrons recombine with the holes nearest of the semiconductor, causing the space charge region. The final result is shown in Figure 2. As can be seen, the band bending forms the Schottky barrier ($\phi_B$) [7]:

...
\[ \phi_B = \frac{E_g}{q} - (\phi_m - \chi) \]  \hspace{1cm} (2)

where \( E_g \) is the band gap of semiconductor and \( q \) is the electric charge. When the metal-semiconductor contact is polarized with a greater potential in the metal, the barrier potential increases and the resistance becomes larger. On the other hand, when the potential in the metal is lower than in the semiconductor, the barrier potential is reduced and the electrons can flow easily.

![Figure 2. Schottky contact, p-type semiconductor.](image)

### 1.1.3 Ohmic contact

Ohmic contacts provide networking of any electronic device to the outside. An ohmic contact is characterized by very low resistance in both directions. Therefore, the contact voltage is low even with currents in the order of milliamperes. In order to implement an ohmic contact any of the following requirements must be fulfilled. First, a barrier should not be formed at the interface; second, if a barrier is formed, the barrier must be sufficiently narrow. When the work function of metal is lower than the work function of n-type semiconductor, there is not barrier and the
electrons flow easily in any direction. Another way is to reduce the barrier width, in that case the electrons flow by means of tunnel effect.

1.1.3.1 Schottky ohmic contacts

If the semiconductor is n-type and the work function of the semiconductor is larger than the work function of metal, the contact is ohmic. Initially, electrons flows from metal to lower energy states of the semiconductor until the equilibrium is reached. Then, the surface acquire a greater concentration of electrons at the surface than in the bulk of the semiconductor (see Figure 3).

![Figure 3. Schottky ohmic contact, n-type semiconductor](image)

In Figure 4 are displayed the two types of polarization. In this regard, it is important to note the junction has a low resistance with either polarity of voltage. If the semiconductor is p-type, the work function of the semiconductor must be lower than the work function of metal so that a process similar to the n-type semiconductor takes place.
1.1.3.2 Tunnel Effect

The barrier height ($\phi_B$) does not depend on the doping density ($N_D$), but the barrier width ($W$) is inversely proportional to the root of the doping density [1]:

$$ W = \sqrt{\frac{2 \varepsilon_s (V_{bi} \pm V)}{q N_D}} $$

(3)

where $\varepsilon_s$ is the permittivity of the semiconductor, $V_{bi}$ is the built-in potential in the semiconductor depletion region and $V$ is the applied forward bias. If the density of dopants increases, the barrier width decreases and the electrons can go through the barrier by tunnel effect. The thermal energy ($kT$) is another influential factor. Three different regions (thermionic emission (TE), thermionic-field emission (TFE) or field emission (FE)) can be differentiated according to relation between the thermal energy and the characteristic energy which is defined as [5]:

$$ E_{00} = \frac{q \hbar}{2} \sqrt{\frac{N_D}{m^* \varepsilon_s}} $$

(4)

where $\hbar$ is the the reduced Planck constant and $m^*$ is the effective mass of electrons. If $kT \gg E_{00}$, the main component of the current will be electrons thermally excited over the barrier (TE). When $kT \ll E_{00}$, the current is caused by tunneling electrons (FE) due to a narrow barrier. While $kT \approx E_{00}$, both components are involved in the conduction process (see Figure 5).
Figure 5. $E_{00}$ and $kT$ as a function of doping density for Ga$_x$In$_{1-x}$As$_y$Sb$_{1-y}$ with $m^*_{\text{tun}}/m = 0.005$. $T = 300$ K.

1.1.4 Non-ideal contacts

At the previous analysis were not considered the characteristics of the surface. The metal surface and the semiconductor surface have broken bonds. It leads to additional allowed states on the surface. That extra allowed states are not in the bulk and are called surface states [10]. One way to understand the effect of surface states on the characteristics of contact is through a mathematical analysis. According to Figure 6, the barrier height is given by [10]:

$$\phi_B = \phi_m - \chi - V_i - \Delta \phi_n$$

where $\Delta \phi_n$ is the image force barrier lowering, and $V_i$ is the voltage across "$\delta$" and it is given by [10]:

$$V_i = \frac{Q_{ss} + Q_{sc}}{C_i}$$

where $Q_{sc}$ is the space-charge density in semiconductor, $Q_{ss}$ is the surface state charge density on semiconductor, and $C_i$ is the capacitance of interfacial layer which is given by [10]:

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Figure 6. Energy band diagram of a metal-n-type-semiconductor contact with an interfacial layer and surface state charge density on semiconductor.

\[ C_i = \frac{\varepsilon_r \varepsilon_0}{\delta} \]  \hspace{1cm} (7)

where \( \varepsilon_0 \) is the permittivity in vacuum, and \( \varepsilon_r \) is the relative permittivity of the interfacial layer. Moreover, it is possible to approximate the surface state charge density to [10]:

\[ Q_{ss} = qD_{ss} (E_F - E_0) = qD_{ss} (E_g - \phi_B - \phi_0) \]  \hspace{1cm} (8)

where \( D_{ss} \) is the surface states density, \( E_g \) is the band gap of the semiconductor, \( E_F \) is the Fermi energy, and \( \phi_0 \) is the difference between the energy at which a pronounced peak appears in the surface states density (\( E_0 \)) and the energy of the top of the valence band (\( E_v \)).

From the equations (5), (7) and (8) [10]:

\[ \phi_B = \phi_m - \chi + \frac{qD_{ss}}{C_i} (E_g - \phi_B - \phi_0) - \frac{Q_{sc}}{C_i} \]  \hspace{1cm} (9)

Rearranging [10]:
\[ \phi_B = \gamma(\phi_m - \chi) + (1 - \gamma)(E_g - \phi_0) - \frac{\gamma Q_{sc}}{C_i} \] 

(10)

where [10]:

\[ \gamma = \frac{1}{1 + \frac{qD_{ss}}{C_i}} = \frac{1}{1 + \frac{qD_{ss}\delta}{\varepsilon_r\varepsilon_0}} \] 

(11)

Therefore, within the boundaries of the surface states density, there are two cases. If \( D_{ss} \to \infty \) [10]:

\[ \phi_B = E_g - \phi_0 \] 

(12)

and the barrier height is independent of the metal work function, this is known as Bardeen's limit of \( \phi_B \). Otherwise, if \( D_{ss} \to 0 \) or/and \( \delta \to 0 \) [10]:

\[ \phi_B = \phi_m - \chi \] 

(13)

This is the Schottky's limit of \( \phi_B \). In semiconductors such as silicon, germanium, gallium arsenide, gallium phosphide and other semiconductor compounds, the quantity \( \phi_0 \) is found experimentally to be about equal to \( 1/3 E_g \), so that the barrier height \( \phi_B \) is typically close to \( 2/3 \) of the band gap [11]. At this point, the conclusion is clear, to get an ohmic contact is necessary to decrease the surface states density and/or decrease the contact length \( \delta \).

1.2 Contact resistance

For practical purposes and comparison, the contact resistance \( R_c \) (in \( \Omega \)) and the specific contact resistivity \( \rho_c \) are necessary. The specific contact resistivity includes the regions immediately above and below the interface. For theoretical
purposes, specific interfacial resistivity $\rho_i$ (in $\Omega \cdot cm^2$) appears and it is defined by [5]:

$$\rho_i = \frac{\partial V}{\partial J} \bigg|_{V=0}$$  \hspace{1cm} (14)

or

$$\rho_i = \frac{\partial V}{\partial J} \bigg|_{A \rightarrow 0}$$  \hspace{1cm} (15)

where $A$ is the contact area. The specific interfacial resistivity is not actually measurable. The parameter determined from measured contact resistance is the specific contact resistivity.

The current density $J$ of a metal-semiconductor contact depends on the applied voltage ($V$), the barrier height ($\phi_B$) and the doping density ($N_D$). According to the dominant current component, there is a theoretical expression more or less acceptable for the specific interfacial resistivity. If FE dominates, the specific interfacial resistivity is given by [2]:

$$\rho_i = \frac{K sen(\pi C_1 K T)}{A^* \pi q T} \exp \left( \frac{q \phi_B}{E_{00}} \right)$$  \hspace{1cm} (16)

$$C_1 = \frac{1}{2E_{00}} \ln \left( \frac{4\phi_B}{-V_n} \right)$$  \hspace{1cm} (17)

($V_n$ is negative for degenerate semiconductor). If TFE dominates, $\rho_i$ is given by [2]:

$$\rho_i = \frac{K \sqrt{E_{00} \cosh \left( \frac{E_{00}}{K T} \right)}}{A^* T_q \sqrt{\pi q (\phi_B - V_n)}} \exp \left[ \frac{q (\phi_B - V_n)}{E_{00} \cot h \left( \frac{E_{00}}{K T} \right)} + \frac{q V_n}{K T} \right]$$  \hspace{1cm} (18)

If TE dominates [2]:

$$\rho_i = \frac{K}{A^* T_q} \exp \left( \frac{q \phi_B}{K T} \right)$$  \hspace{1cm} (19)
Some relevant ideas about the above equations are listed below:

- The specific interfacial resistivity depends on the effective masses, the barrier height, and other parameters. The barrier height depends also on the contact metal, and it is impossible to derive “universal” $\rho_c$ versus $N_D$ curve.
- The main parameters are the barrier height and the doping concentration.
- For TE, $\rho_i$ is independent of the doping concentration and depends only on $\phi_B$.
- In the other extreme of FE, in addition to $\phi_B$, $\rho_i$ has a dependency of proportionality $\exp\left(N^{-\frac{1}{2}}\right)$.

It is clear that for good ohmic contact, the barrier heights must be minimized. There are two factors that control the barrier height, namely the metal work function and the interfacial properties.

### 1.3 Passivation of III-V semiconductor surfaces

This section is focused on the passivation as a technique to reduce the surface states density in III-V semiconductors. Once the surface is passivated, the metal-semiconductor contact may be ohmic [12]. The term “passivation” signifies that a semiconductor surface becomes less chemically active and few active recombination centers are formed on the surface and/or these centers themselves become less active in the process [13]. Since mid-1980’s, passivation of III-V semiconductor surface through treatment of the surface with sulfur or selenium atoms has been widely studied [14]. This method is known like chalcogenide passivation. Chalcogenide passivation simultaneously achieves [14 - 15]:

- Chemical and electronic passivation of a surface.
• To decrease substantially not only the density of surface states in the band gap but the surface recombination velocity.
• To slow down considerably the oxidation of a semiconductor surface in the atmosphere.

1.3.1 Chemical process of passivation

If the solution is properly prepared, when the semiconductor enters in contact with the solution, two events will occur: 1) the layer oxide will be etched and 2) on the surface a passivating layer will be formed. In the presence of an aqueous solution based on sulfur, the chemical reaction leading to the formation of a sulfide coating can be written in the following form [13]:

$$A^{III}B^{V} + HS^- + H_2O \rightarrow (A^{III})_x S_y^-, + (B^{V})_x''S_y'' + HO^- + H_2 \quad (20)$$

In general, values from 1 to 5 is assumed for the stoichiometric coefficients $x'$, $y'$, $x''$ and $y''$. Finally, the surface will be a mixture of different sulfides.

Throughout the course of the sulfidization reaction, the semiconductor oxidizes and hydrogen is reduced, this reaction can be written in the form of two half-reactions [13]:

$$A^{III}B^{V} \rightarrow (A^{III})^3+ (B^{V})^3+ + 6e^- \quad (21)$$

$$6H^+ + 6e^- \rightarrow 3H_2 \uparrow \quad (22)$$

Specifically, the process is as follows. First, bonds between III and V atoms are broken and $HS^-$ ions are dissociated; then, electrons from the semiconductor are transferred into the solution; finally, the sulfur atoms form chemical bonds with the semiconductor atoms on the surface. At the second step, absorption of light with phonon energy greater than the band gap of the semiconductor can serve as the
source of energy required to transfer an electron into the conduction band or to the level of a surface state (see Figure 7).

![Figure 7. Schematic diagram of the processes occurring during the formation of a sulfide passivating coating on GaSb surface. a) Rupture of bonds between Ga and Sb atoms, removal of oxide layer, and dissociation of HS\(^{-}\) ions; b) transfer of electrons from the semiconductor into the solution; c) formation of chemical bonds between Sb and sulfur atoms.](image)

As the process involves an electrochemical reaction, the sulfide coating is formed more quickly on n-type semiconductor than on p-type semiconductor. Other factors that affect the rate of formation of the coating are:

- Temperature
- Light intensity incident on the semiconductor/electrolyte interface
- Concentration of sulfur atoms in the solution
- pH of the solution

### 1.3.2 Chalcogenide passivation

Some chemical solutions have been used to passivate III-V semiconductor surfaces. Those solutions and their effects are listed below [14]:

---

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• Aqueous solution of sodium sulfide \((\text{Na}_2\text{S}:\text{H}_2\text{O})\) with concentration 0.5 – 1.0 \(M\) was tested on AlGaAs/GaAs bipolar transistor, and it improved the device characteristics.

• Aqueous solution of ammonium sulfide \((\text{NH}_2)_2\text{S}\) with 6% excess sulfur. This method did not leave any visible film on the semiconductor surface.

• Treatment in \(\text{P}_2\text{S}_5/\text{NH}_4\text{OH}\) solution improved the stability of the luminescence properties compared to sodium sulfide solution.

• Passivated GaAs with \(\text{P}_2\text{S}_5/(\text{NH}_4)_2\text{S}\) solution was able to improve the photoluminescence intensity in relation to passivated GaAs in pure \((\text{NH}_4)_2\text{S}\).

• Aqueous solutions of \(\text{K}_2\text{Se}\) as well as the solutions \(\text{Na}_2\text{S}+\text{RuCl}_3\), \(\text{Na}_2\text{Se}/\text{NH}_4\text{OH}\), \(\text{SeS}_2\), \(\text{S}_2\text{Cl}_2\) and \(\text{Se}/\text{NH}_4\text{OH}\) were tested on GaAs surfaces.

• Thiols dissolved in nonaqueous solvents and [\(\text{CH}_3(\text{CH}_2)_{17}\)]\(_2\text{NCSSNa}\) were used for GaAs surface passivation. With this treatment, the surface was characterized by high stability against heating and standing in the atmosphere.

• Sodium sulfide and ammonium sulfide solutions in ethanol, isopropanol [16], butanol and tertbutanol were tested also. Those solutions increase the photoluminescence intensity of sulfidized GaAs.

### 1.4 Physical vapor deposition by evaporation

Physical vapor deposition is a method that involves heating a source of material to be deposited until the evaporation is caused. Subsequently, the molecules or atoms reach the substrate surface and deposit there. The degree of impact of molecules or atoms on the substrate or against the walls of the chamber depends on the pressure in the chamber. The rate of mass lost from the source per unit area per unit time \(R\), as a result of such evaporation, can be estimated from the Langmuir-Knudsen relation [6]:

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\[ R = 5.83 \times 10^{-2} \left( \frac{M}{T} \right)^{1/2} P_e \]  

where \( M \) is the gram-molecular mass, \( T \) is the temperature and \( P_e \) is the vapor pressure.

Many metals have been deposited by this method (Figure 8) and some characteristics of the films obtained are:

- High rates of deposit
- Least damage to the substrate surface
- Reduction of contamination of the deposited film due to high levels of vacuum in the chamber
- The substrate is heated only by the impacts of the molecules or atoms that reach the surface

The quality of a thin film deposited on a substrate is measured by:

- Control over the rate of deposit
- The film thickness uniformity across the substrate area
- Good step coverage

Figure 8. Vapor pressure of metals commonly deposited by evaporation (from Wolf et al. [6]).
To achieve those goals, the rate of mass lost of the source and the direction of the evaporated atoms must be known. The equation (23) reveals the rate of mass lost; some theoretical approaches have been developed to know the directions of the evaporated atoms. As the source is extended, this is not a uniform deposition at the area surrounding the source. To resolve that drawback, the wafers are placed on a planetary system inside a vacuum chamber. During evaporation, both the planetary system and the wafer rotate about their respective axis. Although the planetary system achieves film uniformity across the area, it does not get good step coverage.

1.4.1 Evaporation methods

To evaporate a metal is necessary to heat the metal to carry it to its boiling point, passing through a molten phase. This process is carried out in a high vacuum environment, typically lower than $5 \times 10^{-7} \text{Torr}$. The method for heating metal has changed over time. Initially, the metal to be evaporated was placed on strips of wire; then, wire strips were resistively heated until the metal was evaporated. Although the method is easy to apply, it does not have tolerable levels of contamination in microelectronics; also, it has both a limited number of metals which can be evaporated and a limited quantity of metal to be evaporated. Now, the area of microelectronics is using two alternative methods: Electron-Beam Evaporation and Inductive Heating Evaporation.

1.4.1.1 Electron-Beam Evaporation

Electron-Beam Evaporation is carried out in a chamber under high vacuum conditions (about $5 \times 10^{-5} \text{Torr}$ or less), and it uses the following items:

- Electron beam evaporation gun
- A system controller
• A power supply
• Crucibles for the evaporation material
• Materials for evaporation
• Material to be coated

![Electron Beam Evaporation](image)

**Figure 9.** Electron Beam Evaporation.

The electron beam evaporation gun consists basically of a tungsten filament and either permanent magnets or electromagnets which are responsible for generating an electric or magnetic field. First, the filament is heated by means of an electric current until it begins to emit electrons. The electric or magnetic field deflects and accelerates the electrons toward the material to be evaporated. With successive impacts, the kinetic energy of the electron beam ($5 - 30 keV$) is transferred to the metal as heat. The increase in temperature causes the melting and subsequent evaporation of metal (Figure 9). The DC voltage of the power supply is typically $10 - 30 kV$ and its power is of $1200 kW$ or more. For that reason, deposit rates of $0.5 \mu m/min$ are possible with this method.
Electron beam evaporation has advantages over other methods. This method is cleaner because the electron beam evaporation gun is covered and the crucible is made of materials with high melting point, for example carbon. To contribute to the uniformity of the deposit, movements are performed in the electron beam by electromagnetic deflection. In addition, with electron beam is possible to melt and to evaporate a greater number of metals.

1.4.1.2 Inductive Heating Evaporation

High rate evaporation deposition can also be accomplished by heating the source with rf energy. As can be seen in Figure 10, an rf induction heating coil surround a crucible containing the evaporation source. The main advantage of inductive heating over e-beam heating is that the wafers are not subject to ionizing radiation. This method has two disadvantages. First, this method must use a crucible that is in direct contact with the molten evaporant. Second, both rf equipment and the process development are complex [6].

![Figure 10. Induction heating (3 kW) (courtesy Glyndwr University).](image)
1.5 Rapid thermal processing

A rapid thermal process includes a heating system, a sample and physical processes. In the last section of this chapter will be released some characteristics of the sample, so this section will focus on the heating system [17 - 18] and the physical processes involved in the heating of the sample.

1.5.1 Heating system

During a rapid thermal process a wafer is carried to high temperatures (1200 °C) in a few seconds (at a rate in the range of 40 – 200 °C per second), and then, it is cooled taking care not to fracture it. Historically, furnaces have been used in thermal processes. Currently, RTP is moving to the furnaces. RTP allows processes in a short time, more uniformity of temperature, high temperatures, among other advantages. To achieve these qualities, when an RTP system is designed, some aspects such as the heat source, the chamber characteristics, the mechanism for measure the temperature and additional elements to provide uniform heating must be taken into account.

As heating source, typically a linear or honeycomb array of tungsten-halogen lamps are used. According to the design, the array of lamps may be either above, below or both sides of the wafer. These lamps are heated and emit infrared light which incidents on the wafer and heats it. The chamber should help minimize the reflected radiation. For that matter, some accessories are placed around the wafer, such as a thermal shield to reduce the effects of radiation. Typically, RTP systems use pyrometers which sense the emissivity of the wafer. An array of several pyrometers operating in the infrared range is placed strategically. These pyrometers provide to a system of control the information necessary to control the power of the lamps and to achieve uniform heating. Lately, thermocouples have
started to be used as a temperature gauge. One thermocouple is placed in direct contact with the wafer.

![Schematic diagram of a RTP system with laps below the wafer and quartz tube as support.](image)

**Figure 11.** Schematic diagram of a RTP system with laps below the wafer and quartz tube as support.

The basic understanding of physics of heat transfer in RTP is to recognize that it consists of number of radiating bodies at different temperatures, each with its characteristic energy spectrum. The lamps may be at $2000 - 3000 \, ^\circ C$ (filament), the wafer temperature around $25 - 1200 \, ^\circ C$, and the chamber walls between $20 - 400 \, ^\circ C$ depending on system design and wafer set temperature [19].

### 1.5.2 Physical processes

When a sample is heated by RTP, the physical processes can be summarized in four: 1) radiation of a source, 2) absorption of radiation, 3) conversion of radiation into heat and 4) thermal conduction inside sample.

#### 1.5.2.1 Radiation of a source

All hot objects emit radiation and the radiation distribution is well defined. For an ideal black body radiator, this distribution is given by Planck's formula as follows [20]:

$$S(v) = \frac{2h v^3}{c^2} \frac{1}{e^{\frac{h v}{k T}} - 1}$$
\[
\rho_\omega(T) = \frac{8\pi \hbar \omega^3}{c^3} \frac{1}{e^{\frac{\hbar \omega}{k_B T}} - 1}
\] (24)

where \(\rho_\omega(T)\) is the energy density as a function of absolute temperature \((T)\) for a given frequency \(\omega\), \(\hbar\) is the reduced Planck constant and \(k_B\) is the Boltzmann constant. Figure 12 shows the curves of the energy density obtained by variation of the frequency for temperatures from \(1\ K\) to \(10^8\ K\). Note that as the temperature increases, the peak shifts to the right and turn increases. That is, the number of photons with frequencies around the peak increases.

![Figure 12. Energy density curves of a black body radiator to nine different temperatures as the frequency varies.](image)

However, the real components of a system are not perfect black bodies. They emit less radiation at each wavelength than a black body. An approximation to the real emission behavior can be done by scaling blackbody radiation by constant factor called emissivity \(\varepsilon\). Such "real" or "grey" body has the total emitted power equals to \(\varepsilon\) times that of a black body at the same temperature [19].
1.5.2.2 Absorption of radiation

When a radiation reaches the surface of a real body, a fraction of the radiation is absorbed (enters the body) and the other is reflected. So that if $A$ is the fraction absorbed and $R$ is the fraction reflected, it holds that $A + R = 1$. Moreover, by principles of thermal equilibrium, if $I$ is the incident radiation, $E$ the radiation emitted by the body and $R$ the reflected radiation, then, the sum of emitted and reflected radiations must be equal to the incident radiation ($R + E = I$).

As important result of that, the average emissivity of real sources of radiation source may not always be equal to the average absorptivity. The reason behind this is due to different spectral distributions from the emitted radiation (GaSb wafer) and the incident radiation (lamps) [20].

1.5.2.3 Conversion of radiation into heat

In order to increase the temperature in a sample, certain amount of heat must be transferred to it. When radiation reaches the sample, the free electrons absorb that radiation. In that process the electric field of the incident radiation accelerates the free electrons, which in turn are decelerated by collisions with the lattice. Thus the electric field energy is converted into heat.

It should be noted that if the number of free electrons increases, the absorption of radiation will be increased. For that reason, if the energies of the incident photons are above the threshold of energy for electrons promote across the band gap, it will generate more free electrons and the sample is heated further.
1.5.2.4 Thermal conduction inside sample

Although an average temperature across sample remains constant, small variations in temperature can develop across the sample due to a different balance between emission and absorption. Most common factors are outlined below [20]:

- The different geometrical and radiation situations at the edge as compared with the center of a wafer.
- The different energy balances that occur in regions as a result of different film stack, over layers, and pattern definition.

1.6 Measurement techniques

Undoubtedly, the electrical measurements play an important role in this research. The results of the measurements show the quality of the manufacturing process of contacts. For that reason, this section focuses on discerning the most appropriate measurement technique to Characterize the metal-semiconductor contacts which are the aim of this work. At this point, it is important to note that details about all the techniques of measurement are not one of the purposes, only evaluate their advantages and disadvantages. Thereupon, the choice of one or more technique will be justified. Finally, each of the selected techniques will be developed theoretically.

The success of these measurements depends on the specifications of the instruments and that the measurement technique is performed correctly. The next chapter will approach the instruments and the equipments; therefore, this section will not address this subject.

In terms of measurement techniques, to make contacts involves a process that can be extended by the measurement technique used. In that regard and trying to
reduce the number of manufacturing steps, techniques as Vertical Kelvin are not suitable for this research. Other aspects evaluated are the requirements, accuracy and the parameters obtained in the execution of each technique. Techniques such as Two contacts Two terminals, although easy to implement, require data of the substrate or film and are unreliable. Multiple contacts Two terminals is a technique in which there are many details to consider and does not provide enough parameters. Linear transmission line method (LTLM) and six-terminal contact resistance suffer from crowding current on contacts; there is lateral flow, as well as any misalignment alters the measurement. Compared with circular transmission line method (CTLM), the theoretical considerations of these two techniques are higher. For those reasons, CTLM has been chosen as the main technique for evaluating the manufacturing process. A summary of the advantages and disadvantages of each of the techniques is listed in Table 1.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two contacts Two terminals</td>
<td>The earliest method.</td>
<td>Questionable accuracy. The spreading resistance must be smaller than the contact resistance. Bulk Resistance and layer sheet resistance need be known.</td>
</tr>
<tr>
<td>Multiple contact Two terminals:</td>
<td>Neither the bulk resistance nor the layer sheet resistance need be known. It is easy to implement. It can be used to determine the specific contact resistivity by iteration.</td>
<td>Occasionally negative contact resistances are obtained by this method. The specific contact resistivity cannot be directly extracted. The analysis becomes more difficult due to lateral current flow, current crowding at the contacts, and sample geometry.</td>
</tr>
<tr>
<td>- Contact front resistance</td>
<td></td>
<td></td>
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<tr>
<td>- Contact end resistance</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Cross bridge Kelvin resistance</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Structure</td>
<td>Details</td>
<td>Notes</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Circular TLM structure</td>
<td>The problem of $W \neq Z$ can be avoided. It is not necessary to isolate the layer to be measured. It can be used to determine the contact resistance, the specific contact resistivity, the layer sheet resistance and the transfer length.</td>
<td>The correction factor is necessary to compensate the difference between the linear and circular TLM layouts to obtain a linear fit with the experimental data.</td>
</tr>
<tr>
<td>Linear TLM structure</td>
<td>It can be used to determine the contact resistance, the specific contact resistivity, the sheet resistance between and under the contacts and the transfer length.</td>
<td>The sheet resistance under the contacts is uncertain. Constant electrical and geometrical contact parameters across the sample are not the same.</td>
</tr>
<tr>
<td>Vertical Kelvin structure</td>
<td>Overcome the lateral current flow problems of the conventional Kelvin structure. It can be used to determine the contact resistance and the specific contact resistivity. Additional contacts can be used to reduce experimental errors.</td>
<td>The device requires one additional mask level during its fabrication compared to conventional Kelvin structures.</td>
</tr>
<tr>
<td>Six-terminal contact resistance</td>
<td>The structure allows determining the contact resistance, the specific contact resistivity, the contact end resistance, the contact front resistance, and the sheet resistance under the contact.</td>
<td>The two-dimensional complications are manifested.</td>
</tr>
</tbody>
</table>

CTLM structure consists of a conducting circular inner region of radius $R_1$, a gap of width $S$, and a conducting outer $R_2$ (see Figure 13). The conducting regions are usually metallic and the gap typically varies from a few microns to tens of microns. For equal sheet resistances under the metal and in the gap, and for the geometry of the circular contact resistance structure in Figure 13, the total resistance between the internal and the external contacts is [5]:
\[ R_T = \frac{R_{sh}}{2\pi} \left[ \frac{L_T}{R_1} \frac{I_0(R_1/L_T)}{I_1(R_1/L_T)} + \frac{L_T}{R_1+S} \frac{K_0(R_1/L_T)}{K_1(R_1/L_T)} + \ln \left( 1 + \frac{S}{R_1} \right) \right] \]  

(25)

**Figure 13.** Circular transmission line method structure.

where \( I \) and \( K \) denote the modified Bessel functions of the first order, \( R_{sh} \) is the sheet resistance of the semiconductor on which the contact is made and \( L_T \) is the transfer length. For \( R_1 \gg 4L_T \), the Bessel function ratios \( I_0/I_1 \) and \( K_0/K_1 \) tend to unity and \( R_T \) becomes [5]:

\[ R_T = \frac{R_{sh}}{2\pi} \left[ \frac{L_T}{R_1} + \frac{L_T}{R_1+S} + \ln \left( 1 + \frac{S}{R_1} \right) \right] \]  

(26)

At the circular transmission line test structure in Figure 13, for \( R_1 \gg S \), the equation (26) simplifies to [5]:

\[ R_T = \frac{C R_{sh}}{2\pi R_1} (S + 2L_T) \]  

(27)

where \( C \) is the correction factor given by [5]:

\[ C = \frac{R_1}{S} \ln \left( 1 + \frac{S}{R_1} \right) \]  

(28)

The Figure 14 shown the correction factor depending on \( S/R_1 \). For \( S/R_1 \ll 1 \), the correction factor becomes equal to 1 and the total resistance can be given by [5]:

29
\[ R_T = \frac{R_{sh}}{2\pi R_1} (S + 2L_T) \]  

(29)

When the gap \( S \) is greater than approximately one tenth of the radius \( R_1 \), it is necessary to apply the correction factor to the data. Failure to apply the correction factor, the data will not conform to a straight line, as it is shown in Figure 15. Furthermore, the specific contact resistance will be overestimated [21].

Figure 14. Correction factor vs. \( S/R_1 \).

Figure 15. Resistance for the CTLM test structure before and after data correction.
1.7 Antimonide-based compound

The previous sections were focused on the theoretical aspects regarding ohmic contacts and some of the processes performed on a sample of semiconductor material in order to get them. The purpose of this section is to introduce the semiconductor materials of this research.

As can be seen from literature, III-V compounds let tuning the magnitude of the forbidden gap so as to optimize it; for that reason, III-V compounds are attractive for many applications in the mid and long infrared as night vision, medical imaging, sensitive pollution gas monitoring, etc. In III-V compounds, there is a group based on antimony, which tend to shift the HgCdTe for those applications [22]. This research focuses on a binary compound (GaSb), and a quaternary compound (Ga$_x$In$_{1-x}$As$_y$Sb$_{1-y}$), all belonging to that group.

The last lines of this chapter will be devoted to the structural and electrical properties of those semiconductor materials.

![Figure 16. Bandgap as a function of lattice constant for III-V compounds and their ternary and quaternary alloys (from Dutta et al. [23])](image)
1.7.1 Gallium Antimonide

The gallium antimonide (GaSb), such as other semiconductors, is a material whose properties are useful in various applications. Among III-V semiconductor compounds, GaSb is particularly interesting as a material substrate because its lattice parameter matches solid solution of various ternary and quaternary III-V compounds whose band gaps cover a wide spectral range from 0.3 to 1.58 eV as depicted in Figure 16. It has stimulated a lot of interest in GaSb for basic research as well as device fabrication. Some parameters of GaSb are listed in Table 2.

Table 2. Some parameters of GaSb (from Dutta et al. [23])

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant (Å)</td>
<td>6.0959</td>
</tr>
<tr>
<td>Density (g · cm⁻³)</td>
<td>5.6137</td>
</tr>
<tr>
<td>Melting point (K)</td>
<td>985</td>
</tr>
<tr>
<td>Debye Temperature (K)</td>
<td>266</td>
</tr>
<tr>
<td>Coefficient of thermal expansion at 300 K (10⁻⁶ K)</td>
<td>7.75</td>
</tr>
<tr>
<td>Thermal conductivity at 300 K (W cm⁻¹ K⁻¹)</td>
<td>0.39</td>
</tr>
<tr>
<td>Direct energy gap at 300 K (eV)</td>
<td>0.725</td>
</tr>
<tr>
<td>Work function φ (eV)</td>
<td>4.76</td>
</tr>
<tr>
<td>Photoelectric threshold Φₚ (eV)</td>
<td>4.76</td>
</tr>
<tr>
<td>Direct transition threshold Φₜ (eV)</td>
<td>5.24</td>
</tr>
<tr>
<td>Electron affinity χ (eV)</td>
<td>4.06</td>
</tr>
<tr>
<td>Effective mass of electrons (in units of mₑ)</td>
<td>0.0412</td>
</tr>
<tr>
<td>Effective masses of holes (in units of mₒ)</td>
<td>0.28</td>
</tr>
<tr>
<td>Heavy hole mass</td>
<td>0.28</td>
</tr>
<tr>
<td>Light hole mass</td>
<td>0.05</td>
</tr>
<tr>
<td>Spin-orbit split mass</td>
<td>0.13</td>
</tr>
<tr>
<td>Refractive index (near band-gap energy)</td>
<td>3.82</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td></td>
</tr>
<tr>
<td>ε(0)</td>
<td>15.69</td>
</tr>
<tr>
<td>ε(∞)</td>
<td>14.44</td>
</tr>
</tbody>
</table>
1.7.1.1 Structural properties

The crystalline structure of GaSb is zinc-blende. This zinc-blende structure is identical to that of the diamond lattice except that each Ga atom has four tetrahedrally arranged Sb neighbors and vice versa. The crystalline structure of GaSb, unlike that of Ge, does not possess a centre of inversion, and opposite directions in the crystal are not necessarily equivalent. The structure and the 0.33 ionic character of the bonds generate interesting arrangements of atoms in the (100), (110) and (111) planes. For example, the (111) planes are formed by atoms of the same element, either Ga or Sb, and each exhibits striking differences in their chemical, electrical and mechanical properties.

1.7.1.2 Electrical properties

To understand some electrical properties of GaSb, in principle, one must know the structure of bands. The band structure of GaSb obtained by nonlocal pseudopotential calculation is shown in Figure 17. GaSb is a direct-band semiconductor and its band structure reveals a set of three minima in the conduction band. Theoretically, the bandwidth in $\Gamma_{6c}$ is $0.86 \, eV$, in $L_{6c}$ is $1.22 \, eV$ and in $X_{6c} 1.72 \, eV$ (energies relative to the top of valence band).

![Figure 17. Band structure of GaSb (from Dutta et al. [23]).](image)
The effective masses of electrons and holes have been evaluated by cyclotron resonance technique and from the density state analysis of transport data. In Table 3, the effective masses for electrons \( m_\text{e} \) in the \( \Gamma \), \( L \) and \( X \) conduction bands and that for holes \( m_\text{p} \) in heavy and light hole valence bands along with the density of state masses are listed.

**Table 3. Effective masses of electrons and holes (in terms of free electron mass, \( m_\text{o} \)) (from Dutta et al. [23])**

<table>
<thead>
<tr>
<th>Notation</th>
<th>Value</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>( m_\text{e} (\Gamma) )</td>
<td>0.0412</td>
<td>from cyclotron resonance of hot electrons in the temperature range of 1–30 [K]</td>
</tr>
<tr>
<td>( m_\text{e} (\Gamma) )</td>
<td>0.0396</td>
<td>same data as above but by taking into account the nonparabolicity and polaron effect</td>
</tr>
<tr>
<td>( m_\text{e} (L)_\perp )</td>
<td>0.11</td>
<td>from transverse conductivity</td>
</tr>
<tr>
<td>( m_\text{e} (L)_\parallel )</td>
<td>0.95</td>
<td>from longitudinal conductivity</td>
</tr>
<tr>
<td>( m_\text{de} (L) )</td>
<td>0.226</td>
<td>density of state mass</td>
</tr>
<tr>
<td>( m_\text{e} (X)_\perp )</td>
<td>0.22</td>
<td>from transverse conductivity</td>
</tr>
<tr>
<td>( m_\text{e} (X)_\parallel )</td>
<td>0.51</td>
<td>from longitudinal conductivity</td>
</tr>
<tr>
<td>( m_\text{p} (h) )</td>
<td>0.28</td>
<td>from conductivity data</td>
</tr>
<tr>
<td>( m_\text{p} (l) )</td>
<td>0.05</td>
<td>from conductivity data</td>
</tr>
<tr>
<td>( m_\text{de} )</td>
<td>0.82</td>
<td>density of state mass</td>
</tr>
</tbody>
</table>

**1.7.2 III-V quaternary compounds**

Important parameters of III-V compound alloys are not known accurately yet. It necessitates the use of some kind of interpolation scheme. Depending on the relationship on the molar fraction and the type of III-V compound, there are several interpolation schemes. Those schemes are summarized in Table 4. Briefly, these interpolation schemes can derive mathematically parameters of quaternary compounds from the parameters of the binary compounds. Using that method, expressions in terms of mole fractions have been obtained for much of the
parameters of quaternary compounds. Some of those expressions will be presented below, inside the exhibition of the properties of Ga$_x$In$_{1-x}$As$_y$Sb$_{1-y}$.

**Table 4.** Interpolation schemes for ternary and quaternary compounds (from Kasap et al. [24])

<table>
<thead>
<tr>
<th>Compound</th>
<th>Relation</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_xB_1\cdots C_yD_{1-y}$</td>
<td>Linear</td>
<td>$Q(x, y) = xyB_{AC} + x(1-y)B_{AD} + (1-x)yB_{BC} + (1-x)(1-y)B_{BD}$</td>
</tr>
<tr>
<td></td>
<td>Quadratic</td>
<td>$Q(x, y) = xyB_{AC} + x(1-y)B_{AD} + (1-x)yB_{BC} + (1-x)(1-y)B_{BD} + C_{A-B}x(1-x) + C_{C-D}y(1-y)$</td>
</tr>
<tr>
<td>$A_xB_yC_{1-x-y}D$</td>
<td>Linear</td>
<td>$Q(x, y) = xB_{AD} + yB_{BD} + (1-x-y)B_{CD}$</td>
</tr>
<tr>
<td></td>
<td>Quadratic</td>
<td>$Q(x, y) = xB_{AD} + yB_{BD} + (1-x-y)B_{CD} + C_{A-B-C}xy(1-x-y)$</td>
</tr>
</tbody>
</table>

### 1.7.3 Gallium Indium Arsenide Antimonide Ga$_x$In$_{1-x}$As$_y$Sb$_{1-y}$

In this research, Ga$_x$In$_{1-x}$As$_y$Sb$_{1-y}$ epilayers grown by liquid phase epitaxy on GaSb substrates are investigated. Ga$_x$In$_{1-x}$As$_y$Sb$_{1-y}$ is the result of making an alloy between GaSb and InAs and can be rich in GaSb or InAs according to $x$ and $y$ composition factors. Two important qualities of Ga$_x$In$_{1-x}$As$_y$Sb$_{1-y}$ motivate their research:

- Ga$_x$In$_{1-x}$As$_y$Sb$_{1-y}$, as a contacting layer, can be lattice-matched to GaSb, and its smaller band gap allows it to be directly incorporated into a device design, such as the base layer in a TPV p-n junction.
- Ga$_x$In$_{1-x}$As$_y$Sb$_{1-y}$ materials have miscibility gap (see Figure 19) with a critical temperature estimated to be 1467 °C [4], which is pretty interesting.

Every Ga$_x$In$_{1-x}$As$_y$Sb$_{1-y}$ epilayer has specific properties according to the parameters used in their growth and the $x$ and $y$ composition factors resulting. So the purpose of this section is to specify a range of values for any property of any epilayer. Some parameters of Ga$_x$In$_{1-x}$As$_y$Sb$_{1-y}$ are listed in Table 5.
Table 5. Some parameters of Ga$_x$In$_{1-x}$As$_y$Sb$_{1-y}$ (from Levinshtein et al. [4])

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant at 300 K (Å)</td>
<td>6.0959</td>
</tr>
<tr>
<td>Density (g · cm$^{-3}$)</td>
<td>$\rho = 5.69 - 0.08x$</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>$T_m \approx 1100$</td>
</tr>
<tr>
<td>Debye Temperature (K)</td>
<td>$\theta \approx 270$</td>
</tr>
<tr>
<td>Specific heat (J/g °C)</td>
<td>$\cong 0.25$</td>
</tr>
<tr>
<td>Bulk modulus [dyn/cm$^2$]</td>
<td>$B = 5.7 \times 10^{11}$</td>
</tr>
<tr>
<td>Electron affinity</td>
<td>$\chi = (4.87 - 0.81x)$</td>
</tr>
<tr>
<td>Dielectric constant at 300 K</td>
<td></td>
</tr>
<tr>
<td>$\epsilon(0)$</td>
<td>$\epsilon(0) = 15.3 + 0.4x$</td>
</tr>
<tr>
<td>$\epsilon(\infty)$</td>
<td>$\epsilon(\infty) = 12.6 + 1.8x$</td>
</tr>
</tbody>
</table>

1.7.3.1 Structural properties

As expected, the parameters of quaternary alloys such as Ga$_x$In$_{1-x}$As$_y$Sb$_{1-y}$ have complicated expressions. Therefore, Ga$_x$In$_{1-x}$As$_y$Sb$_{1-y}$ has not detailed information about their structural properties. It is known that its crystal structure is zinc-blende, and its lattice constant at 300 K is 6.0959 Å. Further, Guti and O’Reilly [25] presented contours of constant lattice-mismatch as a function of $x$ and $y$ in Ga$_x$In$_{1-x}$As$_y$Sb$_{1-y}$ system grown on a GaSb substrate (see Figure 18).

7.2.2.2 Electrical properties

In Ga$_x$In$_{1-x}$As$_y$Sb$_{1-y}$, the energy gap at 300 K increases progressively from 0.3 $eV$ to 0.7 $eV$ approximately as the $x$ composition factor is increased. Karouta et al. [26] derived an expression for this behavior at 300 K and it is shown below:

$$E_g \cong 0.725x + 0.290(1 - x) - 0.6x(1 - x) \ (eV) \quad (30)$$
Furthermore, the energy gap has a miscibility region within which changes its trend (for details see Figure 19).
The behavior of the energy separation between the conduction band minimum and the top of the valence band with the $x$ composition factor is shown in Figure 20. Additionally, the Figure 21 shows the variation of the energy spin-orbital splitting with $x$ composition factor. With these data, the Ga$_x$In$_{1-x}$As$_y$Sb$_{1-y}$ band structure is more or less specified.

**Figure 20.** Ga$_x$In$_{1-x}$As$_y$Sb$_{1-y}$. Energy separations between $\Gamma$, $L$ and $X$ condition band minima and top of the valence band vs. composition parameter $x$ for lattice-matched to GaSb (from Levinshtein et al. [4]).

**Figure 21.** Energy of spin-orbital splitting $E_{so}$ vs. composition parameter $x$ for GaInAsSb lattice-matched to GaSb (from Levinshtein et al. [4]).
Mikhailova in Levinstein et al. [4] obtained the variation of the intrinsic carrier concentration with temperature for some specific factors of composition. His results are reflected in Figure 22. Other important parameters are reported in Table 6.

**Figure 22.** Intrinsic carrier concentration vs. temperature for Ga$_x$In$_{1-x}$As$_y$Sb$_{1-y}$ alloys lattice-matched to GaSb. 1. $x = 0$; 2. $x = 0.2$; 3. $x = 0.8$ and 4. $x = 1.0$ (from Levinshtein et al. [4]).

**Table 6.** Some electrical parameters of Ga$_x$In$_{1-x}$As$_y$Sb$_{1-y}$ (from Levinshtein et al. [4])

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effective density of states in the conduction band $N_c$ ($cm^{-3}$)</td>
<td>$N_c = 4.82 \times 10^{15} (0.022 + 0.03x - 0.012x^2)^{3/2}T^{3/2}$</td>
</tr>
<tr>
<td>Effective density of states in the valence band $N_v$ ($cm^{-3}$)</td>
<td>$N_v = 4.82 \times 10^{15} (0.41 + 0.16x - 0.23x^2)^{3/2}T^{3/2}$</td>
</tr>
<tr>
<td>Effective electron mass $m_e$</td>
<td>$m_e = (0.022 + 0.03x - 0.012x^2)m_o$</td>
</tr>
<tr>
<td>Effective mass of density states $m_v$</td>
<td>$m_v = (0.41 + 0.16x + 0.023x^2)m_o$</td>
</tr>
<tr>
<td>Effective hole masses (heavy) $m_h$</td>
<td>$m_h \equiv 0.4m_o$</td>
</tr>
<tr>
<td>Effective hole masses (light) $m_{lp}$</td>
<td>$m_{lp} = (0.025 + 0.025x)m_o$</td>
</tr>
</tbody>
</table>
Chapter 2

EXPERIMENTAL PROCEDURES

In this chapter, the reader will find the performed procedures in order to get ohmic contacts on substrates of GaSb and Ga\textsubscript{x}In\textsubscript{1-x}As\textsubscript{y}Sb\textsubscript{1-y} epilayers grown on GaSb substrates. The experimental work will be exhibited in two steps. The first step is to introduce the reader to the proposal of this research so that the contacts are ohmic. For this, the general process will be deployed as a set of steps or procedures. Secondly, each procedure in the process will be described briefly and concisely.

2.1 Processes

To make ohmic contacts is necessary to know in detail the physical aspects involved and the procedures to minimize or accentuate any of those aspects. Within the physical properties mentioned in the first chapter are the work function of the metal or alloy, the work function of the semiconductor and the surface characteristics of the semiconductor. With this in mind, the next step is to select the physical mechanism that makes ohmic contact. The mechanisms are summarized in two, Schottky ohmic contact and tunneling. In this regard, several methods that improve the contact resistance will be discussed below. When a method or a combination of methods is selected, definitively, it must be specified a procedure for reducing the density of states on the semiconductor surface. Without a suitable passivation method, the contact will be probably a Schottky barrier. Finally, some steps to improve the contact resistance must be added to the process.
A variety of configurations is possible in the fabrication of devices based III-V semiconductor compounds. Within that, Hurtado [27] proposed the configuration shown in Figure 23. To fabricate and characterize the device, ohmic contacts on n-type Ga$_x$In$_{1-x}$As$_y$Sb$_{1-y}$ epilayer and p-type InAs$_x$Sb$_{1-x}$ epilayer must be gotten. Based on the above statement, this research has tried different procedures on GaSb substrates and Ga$_{0.86}$In$_{0.14}$As$_{0.13}$Sb$_{0.87}$ epilayers growth on GaSb. Noteworthy that it is not necessary to present the process, the results and the respective analysis to say that obtaining ohmic contacts on those compounds is not an easy task. Perhaps for that reason Rideout [11] wrote, “It is probably a fair assessment, however, that the ohmic contact technology has developed thus far more as a technical art than as a science.”

Looking at the Figure 23, if the contact was ohmic on Ga$_{0.86}$In$_{0.14}$As$_{0.13}$Sb$_{0.87}$ epilayer, it would be due to the tunnel effect by the high concentration of carriers in the semiconductor. In the design of the device, Ga$_{0.86}$In$_{0.14}$As$_{0.13}$Sb$_{0.87}$ epilayer has two functions. One is to serve how a buffer layer between the GaSb substrate and the n-type InAsSb epilayer; the other, equally important, is to change the conductivity from p-GaSb substrate to n-Ga$_{0.86}$In$_{0.14}$As$_{0.13}$Sb$_{0.87}$ epilayer. On the other hand, seeing it from the theory of contact, Ga$_{0.86}$In$_{0.14}$As$_{0.13}$Sb$_{0.87}$ epilayer originates an interfacial semiconductor–semiconductor heterojunction with the lower-band gap semiconductor in contact with the metal. Furthermore, it is important to mention that the metal contact must include layers acting as diffusion barriers in order to ensure the integrity of the device.

**Figure 23.** Schematic diagram of the mesa structure (from Hurtado [27]).
The general process followed in this research consists of the following procedures:

1. Cleaning
2. Passivation
3. Pre-metallization thermal annealing process
4. Photolithography
5. Deposition of metal by evaporation
6. Metallization lift-off process
7. Post-metallization thermal annealing process

The Table 7 shows how the samples were labeled and the received process.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Label</th>
<th>Dimensions</th>
<th>Steps</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-GaSb substrate</td>
<td>A</td>
<td>5mmx5mmx513(\mu m)</td>
<td>1, 2, 3, 4, 5, 6 and 7 Note: Step 7 at 300 °C</td>
</tr>
<tr>
<td>n-GaSb substrate</td>
<td>B</td>
<td>4.5mmx4.5mmx513(\mu m)</td>
<td>1, 2, 4, 5, 6 and 7 Note: Step 7 at 300 °C</td>
</tr>
<tr>
<td>n-GaSb substrate</td>
<td>C</td>
<td>4mmx4mmx513(\mu m)</td>
<td>1, 4, 5, 6 and 7 Note: Step 7 at 300 °C</td>
</tr>
<tr>
<td>n-GaSb substrate</td>
<td>D</td>
<td>4mmx4mmx513(\mu m)</td>
<td>1, 2, 3, 4, 5 and 6</td>
</tr>
<tr>
<td>n-GaSb substrate</td>
<td>E</td>
<td>4mmx4mmx513(\mu m)</td>
<td>1, 2, 3, 4, 5, 6 and 7 Note: Step 7 at 350 °C</td>
</tr>
<tr>
<td>n-GaSb substrate</td>
<td>F</td>
<td>4mmx4mmx513(\mu m)</td>
<td>1, 2, 4, 5, 6 and 7 Note: Step 7 at 350 °C</td>
</tr>
<tr>
<td>n-GaSb substrate</td>
<td>G</td>
<td>4.5mmx4.5mmx513(\mu m)</td>
<td>1, 4, 5, 6 and 7 Note: Step 7 at 350 °C</td>
</tr>
<tr>
<td>n-GaSb substrate</td>
<td>H</td>
<td>5mmx5mmx513(\mu m)</td>
<td>1, 2, 3, 4, 5, 6 and 7 Note: Step 7 at 400 °C</td>
</tr>
<tr>
<td>n-GaSb substrate</td>
<td>J</td>
<td>5mmx5mmx513(\mu m)</td>
<td>1, 2, 4, 5, 6 and 7 Note: Step 7 at 400 °C</td>
</tr>
<tr>
<td>n-GaInAsSb films</td>
<td>CE205</td>
<td>3mmx4mmx515(\mu m)</td>
<td>1, 2, 3, 4, 5, 6 and 7 Note: Step 7 at 350 °C</td>
</tr>
<tr>
<td></td>
<td>CE229</td>
<td>3.5mmx3.5mmx515(\mu m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CE240</td>
<td>3.5mmx4.5mmx515(\mu m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CE241</td>
<td>3.5mmx4mmx515(\mu m)</td>
<td></td>
</tr>
</tbody>
</table>
2.2 Cleaning and passivation

At the first pages of this thesis, the effects of native oxide and surface density of states on a metal-semiconductor contact have been clearly exposed. Now is the time of submitting the proposal of this research to reduce its effects. The cleaning and passivation procedures, developed by the Laboratory of Liquid Phase Epitaxy at CINVESTAV, have been tested on GaSb substrates and Ga$_{0.86}$In$_{0.14}$As$_{0.13}$Sb$_{0.87}$ epilayers.

The samples used in those experiments were n-GaSb (100) substrates doped around $8 \times 10^{15} \text{ cm}^{-3}$ (from measurements using the four-point method) and n-Ga$_{0.86}$In$_{0.14}$As$_{0.13}$Sb$_{0.87}$ epilayers doped in the range of $5 \times 10^{15} - 8 \times 10^{16} \text{ cm}^{-3}$, both doped with Te. All the samples were initially degreased in two steps. First, they were dipped in boiling acetone; then, they were dipped in boiling methanol. The organic strips were removed by dipping the samples in sulfuric acid (H$_2$SO$_4$) and with successive rinses in methanol. The native oxide was removed with hydrofluoric acid (HF) and hydrochloric acid (HCl), one after the other. Ending the cleaning procedure, the samples were dipped in isopropanol (for additional information see [28 - 29]). The treatment times are summarized in Table 8.

Table 8. Summary of cleaning time

<table>
<thead>
<tr>
<th>Samples</th>
<th>Chemical name</th>
<th>Chemical formula</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaSb substrates</td>
<td>Acetone</td>
<td>$CH_3(CO)CH_3$</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Methanol</td>
<td>$CH_3OH$</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Sulfuric acid</td>
<td>$H_2SO_4$</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Hydrofluoric acid</td>
<td>$HF$</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Hydrochloric acid</td>
<td>$HCl$</td>
<td>5</td>
</tr>
<tr>
<td>Ga$<em>{0.86}$In$</em>{0.14}$As$<em>{0.13}$Sb$</em>{0.87}$ epilayers</td>
<td>Acetone</td>
<td>$CH_3(CO)CH_3$</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Methanol</td>
<td>$CH_3OH$</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Sulfuric acid</td>
<td>$H_2SO_4$</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Hydrofluoric acid</td>
<td>$HF$</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Hydrochloric acid</td>
<td>$HCl$</td>
<td>2</td>
</tr>
</tbody>
</table>
The substrate surfaces, except C and G substrates, and the epilayers were passivated with sulfur. Specifically, an aqueous solution of sodium sulfide (Na$_2$S:9H$_2$O) ($pH$~14) with molarity of 1.0 $M$ at room temperature was deposited on each surface. After 6 minutes, samples were dropped, rinsed with deionized water and blown dry with nitrogen (N$_2$).

### 2.3 Pre-metallization thermal annealing procedure

A pre-metallization experimental annealing was included in the process. Some of the samples of GaSb and the whole of Ga$_{0.86}$In$_{0.14}$As$_{0.13}$Sb$_{0.87}$ epilayers were annealed at 125 $^\circ$C in a nitrogen atmosphere. The thermal annealed was carried out in the *MILA-5000*, made by ULVAC-RIKO (see Figure 24). As can be seen in Figura 25, the *MILA-5000* consists of infrared lamps installed on bottom of the chamber, a thermally insulated chamber within which the process is accomplished, a quartz tube sample holder, a thermal shield, a cooling system and inlet and outlet ports of water and gasses. The system is cooled by both water circulation and nitrogen flow. A thermocouple senses the temperature of the sample and transfers such information to the control system.

*Figure 24. Model MILA-5000 Infrared Lamp Heating System.*
The graphs displayed by *CX-THERMO* software [31] are shown in Figure 26 and Figure 27. In Table 9 are listed the main parameters of process.

**Table 9. Parameters of pre-metallization thermal annealing process.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value or Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial temperature (°C)</td>
<td>18.5</td>
</tr>
<tr>
<td>Heating rate (°C/s)</td>
<td>21.3</td>
</tr>
<tr>
<td>Process temperature (°C)</td>
<td>125</td>
</tr>
<tr>
<td>Cooling ramp to 53 °C (°C/min)</td>
<td>5.25</td>
</tr>
<tr>
<td>Process time (min)</td>
<td>60</td>
</tr>
<tr>
<td>Initial pressure (Torr)</td>
<td>$3.45 \times 10^{-5}$</td>
</tr>
<tr>
<td>Process pressure (Torr)</td>
<td>$6.45 \times 10^1$</td>
</tr>
<tr>
<td>Initial speed turbo pump (rpm)</td>
<td>90000</td>
</tr>
<tr>
<td>Process speed turbopump (rpm)</td>
<td>1800</td>
</tr>
<tr>
<td>Nitrogen flow (slm)</td>
<td>1.0</td>
</tr>
<tr>
<td>PID controller constants:</td>
<td></td>
</tr>
<tr>
<td>Proportional</td>
<td>5.0</td>
</tr>
<tr>
<td>Integral</td>
<td>5.0</td>
</tr>
<tr>
<td>Derivative</td>
<td>1.2</td>
</tr>
<tr>
<td>GaSb samples</td>
<td>A, D, E and H</td>
</tr>
<tr>
<td>Ga$<em>{0.86}$In$</em>{0.14}$As$<em>{0.15}$Sb$</em>{0.87}$ epilayers</td>
<td>CE205, CE229, CE240 and CE241</td>
</tr>
</tbody>
</table>
Figure 26. Temperature profile of a pre-metallization thermal annealing procedure. B, C, D, E, F, G and J GaSb substrates and Ga$_{0.86}$In$_{0.14}$As$_{0.13}$Sb$_{0.87}$ epilayers. The horizontal axis is the time and the vertical axis is the temperature.

Figure 27. Temperature profile of a pre-metallization thermal annealing procedure. A and H GaSb substrates. The horizontal axis is the time and the vertical axis is the temperature.
2.4 Photolithography

In photolithography, there are two basic questions. What were elements used and what was the procedure? In this research, a set of special accessories for small samples was used. The set includes a special chuck for the spinner (see Figure 28), three small beakers and two tweezers, a metallic and other one of Teflon. A negative photoresist was used. The photoresist \( AZ\ nLOF\ 2070 \), made by AZ Electronic Materials, is special for metal lift-off applications \[32\]. The developer \( AZ\ 326\ MIF \), also made by AZ Electronic Materials, was used for develop the photoresist \[33\]. Samples with photoresist were exposed to ultraviolet light in a mask aligner to 3-inch wafers (see Figure 29). The initial proposal was to expose the samples on a mask aligner set up for 2.5 inch wafers, but some drawbacks motivated the execution of tests with the \( SUSS\ MA\ 56M\ Mask\ Aligner \), made by KARL SUSS, set up for 3-inch wafers \[34\]. For that reason, the mask is 2.5-inch. The design and structure of each die in the mask is shown in Figure 30.

![Figure 28. Chuck placed on spinner. a) Chuck without sample; b) chuck with sample.](image-url)
In short, the photolithographic procedure, for each sample, was as follows:

- **Initial heating**: In order to reduce the humidity of the sample, the sample was placed on a hot-plate to 110 °C for 30 s.
- **Deposit of photoresist**: A drop of photoresist was applied on the surface of the sample with a dropper; then, the spinner was activated at 5000 rpm for 30 s.
- **Softbake**: The sample was placed on hot-plate to $110 \, ^{\circ}C$ for $1 \, \text{min}$.
- **Exposure**: After the sample was positioned at the mask aligner correctly, and the vacuum was reached, the sample was exposed to ultraviolet radiation for $10 \, \text{s}$.
- **Post-exposure bake**: The sample was placed on hot-plate to $110 \, ^{\circ}C$ for $40 \, \text{s}$.
- **Developed**: the sample was dipped in the developer for $40 \, \text{s}$. Finally, the sample was rinsed with water and, then, it was dried in a dry nitrogen flow.

As can be seen in Figure 31, the mask patterns have been faithfully transferred to GaSb substrates.

### 2.5 Deposition of metal by evaporation

To manufacture ohmic contacts on III-V semiconductor compounds not only the contacts must be ohmic but also the metal, the metal alloy and/or the combination of metal films must satisfy certain requirements. Then, the choice of metals must take into account that the contact is ohmic and satisfies the requirements. The requirements for an ohmic contact have been already discussed during the thesis, but not the general and specific requirements that the contacts must achieve in this research. The main requirements are:

- Low specific contact resistivity (of the order of $10^{-4} \, \Omega \cdot cm^2$)
- Shallow contacts (less than $1 \, \mu m$)
- Good adhesion to the substrate or epilayer
- Stable over time
- Resistant to corrosion
• Controllable thickness and uniformity of the deposit

![Image of samples](image)

**Figure 31.** Photographs taken to samples after the photolithography procedure. a) Unpassivated surface of silicon sample; b) unpassivated surface of GaSb substrate; c) passivated surface of GaSb substrate.

Rideout [11] proposed indium (In) as contact material for GaSb, both n-type and p-type. In Figure 32 is shown the band diagram for In and GaSb, both before and after contact; while, in Figure 33 is shown the band diagram for In and GaInAsSb, both before and after contact. Although those figures reflect the formation of a Schottky ohmic contact, segregation coefficient of In in GaSb is 1, therefore it is expected that In diffuse into GaSb; furthermore, the resistivity of In is three times
greater than Al. To prevent diffusion of In is well known that palladium (Pd) acts as a diffusion barrier. Pd is effective in that work, and it does not alter the formation of the contact as long as its thickness does not exceed a few nanometers [35 - 36]. If that premise is unfulfilled, the junction will form a barrier Shottky (see Figure 34 and Figure 35). In order to reduce the contact resistance and increase resistance to corrosion, this research considered Au-Ge and Au as metal layers.

**Figure 32.** Band diagram for contact between In and GaSb, before (left) and after (right) contact.

**Figure 33.** Band diagram for contact between In and GaInAsSb, before (left) and after (right) contact.
Given the list of requirements and the above analysis, in this work has been proposed Pd/In/Pd/Au-Ge/Pd/Au (40/400/40/500/40/1000 Å) ohmic contacts to n-GaSb substrates and n-Ga_{0.86}In_{0.14}As_{0.13}Sb_{0.87} epilayers doped with Te. Pd provides good adhesion and acts as a diffusion barrier [37]. Additionally, Pd presents intrinsic stability at high temperatures and some studies show that with the inclusion of a Pd layer, the contact region is less than 10 nm [37]. In is the crucial metal which undergoes a solid phase regrowth forming the ohmic contact. During the post-metallization thermal annealing process is expected that Sb atoms reach the In layer and form together with In atoms a semi-metallic film of InSb (see Figure 36). As can be seen in Figure 37 and Figure 38, the interfacial layer is
GaInSb; then, this is other way to make ohmic contacts. The intermediate Pd layer is exclusively a barrier for subsequently deposited metals. The Au-Ge alloy contributes doping with Ge. Summarizing this part, it is expected that, intermediate Pd layer obstructs the Au atoms mainly due to the difference in atomic weight of Ge, Pd and Au atoms. The third layer of Pd is again a barrier for Au atoms of the last layer.

**Figure 36.** a) Auger sputtering profile of Pd/Ge/Pd/In/Pd contacts to GaSb:Te as deposited. b) Auger sputtering profile of Pd/Ge/Pd/In/Pd contacts to GaSb:Te after 300 °C sintering (from Ikossi et al. [37]).

**Figure 37.** Ohmic contact between InSb and GaSb.
All the metallizations were performed sequentially in e-beam evaporator, made by BALZERS (see Figure 39) [38], using elemental sources only and under high vacuum \( (1 \times 10^{-5} \text{ Torr}) \). Since the samples are at most 4mmx4mm, they do not fit directly to the planetary; then, it was necessary to design a layout in CircuitCAM and to manufacture it on an aluminum foil. The design is shown in the Figure 40, while the location of the samples on foil is shown in Figure 41. Some additional data about each evaporated metal are included in Table 10 and Table 11.
**Figure 40.** Schematic layout of the sample holder designed over CircuitCAM a) bottom layer b) top layer.

**Figure 41.** Location of samples on aluminum foil before and during the evaporation.

**Table 10.** Data of the top contact metallization of the sample

<table>
<thead>
<tr>
<th>Layer</th>
<th>Metal</th>
<th>Programming</th>
<th>Current range (mA)</th>
<th>Deposit ratio (Å/s)</th>
<th>Time (min)</th>
<th>Thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First</td>
<td>Palladium</td>
<td>Density: 12.038 (g/cm³) Z-ratio: 0.357</td>
<td>40 – 50</td>
<td>1 – 2</td>
<td>0.5</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tooling: 103.7 %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Second</td>
<td>Indium</td>
<td>Density: 7.300 (g/cm³) Z-ratio: 0.841</td>
<td>7 – 8</td>
<td>3 – 4</td>
<td>2.0</td>
<td>408</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tooling: 103.7 %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Third</td>
<td>Palladium</td>
<td>Density: 12.038 (g/cm³) Z-ratio: 0.357</td>
<td>40 – 50</td>
<td>1 – 2</td>
<td>0.6</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tooling: 103.7 %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fourth</td>
<td>Gold-Germanium</td>
<td>Density: 19.300 (g/cm³) Z-ratio: 0.381</td>
<td>40 – 45</td>
<td>2 – 3</td>
<td>3.4</td>
<td>502</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tooling: 103.7 %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fifth</td>
<td>Palladium</td>
<td>Density: 12.038 (g/cm³) Z-ratio: 0.357</td>
<td>40 – 50</td>
<td>1 – 2</td>
<td>0.6</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tooling: 103.7 %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sixth</td>
<td>Gold</td>
<td>Density: 19.300 (g/cm³) Z-ratio: 0.381</td>
<td>50 – 65</td>
<td>4.9 – 5</td>
<td>3.5</td>
<td>1002</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tooling: 103.7 %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 11. Data of the bottom contact metallization of the sample

<table>
<thead>
<tr>
<th>Layer</th>
<th>Metal</th>
<th>Programming</th>
<th>Current range (mA)</th>
<th>Deposit ratio (Å/s)</th>
<th>Time (min)</th>
<th>Thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First</td>
<td>Palladium</td>
<td>Density: 12.038 (g/cm³)</td>
<td>40 – 50</td>
<td>1 – 2</td>
<td>0.5</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Z-ratio: 0.357</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tooling: 103.7 %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Second</td>
<td>Indium</td>
<td>Density: 7.300 (g/cm³)</td>
<td></td>
<td>Lack</td>
<td>2.3</td>
<td>580</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Z-ratio: 0.841</td>
<td></td>
<td>Lack</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tooling: 103.7 %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Third</td>
<td>Palladium</td>
<td>Density: 12.038 (g/cm³)</td>
<td>40 – 50</td>
<td>1 – 2</td>
<td>1.2</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Z-ratio: 0.357</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tooling: 103.7 %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fourth</td>
<td>Gold-Germanium</td>
<td>Density: 19.300 (g/cm³)</td>
<td>40 – 45</td>
<td>2 – 3</td>
<td>3.4</td>
<td>502</td>
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<tr>
<td></td>
<td></td>
<td>Z-ratio: 0.381</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tooling: 103.7 %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fifth</td>
<td>Palladium</td>
<td>Density: 12.038 (g/cm³)</td>
<td>45 – 50</td>
<td>1 – 2</td>
<td>1.2</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Z-ratio: 0.357</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td>Tooling: 103.7 %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sixth</td>
<td>Gold</td>
<td>Density: 19.300 (g/cm³)</td>
<td>50 – 65</td>
<td>4.9 – 5</td>
<td>3.5</td>
<td>1002</td>
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<tr>
<td></td>
<td></td>
<td>Z-ratio: 0.381</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tooling: 103.7 %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.6 Metal lift-off process

As technique of defining metal pattern on the GaSb substrates and the Gaₐ₀.₈₆In₀.₁₄As₀.₁₃Sb₀.₈₇ epilayers a lift-off process has been used. This technique is not new, and even though it has been modified in some aspects, the basic idea is still maintained. As can be seen in Figure 42, metal lift-off process consists of three basic steps:

- Photoresist pattern definition
- Metal evaporation
- Photoresist stripping, thereby lifting off the overlying metal
The first two steps were shown in previous subsections, now the third step will be tackled. The procedure consists in dipping the samples in a small beaker with acetone and ultrasonic vibrator during the time required. After that the samples are rinsed in isopropanol and finally blown dry with nitrogen. The success depends on some considerations [39] and the experience of the person who implements it. The main considerations are related with the metal thickness on the bottom of photoresist bars and how brittle is the metal. If either the metal at the bottom of photoresist bars is greater than about 100 Å or metal is not sufficiently brittle, it will be difficult to crack the metal deposited on the sides of the photoresist. Moreover, the metal layer thickness should not exceed about 2/3 of the thickness of the photoresist, in order to assure complete separation of the two portions of the metal layer [40]. In this case, it is worth noting that Au is a brittle and ductile metal, and the thickest layer in this work. Other considerations are related to processes of photolithography and evaporation. The beam of ultraviolet light during the exposure process in photolithography must fall perpendicular to the sample surface; furthermore, the most of the metal atoms during e-beam evaporation must be deposited in direction normal to the surfaces of the samples. Regarding the experience with this technique, the main drawback was the process time. The photolithographic process was sequential (a process began until previous process ended); then, when metal and photoresist were lifted off, the first

Figure 42. Schematic illustration of the steps of the metal lift-off process. a) Patterns are defined by deposit of photoresist and photolithography process; b) metal is deposited by e-beam evaporation; c) metal and photoresist are lifted off.
sample had more process time than any other. For that reason, metal lift-off process took from 30 s to 90 s depending on which sample was treated. Some results of the metal lift-off process are shown in Figure 43.

![Figure 43](image)

**Figure 43.** Photographs taken to CE240 sample after the lift-off process. a) Circular contact resistance test structure (CCRTS); b) circular contact.

### 2.7 Post-metallization thermal annealing process

A thermal process was executed on samples after the I-V measurements. Only D sample did not receive this annealing. The annealing purposes are:

- To perform metal alloy
- To restructure the contact interface

Ikossi et al. [37] reported a minimum specific contact resistance of $1.2 \times 10^{-6} \Omega \cdot cm^2$ on GaSb:Te doped to $5.6 \times 10^{17} \text{cm}^{-3}$ sintered at $300 \, ^\circ C$ for 60 s under forming gas flow and realized the research in the range $250 \, ^\circ C$ to $400 \, ^\circ C$; Dutta et al. [23] reported ohmic contacts to p-GaSb doped in the range of $8 \times 10^{16} - 1 \times 10^{19} \text{cm}^{-3}$ with a specific contact resistivity in the range of $10^{-4} - 10^{-6} \Omega \cdot cm^2$
after annealing in the range of $250 - 350 \, ^\circ C$ for $10 - 30 \, min$. From those studies and taking into account the tests to be performed, in this research, three different annealing temperatures were tested in the range $300 \, ^\circ C$ to $400 \, ^\circ C$ for GaSb substrates and only one of $350 \, ^\circ C$ for $\text{Ga}_{0.86}\text{In}_{0.14}\text{As}_{0.13}\text{Sb}_{0.87}$ epilayers (see Table 7).

The thermal process was carried out within the thermally insulated chamber $\text{MILA-5000}$ (RTP), made by ULVAC-RIKO, in nitrogen atmosphere. As can be seen in Figure 45, the samples were placed in the quartz tube sample holder. $\text{Type-K}$ thermocouple, which senses the temperature and transmits this information to the controller E5AR, was put in touch on the central sample in each process. Information about the exact location of the samples in the quartz tube sample holder is displayed in Figure 45. After closing the chamber door of the $\text{MILA-5000}$, the $\text{HiCube}$ turbopumping stations (see Figure 46) [41 - 44], made by PFEIFFER VACUUM, started to operate and thus to achieve high vacuum. Once the camera reaches the high vacuum, the speed of the turbopump was reduced to $90000 \, rpm$ to $1800 \, rpm$. Only until then, the valve that allows the entry of nitrogen was opened. Soon thereafter (maximum one minute) the schedule process in the $\text{CX-THERMO}$ software was started. The heating was done with the infrared lamps, while the cooling was performed by water circulation and nitrogen flow. Finally,
when the sample reached room temperature, the chamber door of the MILA-5000 was opened and the samples were removed from the quartz tube sample holder. The graphs displayed by CX-THERMO software are shown in the Figure 47, Figure 48 and Figure 49. The parameters of each rapid thermal process are listed in Table 12.

**Figure 45.** Location of samples in the quartz tube sample holder for each rapid thermal process. a) 300 °C; b) 350 °C; c) 400 °C.

**Figure 46.** The HiCube turbopumping stations.
Table 12. Parameters of each post-metallization rapid thermal process.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>RTP to 300 °C</th>
<th>RTP to 350 °C</th>
<th>RTP to 400 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial temperature (°C)</td>
<td>18.0</td>
<td>18.0</td>
<td>17.9</td>
</tr>
<tr>
<td>Heating rate (°C/s)</td>
<td>40.3</td>
<td>36.9</td>
<td>38.2</td>
</tr>
<tr>
<td>Cooling ramp (°C/min)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>to 225 (°C)</td>
<td>35.0</td>
<td>64.3</td>
<td>80</td>
</tr>
<tr>
<td>to 100 (°C)</td>
<td>16.3</td>
<td>17.0</td>
<td>17.3</td>
</tr>
<tr>
<td>Process time (s)</td>
<td>60</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Initial pressure (Torr)</td>
<td>3.45 × 10⁻⁵</td>
<td>3.45 × 10⁻⁵</td>
<td>4.05 × 10⁻⁵</td>
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<td>Process pressure (Torr)</td>
<td>6.45 × 10¹</td>
<td>6.45 × 10¹</td>
<td>6.45 × 10¹</td>
</tr>
<tr>
<td>Initial speed turbopump (rpm)</td>
<td>90000</td>
<td>90000</td>
<td>90000</td>
</tr>
<tr>
<td>Process speed turbopump (rpm)</td>
<td>1800</td>
<td>1800</td>
<td>1800</td>
</tr>
<tr>
<td>Nitrogen flow (slm)</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>PID controller constants:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Proportional</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Integral</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Derivative</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>GaSb samples</td>
<td>A, B and C</td>
<td>D, E, F and G</td>
<td>H and J</td>
</tr>
<tr>
<td>Ga₀.₈₆In₀.₁₄As₀.₁₃Sb₀.₈₇ epilayers</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.8 Experiments

For the case of Ga₀.₈₆In₀.₁₄As₀.₁₃Sb₀.₈₇ epilayers, some modifications were made to some procedures of the process. When the results of the measurements were displayed and analyzed, some questions arose. To resolve them, three tests on three additional samples were carried out. Three procedures were modified:

- Both the chemicals and the reaction time during the cleaning procedure.
- The temperature of the pre-metallization thermal annealing procedure.
- The metal layers during deposition of metals by evaporation.
Samples of CE240 and CE241 growth processes were used for these experiments. The first experiment was to modify the reaction time. To do this, the CE241 sample was used and the time was varied from 2 min to 5 min. That experiment allowed us to identify the effects of the reaction time on the metal-semiconductor contact. To recognize and extend the quality of the passivation process, two more experiments were planned; the first was to remove the hydrochloric acid (HCl) of the cleaning procedure, and the second was to increase the temperature to 250 °C during the pre-metallization thermal annealing procedure. In this case, two CE240 samples were used. Regarding the metallization scheme, Pd/Au-Ge/Pd/Au layers were deposited on all the samples (one CE241 sample and two CE240 samples). In this case was considered that indium is not necessary because Ga$_{0.86}$In$_{0.14}$As$_{0.13}$Sb$_{0.87}$ epilayers already contain indium [45 - 46]. To prevent confusion with the other samples of CE240 and CE241 growth processes, the samples from these experiments have been named CE2401, CE2402 and CE2411. The Figure 47, Figure 48 and Figure 49 show the temperature profiles of the thermal process. The Table 13 and Table 14 summarize the main details of the experiments.

![Figure 47. Temperature profile of a pre-metallization rapid thermal process to 125 °C (CE2401 sample). The horizontal axis is the time and the vertical axis is the temperature.](image-url)
Figure 48. Temperature profile of a pre-metallization rapid thermal process to 250 °C (CE2411 and CE2402 samples). The horizontal axis is the time and the vertical axis is the temperature.

Figure 49. Temperature profile of a Post-metallization rapid thermal process to 350 °C (CE2411, CE2401 and CE2402 samples). The horizontal axis is the time and the vertical axis is the temperature.
Table 13. Summary of the cleaning procedure.

<table>
<thead>
<tr>
<th>Samples of Ga_{0.86}In_{0.14}As_{0.13}Sb_{0.87}</th>
<th>Chemical name</th>
<th>Chemical formula</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CE2411</td>
<td>Acetone</td>
<td>CH_{3}(CO)CH_{3}</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Methanol</td>
<td>CH_{3}OH</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Sulfuric acid</td>
<td>H_{2}SO_{4}</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Hydrofluoric acid</td>
<td>HF</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Hydrochloric acid</td>
<td>HCl</td>
<td>5</td>
</tr>
<tr>
<td>CE2401 and CE2402</td>
<td>Acetone</td>
<td>CH_{3}(CO)CH_{3}</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Methanol</td>
<td>CH_{3}OH</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Sulfuric acid</td>
<td>H_{2}SO_{4}</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Hydrofluoric acid</td>
<td>HF</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 14. Temperatures of the pre-metallization thermal annealing procedure.

<table>
<thead>
<tr>
<th>Samples of Ga_{0.86}In_{0.14}As_{0.13}Sb_{0.87}</th>
<th>Process temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CE2411</td>
<td>250</td>
</tr>
<tr>
<td>CE2401</td>
<td>125</td>
</tr>
<tr>
<td>CE2402</td>
<td>250</td>
</tr>
</tbody>
</table>

Finally, two Ga_{0.86}In_{0.14}As_{0.13}Sb_{0.87} epilayers (CE113 and CE118) at doping density of the order of \(10^{17} \text{ cm}^{-3}\) were tested. The doping density of the CE113 was about \(4 \times 10^{17} \text{ cm}^{-3}\), while the doping density of the CE118 was about \(8 \times 10^{17} \text{ cm}^{-3}\) (data supplied by the Laboratory of Liquid Phase Epitaxy at CINVESTAV). The Table 15 summarizes the complete manufacturing process on CE113 and CE118 samples.
Table 15. Manufacturing process of metal-semiconductor contacts on Ga$_{0.86}$In$_{0.14}$As$_{0.13}$Sb$_{0.87}$ epilayers with a doping level of the order of 10$^{17}$ cm$^{-3}$ (CE113 and CE118 samples).

<table>
<thead>
<tr>
<th>Cleaning procedure</th>
<th>Chemical name</th>
<th>Chemical formula</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>$CH_3(CO)CH_3$</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>$CH_3OH$</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>$H_2SO_4$</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Hydrofluoric acid</td>
<td>$HF$</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Passivation procedure</th>
<th>Chemical name</th>
<th>Chemical formula</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution of sodium sulfide</td>
<td>Na$_2$S:9H$_2$O</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pre-metallization thermal annealing procedure</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Nitrogen flow (slm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>60</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metal layers</th>
<th>Layer</th>
<th>Metal</th>
<th>Thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First</td>
<td>Palladium</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Second</td>
<td>Gold-Germanium</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>Third</td>
<td>Palladium</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Fourth</td>
<td>Gold</td>
<td>1000</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Post-metallization thermal annealing procedure</th>
<th>Temperature (°C)</th>
<th>Time (s)</th>
<th>Nitrogen flow (slm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>60</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>
Chapter 3

MEASUREMENTS AND RESULTS

In the previous chapter, the specific process for each of the samples was defined; now, the analysis of the results bearing in mind the theoretical fundamentals is necessary. Electrical measurements are a valid tool to characterize metal-semiconductor contacts, because its results reflect the properties of the object under study (both metalized GaSb substrates and metalized Ga_{0.86}In_{0.14}As_{0.13}Sb_{0.87} epilayers). In this research, I-V and C-V electrical measurements were carried out in order to analyze various aspects, including the effects of each step of the process (cleaning, passivation, pre-metallization annealing, metal layers and post-metallization annealing) and the main parameters of the contacts (contact resistance, specific contact resistivity, sheet resistance and transfer length). To accomplish this, not only is enough to measure but also perform data processing taking into account the theory. In this chapter will be exposed the way in which data were obtained and the results of their processing.

3.1 Overview of electrical measurements

Before starting the measurements, each circular contact resistance test structure (CCRTS) was assigned a Roman number, while each circular structure with the same gap distance was assigned a letter (see Figure 50). Indeed, the name of each measurement data specifies the sample type, the specific procedure, measurement type and equipment, test structure, the circular structure and the number of the measurement (see Table 16 and Figure 51).
**Table 16.** Summary of the notation used to store measurement data

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Notation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GaSb</td>
<td>GaSb substrate</td>
</tr>
<tr>
<td></td>
<td>CE205, CE229, CE240, CE241, CE2401, CE2402, CE2411, CE113 or CE118</td>
<td>$\text{Ga}<em>{0.86}\text{In}</em>{0.14}\text{As}<em>{0.13}\text{Sb}</em>{0.87}$ epilayers</td>
</tr>
</tbody>
</table>

**Procedure**

- A, B, C, D, E, F, G, H or J GaSb substrates

<table>
<thead>
<tr>
<th>Measurement Equipment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3 or 4</td>
</tr>
<tr>
<td>5</td>
</tr>
</tbody>
</table>

**Test structure**

- I, II, III, IV, V, VI, VII or VIII

<table>
<thead>
<tr>
<th>Circular structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
</tr>
<tr>
<td>b</td>
</tr>
<tr>
<td>c</td>
</tr>
<tr>
<td>d</td>
</tr>
<tr>
<td>e</td>
</tr>
<tr>
<td>f</td>
</tr>
</tbody>
</table>

**Measurement number**

- 01, 02, 03…

Successive measurements with positional changes of the measurement tips.

In order to apply CTLM, the measurement tips were put on the samples under procedural order; first, they were placed in the area corresponding to the interest CCRTS; once that was done, they were placed on a circular structure in particular, with one tip on the conducting circular inner region and the other tip on the conducting outer region (see Figure 52).
Figure 50. Schematic representation of the names of the structures of CTLM.

Figure 51. Example of the notation used to store the measured data.

Figure 52. Illustration of a) how and b) where were put the measurement tips on a sample.
The measurement range was variable, sometimes was from $-600 \text{ mV}$ to $600 \text{ mV}$ (higher range) and other times from $-200 \text{ mV}$ to $200 \text{ mV}$ (lower range).

### 3.2 I-V electrical measurements

The I-V electrical measurements were performed both before and after the samples were annealed (step 7). All the samples were measured before the annealing. The measurements were performed with the *Keithley 2400 SourceMeter Instrument* [47 - 48]. A couple of graphs of I-V electrical measurements on GaSb substrate, both before and after the sample was annealed, are shown in Figure 53. It is worth mentioning that the behavior was similar in all GaSb substrates. Regarding the $\text{Ga}_{0.86}\text{In}_{0.14}\text{As}_{0.13}\text{Sb}_{0.87}$ epilayers, the best results were obtained with CE113 and CE118 samples. As can be seen in Figure 54, the slope is not the same in both directions, while the magnitude of the current is the same order of that of GaSb substrate. Similarly, Figure 55 and Figure 56 show the effect of the annealing on the electrical behavior of metal-$\text{Ga}_{0.86}\text{In}_{0.14}\text{As}_{0.13}\text{Sb}_{0.87}$ epilayer contact.

During measurements, the depth at which the tips penetrated the metal layers had an impact on results. For that reason, the post-metallization measurements were done with another measuring station. That station has an *Agilent B1500A Semiconductor Device Analyzer* [49] and a video camera that displays the contact of the tip with the sample.
Figure 53. Measurement data on G sample. a) pre-annealing b) post-annealing.

Figure 54. Measurement data on a) CE113 and b) CE118 samples.
Figure 55. Comparative charts of the effects of annealing on $\text{Ga}_{0.86}\text{In}_{0.14}\text{As}_{0.13}\text{Sb}_{0.87}$ epilayers. a) CE205; b) CE229; c) CE240 and d) CE241.

Figure 56. I-V electrical measurements on GaInAsSb films post-annealed. All on circular structures with the same gap distance (30 $\mu$m).
When the I-V electrical measurements were finished, five steps were executed prior to obtaining the parameters of the contacts (except CE205, CE229, CE240, CE241, CE2401, CE2402 and CE2411 samples, whose conduction mechanism is close to thermionic emission). The steps were linear fit of the data for each measurement, exclusion of some measurements, obtaining of the average total resistance for each gap, application of the correction factor and linear fit of the total resistance.

The correction factor, taking into account that the radius of the inner disc contact is 80 \( \mu m \), was calculated for each gap (see equation 28). The Table 17 lists each correction factor. The experimental CTLM data should be divided by these correction factors in order to get values which can be used for a linear fit. Without these correction factors, the specific contact resistance would be underestimated [46]. The Figure 57 illustrates the effects of applying the correction factor to the experimental CTLM data. From Figure 58 to Figure 65, the results of applying the five steps to the experimental CTLM data are shown.

**Table 17.** Correction factors for each gap spacing. The inner radius is constant. \( R_1 = 80 \mu m \).

<table>
<thead>
<tr>
<th>Gap spacing, ( S (\mu m) )</th>
<th>Correction factor, ( C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.96999</td>
</tr>
<tr>
<td>10</td>
<td>0.94226</td>
</tr>
<tr>
<td>15</td>
<td>0.91653</td>
</tr>
<tr>
<td>20</td>
<td>0.89257</td>
</tr>
<tr>
<td>30</td>
<td>0.84921</td>
</tr>
<tr>
<td>50</td>
<td>0.76812</td>
</tr>
</tbody>
</table>
**B SAMPLE**

![Graph with data points](image)

**Figure 57.** Total resistance plotted versus gap spacing before (black squares) and after (red circles) applying the correction factors.

**A SAMPLE**

![Graph with data points and linear fit](image)

**Figure 58.** Measurement result for Au/Pd/Au-Ge/Pd/In/Pd metal contact to A sample.
Figure 59. Measurement result for Au/Pd/Au-Ge/Pd/In/Pd metal contact to B sample.

Figure 60. Measurement result for Au/Pd/Au-Ge/Pd/In/Pd metal contact to C sample.
**E SAMPLE**

**Procedure:**
1. Cleaning
2. Passivation
3. RTP (125 °C)
4. Photolithography
5. Deposition of metal
6. Metal Lift-off
7. RTP (350 °C)

**Corrected CTLM Data**

**Linear Fit to Corrected CTLM Data**

<table>
<thead>
<tr>
<th>Total Resistance, $R_{total}$ (Ω)</th>
<th>Gap spacing, $S$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation $y = a + bx$</td>
<td></td>
</tr>
<tr>
<td>Adj. R-Squar 0.97652</td>
<td></td>
</tr>
<tr>
<td>Intercept 4.74 258.88m</td>
<td></td>
</tr>
<tr>
<td>Slope 122.28k 9.45k</td>
<td></td>
</tr>
</tbody>
</table>

**Table of Parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact Resistance [ohm]</td>
<td>2.37</td>
<td>129.44m</td>
</tr>
<tr>
<td>Specific Resistivity [ohm cm²]</td>
<td>476.33µ</td>
<td>26.03µ</td>
</tr>
<tr>
<td>Transfer Lenght [µm]</td>
<td>19.37</td>
<td>2.77</td>
</tr>
<tr>
<td>Sheet Resistance [ohm/square]</td>
<td>61.47</td>
<td>4.15</td>
</tr>
</tbody>
</table>

**Figure 61.** Measurement result for Au/Pd/Au-Ge/Pd/In/Pd metal contact to E sample.

---

**F SAMPLE**

**Procedure:**
1. Cleaning
2. Passivation
4. Photolithography
5. Deposition of metal
6. Metal Lift-off
7. RTP (350 °C)

**Corrected CTLM Data**

**Linear Fit to Corrected CTLM Data**

<table>
<thead>
<tr>
<th>Total Resistance, $R_{total}$ (Ω)</th>
<th>Gap spacing, $S$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation $y = a + bx$</td>
<td></td>
</tr>
<tr>
<td>Adj. R-Squar 0.98198</td>
<td></td>
</tr>
<tr>
<td>Intercept 18.31 4.49</td>
<td></td>
</tr>
<tr>
<td>Slope 2.82M 170.60k</td>
<td></td>
</tr>
</tbody>
</table>

**Table of Parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact Resistance [ohm]</td>
<td>9.15</td>
<td>2.24</td>
</tr>
<tr>
<td>Specific Resistivity [ohm cm²]</td>
<td>1.84µ</td>
<td>451.05µ</td>
</tr>
<tr>
<td>Transfer Lenght [µm]</td>
<td>3.24</td>
<td>1.06</td>
</tr>
<tr>
<td>Sheet Resistance [ohm/square]</td>
<td>1.42k</td>
<td>85.75</td>
</tr>
</tbody>
</table>

**Figure 62.** Measurement result for Au/Pd/Au-Ge/Pd/In/Pd metal contact to F sample.

---
Figure 63. Measurement result for Au/Pd/Au-Ge/Pd/In/Pd metal contact to G sample.

Figure 64. Measurement result for Au/Pd/Au-Ge/Pd/In/Pd metal contact to H sample.
Figure 65. Measurement result for Au/Pd/Au-Ge/Pd/ln/Pd metal contact to J sample.

Figure 66. Measurement result for Au/Pd/Au-Ge/Pd metal contact to CE113 sample.
Figure 67. Measurement result for Au/Pd/Au-Ge/Pd metal contact to CE118 sample.

The experimental data processing was done in OriginPro 8.0. Contact parameters were obtained from the linear fit of the total resistance for each gap. The mathematical procedure to obtaining the parameters is based on equation 29 and it is presented below.

The contact resistance $R_c$ is given by:

$$R_c = \frac{a}{2}$$  \hspace{1cm} (31)

where $a$ is the intercept of the straight line with the axis of the total resistance ($R_{total}$). The specific contact resistivity ($\rho_c$) is calculated from the contact resistance ($R_c$) and the area of the inner disc contact ($A_c$), as follows:

$$\rho_c = R_c A_c$$  \hspace{1cm} (32)

As the intercept of the straight line with the axis of the gap spacing ($S$) is twice the transfer length ($L_T$), then:
where $b$ is the slope of the straight line. Finally, the sheet resistance is calculated from the slope and the radius of the inner disc contact ($R_1$):

$$R_{sh} = 2\pi R_1 b$$

(34)

### 3.3 Thermionic-Field Emission

Taking into account the carrier concentration of the Ga$_{0.86}$In$_{0.14}$As$_{0.13}$Sb$_{0.87}$ epilayers (see section 3.4), the equation 4, the information in Table 5 and Table 6, and knowing that the $x$ composition factor is 0.86, a range for energy characteristic ($E_{00}$) may be defined from the following calculations:

$$E_{00\text{min}} = 1.86 \times 10^{-11} \sqrt{\frac{5.0 \times 10^{15}}{15.644 \times 5.075 \times 10^{-3}}} = 4.67 \text{ (meV)}$$

(35)

$$E_{00\text{max}} = 1.86 \times 10^{-11} \sqrt{\frac{8 \times 10^{17}}{15.644 \times 5.075 \times 10^{-3}}} = 59.04 \text{ (meV)}$$

(36)

According to previous information and the Figure 5, the conduction mechanism is thermionic/field emission and it is close to thermionic emission in CE205, CE229, CE240, CE241, CE2401 and CE2402 samples. Rideout [11] presents an appropriate diode equation for both thermionic and thermionic-field emission. The equation is as follows:

$$J = J_r \left\{ \exp \left( \frac{qV}{nk_B T} \right) - \exp \left[ \left( \frac{1}{n} - 1 \right) \frac{qV}{k_B T} \right] \right\}$$

(37)

where $J$ is the total current density, $J_r$ is the reverse flux and $n$ is the ideality factor of the diode. The equation 37 is valid for both reverse and forward flux, because image force, interface layers, and tunneling effects transported in either directions.
The Figure 68 shows the variation of current as the doping density increases within the range of TFE, although that figure shows curves for $n = 4$ and $n = 20$, these values are outside the range under which equation 37 is physically valid.

![Figure 68. Normalized current-voltage characteristic according to equation 37.](image)

To obtain the diode ideality factor ($n$) from the equation 37 may be useful to compare the degree to which the field emission dominates over thermionic emission in each sample [50]. With that propose, a different treatment was given to I-V measurements of CE205, CE229, CE240, CE241 CE2401 and CE2402 samples. As the flow enters the film by a metal-$\text{Ga}_{0.86}\text{In}_{0.14}\text{As}_{0.13}\text{Sb}_{0.87}$ epilayer contact and it out the other contact, actually, the data of measurements are the result of an electron density across two Schottky barriers. In a complete way, electrons flow from the metal to semiconductor, and, then they pass from the semiconductor to metal, or vice versa. The inner disc contact was designed with an area of 0.02 $mm^2$, while the conducting outer region has 0.7 $mm^2$ at best (see Figure 52); then, the conducting outer region has a current capacity 35 times greater than the inner disc contact. For that reason, if a small voltage is
applied, the current will reflect the effects of the Schottky barrier in the inner disc contact mainly. Considering the above statement and according to some initial fits of the equation 37 to the data (i.e. different voltage ranges were tested with the data shown in Figure 69), the selected voltage range to fit data was $-50 \text{ mV}$ to $50 \text{ mV}$. Once the voltage range was selected, the data of the I-V electrical measurements with the B15000A Semiconductor Device Analyzer on samples CE205, CE229, CE240, CE241, CE2401 and CE2402 were fitted by means of *OriginPro 8.0* (according to notation, measurement equipment 3).

![Figure 69](image)

**Figure 69.** I-V electrical measurement on CE229 sample post-annealing. The circle structure is located in CCRTS V and circular structure e.

Regard to equation 37, reverse flux $J_r$ is given by [11]:

$$J_r = A^*T^2 \exp(-q\phi_B/kT')$$  \hspace{1cm} (38)

where $A^* = 4\pi qk^2m^*/\hbar^3 = 120(m_e/m)(A/cm^2 \cdot K^2)$ is Richardson's constant, $m$ is the free electron mass and $m_e$ is the effective electron mass (see Table 6). Then, It is possible to calculate the barrier height from the reverse current solving reverse flux and multiplying by the area of the inner disc contact ($A_c$). Specifically:
\[ \phi_B = -\frac{kT}{q} \ln \left( \frac{I_r}{A^*T^2A_c} \right) \]  

(39)

An example of this procedure is shown in the Figure 70. From this procedure, two averages were obtained per sample, one of the reverse current and other of the ideality factor of the diode. These parameters are listed in Table 18 along with the barrier height.

![Figure 70](image)

**Figure 70.** Nonlinear fit to I-V electrical measurements on CE240 sample. The reverse current \(I_r\) and the factor ideality of diode \(n\) were calculated. Barrier height \(\phi_B\) was calculated from equation 39. The circle structure is located in CCRTS I-V and circular structure f.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CE205</th>
<th>CE229</th>
<th>CE240</th>
<th>CE241</th>
<th>CE2401</th>
<th>CE2402</th>
<th>CE113</th>
<th>CE118</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reverse current (I_r) ((\mu A))</td>
<td>7.89</td>
<td>8.04</td>
<td>6.71</td>
<td>7.04</td>
<td>5.26</td>
<td>6.02</td>
<td>477.05</td>
<td>1340</td>
</tr>
<tr>
<td>Ideality factor of the diode (n)</td>
<td>1.15</td>
<td>1.36</td>
<td>1.21</td>
<td>1.20</td>
<td>1.20</td>
<td>1.24</td>
<td>1.89</td>
<td>1.74</td>
</tr>
<tr>
<td>Barrier height (\phi_B) (eV)</td>
<td>0.42</td>
<td>0.42</td>
<td>0.42</td>
<td>0.42</td>
<td>0.43</td>
<td>0.43</td>
<td>0.31</td>
<td>0.29</td>
</tr>
</tbody>
</table>

**Table 18.** Summary of parameters of contacts on Ga\(_{0.86}\)In\(_{0.14}\)As\(_{0.13}\)Sb\(_{0.87}\) epilayers which were obtained from I-V curves and equations 37 and 39. \(A_c = 2 \times 10^{-4} \text{ cm}^2\) and \(T = 300 \text{ K}\).
3.4 C-V electrical measurements

C-V electrical measurements were done for both GaSb substrates and Ga$_{0.86}$In$_{0.14}$As$_{0.13}$Sb$_{0.87}$ epilayer. Initially, I-V electrical measurements were necessary to define the voltage range within which C-V electrical measurements would be done. Unlike previous I-V electrical measurements, in this case the negative terminal was connected to the chuck and the positive terminal was placed into contact with the sample by means of a test probe. Then, the current enters to the semiconductor by the inner disc contact and exits from the semiconductor by the bottom contact of the sample. Two of the I-V electrical measurements are shown in the Figure 71 and Figure 72. According to those figures, the voltage range was selected from $-2 \ V$ to $2 \ V$.

![GaSbB4la](image)

**Figure 71.** I-V electrical measurement on B sample of GaSb. The current was limited to the range of $-100 - 100 \ mA$, therefore the curve described by the data saturate at $-100 \ mA$ and $100 \ mA$. 

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Figure 72. I-V electrical measurement on CE205 sample. The current was limited to the range of $-100$ – $100$ mA, therefore the curve described by the data saturate at $100$ mA.

To carry out the C-V electrical measurements, a testing station and measuring equipment were necessary. The measuring equipment consisted of an *Agilent B1500A* Semiconductor Device Analyzer (SDA) [51 - 52] and an *Agilent N1300A* Multi Frequency Capacitance Measurement Unit (MFCMU) [53], both made by Agilent Technologies. The system software is the *Agilent Technologies EasyExpert* [52]. Through the system software, the parameters of the measurement are defined and the measurement is controlled. To understand more in detail the measurements, it is worth illustrating some aspects such as internal configuration, connections, conditions and programming. The Figure 73 shows a diagram of the internal configuration of the MFCMU and illustrates how to connect the four-terminal pairs to the device under test (DUT). The MFCMU has four terminals:

- *Hcur*: Source of both DC and AC
- *Hpot*: Voltage meter through the DUT
- *Lpot*: Auto balance bridge
- *Lcur*: Current meter through the DUT
The connections between the SDA, the MFCMU and the testing station are shown through the photographs in Figure 74. The \(H_{\text{cur}}\) and \(H_{\text{pot}}\) terminals were connected together, as the \(L_{\text{pot}}\) and \(L_{\text{cur}}\) terminals. In this case, the \(H_{\text{cur}}\) and \(H_{\text{pot}}\) terminals were connected to the chuck, while the \(L_{\text{pot}}\) and \(L_{\text{cur}}\) terminals was placed into contact with the sample by mean of a test probe.

![Figure 74. Some photographs illustrate the connections. a) Connection between the SDA and the MFCMU; b) four-terminal pair configuration and c) connection between the MFCMU and the testing station.](image)

Regarding the conditions of the measurements, the testing station includes a vibration table, a microscope, a vacuum pump, a chuck, test probes, supports for
test probes, and a video camera whose image is displayed on a screen, among others.

For additional information about Agilent Technologies EasyExpert see the user guide [54]. Here, the configuration will only be submitted for C-V sweeps. To access the C-V sweep test setup screen several easy steps are necessary. First, the Agilent Technologies EasyExpert is opened; then, EasyExpert main screen appears, click the Classic Test tab and select the C-V Sweep icon. Finally, the main screen displays the C-V sweep test setup screen. The configuration of the measurements was as follows:

- Measurement parameters: Model: Cp-G; C Name: C and G Name: G
- Sweep parameters: Start: $-2\,\text{V}$, Stop: $2\,\text{V}$ and Step: $10\,\text{mV}$ or Start: $2\,\text{V}$, Stop: $-2\,\text{V}$ and Step: $10\,\text{mV}$
- Frequency: $1\,\text{MHz}$
- AC level: $30\,\text{mV}$
- Integration Time: Mode: PLC and Factor: 2

Figure 75. C-V sweep test setup screen. Programming example.

Some graphs of the C-V electrical measurement are shown in Figure 76. From those graphs it is clear that the CE205, CE229, CE240 and CE242 samples have a capacitive behavior of the MOS type.
Figure 76. Some graphs of the C-V electrical measurements GaSb and GaInAsSb samples. a), b), c) and e) voltage range from $2 - (-2) \, V$; d) and f) voltage range from $-2 - 2 \, V$. 

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The analysis of the graphs in Figure 76 is not simple [55]. According to the manufacturing process, a thin layer of sulfur was formed between the semiconductor and the metal during the passivation procedure; then, the structure in each case (GaSb substrates and \( \text{Ga}_{0.86}\text{In}_{0.14}\text{As}_{0.13}\text{Sb}_{0.87} \) epilayer) is as the Figure 77 shows. On the other hand, the behavior of the contact is Schottky type; therefore, reverse-biased capacitance is the result of two capacitances in series, the capacitance of the Metal-Sulfur-Semiconductor (MSS) structure and the capacitance of the Schottky diode, while the forward-biased capacitance is the capacitance of the MSS capacitor. According to Goodman [5], the capacitance per unit area of a Schottky diode is given by:

\[
\frac{C}{A} = \sqrt{\frac{q\varepsilon_S\varepsilon_0 N_D}{2\left(V_{bi} + V - \frac{k_B T}{q}\right)}}
\]  

(40)

where \( V \) is the reverse-bias voltage. For additional information see Figure 6. The \( k_B T / q \) in the denominator accounts for the majority carrier tail in the space-charge
region which is omitted in the depletion approximation. The built-in potential is related to the barrier height by the relationship [5]:

\[ \phi_B = V_{bi} + \phi_n \]  \hspace{1cm} (41)

as can be seen in Figure 6. \( \phi_n \) is given by [5]:

\[ \phi_n = \left( \frac{k_B T}{q} \right) \ln \left( \frac{N_c}{N_D} \right) \]  \hspace{1cm} (42)

where \( N_c \) is the effective density of states in the conduction band.

Assuming that a Schottky diode has formed on a Ga\(_{0.86}\)In\(_{0.14}\)As\(_{0.13}\)Sb\(_{0.87}\) epilayer with \( N_D = 1 \times 10^{16} \text{ cm}^{-3} \), \( V_{bi} = 0.35 \text{ V} \), \( A = 2 \times 10^{-4} \text{ cm}^2 \) at \( T = 300 \text{ K} \), the equation 40 has been plotted in Figure 78. Plotting \( 1/C^2 \) versus \( V \) gives a curve with the slope \( 2/(A^2q\varepsilon_s\varepsilon_0N_D) \), and with the intercept on the \( V \)-axis, \( V_{int} = -V_{bi} + k_B T/q \) (see Figure 79). With this method, the doping density and the barrier height
can be obtained. Additional parameters such as flat band voltage ($V_{FB}$), thickness of the layer of sulfur ($t_{sul}$) and surface states density ($N_{ss}$) can be obtained from the MSS structure in forward bias. The procedure used in this research is as follows.

![Graph of $1/C^2$ versus voltage](image)

**Figure 79.** Reverse-bias $1/C^2$ versus voltage of the Schottky diode in Figure 78.

The flat band capacitance of the semiconductor ($C_{FBS}$) is given by [5]:

$$C_{FBS} = A \sqrt{\frac{\varepsilon \cdot q^2 N_D}{k_B T}}$$  \hspace{1cm} (43)

Then, the total flat band capacitance ($C_{FB}$) is given by:

$$C_{FB} = \frac{C_{sul} \cdot C_{FBS}}{C_{sul} + C_{FBS}}$$  \hspace{1cm} (44)

where $C_{sul}$ is the capacitance of the sulfur. $C_{sul}$ is obtained from the C-V measurement data. The thickness of the layer of sulfur ($t_{sul}$) is given by:

$$t_{sul} = \frac{\varepsilon_{sul} A}{C_{sul}}$$  \hspace{1cm} (45)
where $\varepsilon_{sul}$ is the permittivity of the sulfur (the relative permittivity of the sulfur is 3.5). Once the total flat band capacitance is calculated, the flat band voltage ($V_{FB}$) can also be obtained from the C-V measurement data. Finally, the surface states density ($N_{ss}$) is calculated from:

$$N_{ss} = \left( \frac{\phi_{ms} - V_{FB}}{q} \right) \frac{C_{su l}}{A}$$  \hspace{1cm} (46)

These two methods have been applied to the C-V measurement data of the Ga$_{0.86}$In$_{0.14}$As$_{0.13}$Sb$_{0.87}$ epilayers and the main parameter are listed in Table 19. Although the total capacitance in reverse bias is approximately the Schottky diode capacitance, the capacitance of the MSS structure has not been neglected. The graphs in Figure 80 show how the method was used to obtain the doping density and the barrier height of a specific structure in the CE240 sample.

**Table 19.** Summary of parameters of Ga$_{0.86}$In$_{0.14}$As$_{0.13}$Sb$_{0.87}$ epilayers which were obtained from C-V curves.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CE205</th>
<th>CE229</th>
<th>CE240</th>
<th>CE241</th>
<th>CE2402</th>
<th>CE2411</th>
</tr>
</thead>
<tbody>
<tr>
<td>Doping density $N_D$ ($cm^{-3}$)</td>
<td>$2.4 \times 10^{16}$</td>
<td>$5.0 \times 10^{15}$</td>
<td>$1.7 \times 10^{16}$</td>
<td>$2.2 \times 10^{16}$</td>
<td>$1.3 \times 10^{16}$</td>
<td>$2.1 \times 10^{16}$</td>
</tr>
<tr>
<td>Barrier height $\phi_b$ (eV)</td>
<td>0.37</td>
<td>0.41</td>
<td>0.36</td>
<td>0.39</td>
<td>0.35</td>
<td>0.47</td>
</tr>
<tr>
<td>Flat band voltage $V_{FB}$ (mV)</td>
<td>50</td>
<td>70</td>
<td>66</td>
<td>70</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Flat band capacitance $C_{FB}$ (pF)</td>
<td>67</td>
<td>38</td>
<td>59</td>
<td>69</td>
<td>55</td>
<td>68</td>
</tr>
<tr>
<td>$\phi_{ms}$ (eV)</td>
<td>0.77</td>
<td>0.73</td>
<td>0.76</td>
<td>0.77</td>
<td>0.76</td>
<td>0.77</td>
</tr>
<tr>
<td>Surface states density $N_{ss}$ ($cm^{-2}$)</td>
<td>$8.5 \times 10^{12}$</td>
<td>$8.3 \times 10^{12}$</td>
<td>$5.4 \times 10^{12}$</td>
<td>$6.8 \times 10^{12}$</td>
<td>$6.2 \times 10^{12}$</td>
<td>$7.6 \times 10^{12}$</td>
</tr>
<tr>
<td>Sulfur capacitance $C_{sul}$ (pF)</td>
<td>384</td>
<td>401</td>
<td>250</td>
<td>314</td>
<td>283</td>
<td>340</td>
</tr>
<tr>
<td>Sulfur thickness $t_{sul}$ (nm)</td>
<td>1.65</td>
<td>1.47</td>
<td>2.50</td>
<td>1.99</td>
<td>2.22</td>
<td>1.83</td>
</tr>
</tbody>
</table>
Figure 80. A example of the method to obtain the doping density and the barrier height. The C-V measurement data are from CE240 sample, CCRTS I-V and circular structure f. a) Reverse bias data from the C-V measurement. b) Reverse-bias $1/C^2$ versus voltage.
Chapter 4

ANALYSIS AND CONCLUSIONS

So far, only a few explanations about the process specifications have been given, but the results have not been explained yet from the theoretical basis in Chapter 1. This chapter seeks to achieve that goal and is organized into two parts. First, the results (graphs and tables presented in the previous chapter) and the particular process of each sample will be analyzed from the theoretical fundamentals. Second, the main conclusions of this research and further work will be listed.

4.1 Analysis of results in GaSb substrates

The results on GaSb substrates were summarized by Figure 53 and Figures 58 to 65. The Table 20, Table 21 and Table 22 have been obtained from such graphs in order to compare processes and evaluate the effects of each procedure. The main aspects to evaluate are the effects of surface passivation, the impact of the thermal annealing procedures and the temperature at which the alloy is carried out. The analysis strategy to be used is to see the results as some procedures are removed from the complete process. As the complete process was developed in the samples A, E and H (see Table 7), those samples are the basis for the main analysis.

By comparing the data in Table 21 with the data within the Table 20 can be seen that the specific contact resistivity is higher when the pre-metallization thermal annealing is not carried out. The pre-metallization thermal annealing procedure has
some functions. One function is to activate bonds between sulfur atoms and antimony atoms on the surface of GaSb. Another function is to reduce the thickness of the sulfur layer by desorption of some sulfur atoms. Furthermore, according to Kunitsyna et al. [54] a reduction of the roughness of the surface would be expected. An indication of the decrease in surface roughness may be the sheet resistance changes in Table 20 to Table 21. For those reasons, the specific contact resistance reduction in A, E and H samples with respect to B, F and J samples respectively is understandable.

**Table 20.** Summary of contact parameters in A, E and H samples.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Complete Process</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature of the post-metallization annealing (°C)</td>
<td>300</td>
<td>350</td>
<td>400</td>
</tr>
<tr>
<td>Contact resistance (Ω)</td>
<td>5.15</td>
<td>2.37</td>
<td>3.34</td>
</tr>
<tr>
<td>Specific contact resistivity (Ω ∙ cm²)</td>
<td>1.03 x 10⁻³</td>
<td>4.76 x 10⁻⁴</td>
<td>6.71 x 10⁻⁴</td>
</tr>
<tr>
<td>Transfer length (µm)</td>
<td>18.15</td>
<td>19.37</td>
<td>21.66</td>
</tr>
<tr>
<td>Sheet resistance (Ω/square)</td>
<td>142.47</td>
<td>61.47</td>
<td>77.45</td>
</tr>
</tbody>
</table>

**Table 21.** Summary of contact parameters in B, F and J samples.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Process without thermal annealing pre-metallization</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature of the post-metallization annealing (°C)</td>
<td>300</td>
<td>350</td>
<td>400</td>
</tr>
<tr>
<td>Contact resistance (Ω)</td>
<td>13.01</td>
<td>9.15</td>
<td>5.88</td>
</tr>
<tr>
<td>Specific contact resistivity (Ω ∙ cm²)</td>
<td>2.61 x 10⁻³</td>
<td>1.84 x 10⁻³</td>
<td>1.18 x 10⁻³</td>
</tr>
<tr>
<td>Transfer length (µm)</td>
<td>18.27</td>
<td>3.24</td>
<td>3.82</td>
</tr>
<tr>
<td>Sheet resistance (Ω/square)</td>
<td>357.88</td>
<td>1.42 x 10³</td>
<td>774.91</td>
</tr>
</tbody>
</table>

On the other hand, the specific contact resistivities in Table 21 and Table 22 are close and no significant difference can be seen there. Then, not only is sufficient to passivate the surface, but the pre-metallization thermal annealing is also
necessary so that the passivation takes effect and improves the contact performance.

Table 22. Summary of contact parameters in C and G samples.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>C Sample</th>
<th>G Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature of the post-metallization thermal annealing (°C)</td>
<td>300</td>
<td>350</td>
</tr>
<tr>
<td>Contact resistance (Ω)</td>
<td>12.51</td>
<td>13.26</td>
</tr>
<tr>
<td>Specific contact resistivity (Ω·cm²)</td>
<td>$2.51 \times 10^{-3}$</td>
<td>$2.67 \times 10^{-3}$</td>
</tr>
<tr>
<td>Transfer length (µm)</td>
<td>1.41</td>
<td>4.68</td>
</tr>
<tr>
<td>Sheet resistance (Ω/square)</td>
<td>$4.45 \times 10^3$</td>
<td>$1.42 \times 10^3$</td>
</tr>
</tbody>
</table>

According to the transfer length, when the complete process is applied, the current is transferred from the semiconductor to the metal or from metal to the semiconductor at a distance around 20 µm, therefore the dimensions of the contacts should not be less than that value. In this research, circular contacts of radius 80 µm were used and therefore that premise was fulfilled. In this regard, it is worth mentioning that as the transfer length increases, the current distributes more widely in the area of contact.

As regards the effects of the post-metallization thermal annealing procedure, the current-voltage behavior is nonlinear before thermal treatment, but thereafter a linear current-voltage characteristic is obtained (see Figure 53). The lower specific contact resistivity was obtained with the complete process to an alloying temperature of 350 °C. Now, assuming that the specific contact resistivity has a second order behavior with respect to the alloying temperature, the lower specific contact resistivity would be obtained at 362 °C approximately.
4.2 Analysis of results in Ga$_{0.86}$In$_{0.14}$As$_{0.13}$Sb$_{0.87}$ epilayers

The results on Ga$_{0.86}$In$_{0.14}$As$_{0.13}$Sb$_{0.87}$ epilayers were summarized by Figure 54, Figure 55, Figure 56, Figure 66, Figure 67 and Figure 76 and by Table 18 and Table 19. In this case, the doping density ($N_D$) plays an important role in the contact characteristics. This research began with very low doping densities. Those doping densities uncovered some peculiarities that were not revealed by the tests on GaSb substrates. One of these peculiarities can be seen in Figure 55 where the curves described by the post-metallization I-V measurements data are below the curves described by the pre-metallization I-V measurement data in forward bias. Apparently, the post-metallization thermal annealing promotes a chemical reaction of the passivated surface with the epilayer, resulting in damage of the surface morphology. Another is related to the nature of the passivation process. As the passivation is a photoelectrochemical process, it also is affected by the doping density. Subsequently, the doping density was increased and other physical phenomena were observed. For example, the ohmic character of the contacts is associated with the degree of dominance of the field emission conduction mechanism over the thermionic emission conduction mechanism.

Before addressing the implications of doping density, it is worth devoting a few lines to explain the electrical behavior of contacts on the sample CE229. In Figure 56, the location of the CE229 sample data is unexpected, but their behavior has an explanation. The CE229 sample has the lowest doping density ($5.0 \times 10^{15} \text{ cm}^{-3}$); therefore, the growth of the sulfur layer during the passivation is slower than in the other samples. As all the samples were remained within the aqueous solution of sodium sulfide (Na$_2$S:9H$_2$O) at the same time; hence, the sulfur layer in the CE229 sample have a smaller thickness than the other samples (see Table 19), which facilitates the transfer of electrons from the metal to the semiconductor or from the semiconductor to the metal in either direction. On the other hand, the CE205,
CE240 and CE241 samples have doping densities very close and within the same order of magnitude. Therefore, the data curves of the CE205, CE240 and CE241 samples are organized according to the doping density.

Interpreting the ideality factors of the diode in Table 18, the dominant conduction mechanism at low doping densities of the order of \(1.0 \times 10^{16} \text{ cm}^{-3}\) is thermionic emission. Again, the sample CE229 has an ideality factor of the diode greater than that of the samples with concentrations of the order of \(1.0 \times 10^{16} \text{ cm}^{-3}\). The reason for this behavior is the same as above. As the doping density increases from \(1.0 \times 10^{16} \text{ cm}^{-3}\), the field emission conduction mechanism begins to dominate over the thermionic emission conduction mechanism. Then, the I-V measurements data on samples with densities in the range from \(1.0 \times 10^{17} - 1.0 \times 10^{18} \text{ cm}^{-3}\) exhibit a behavior increasingly symmetrical. These effects are represented by an increase in the ideality factor of the diode. The values in Table 18 confirm numerically the event while the Figure 54 shows the electric behavior by mean of I-V measurements data from CE113 and CE118 samples which have doping densities of \(4.0 \times 10^{17} \text{ cm}^{-3}\) and \(8.0 \times 10^{17} \text{ cm}^{-3}\) respectively.

At this point, the effects of the passivation and pre-metallization thermal annealing temperature have not been clearly explained yet. As can be seen in the results of the CE229 sample, an optimum thickness of the sulfur layer must exist and probably is lower than the values which were obtained with the experiments. The temperature of the pre-metallization thermal annealing is a good tool to achieve this goal and it was demonstrated through the numerical results of the sample CE2402 in relation to the numerical results of the sample CE240. By increasing the temperature of the pre-metallization thermal annealing from 125 °C to 250 °C, the thickness of the sulfur layer was decreased and the barrier height was lower. Another method would be to reduce the passivation process time, in order to
prevent the formation of a too thick sulfur layer. On the other hand, the surface states density is in the order of $10^{12} \ cm^{-2}$ and additional studies in samples with low doping density must be carried out.

### 4.3 Conclusions about GaSb substrates

Taking into account the previous analysis about the results in GaSb substrates, the main conclusions are listed below:

- Ohmic contacts with the lowest value of $\rho_c = 4.8 \times 10^{-4} \ \Omega \cdot cm^2$ were obtained after annealing at 350 °C for 60 s. At this temperature, it is likely that an interfacial layer of GaInSb and a semimetal of InSb have formed. Under this principle, the electrons do not have to go through or overcome a barrier.
- The pre-metallization thermal annealing procedure at 125 °C for 60 min reduces the contact resistance to somewhat less than half.
- To improve the parameters of the contact is not enough to passivate the surface, the pre-metallization thermal annealing procedure is necessary.
- When a sample is not passivated, changes in the contact parameters due to the alloying temperature are not significant.
- The post-metallization thermal annealing procedure makes the ohmic contact and it increases the current in somewhat more than one order of magnitude.

### 4.4 Conclusions about $\text{Ga}_{0.86}\text{In}_{0.14}\text{As}_{0.13}\text{Sb}_{0.87}$ epilayers

Taking into account the previous analysis about the results in $\text{Ga}_{0.86}\text{In}_{0.14}\text{As}_{0.13}\text{Sb}_{0.87}$ epilayers, the main conclusions are listed below:
• The curves described by the CE113 and CE118 samples data have different slopes in forward and reverse bias, in spite of that, the linear region of forward bias was used to characterize the contacts. According to the parameters of contacts on CE113 and CE118 samples, the best result in terms of specific contact resistivity were obtained with the CE118 sample and its value was \( \rho = 5.0 \times 10^{-4} \, \Omega \cdot cm^2 \) after annealing at 350 °C for 60 s.

• A Schottky barrier was formed; then, as the doping density is increased, the electric behavior of the contacts shifts by the three regions in Figure 5 (thermionic emission (TE), thermionic-field emission (TFE) and field emission (FE)).

• There are two ways to reduce the contact resistance. One is to increase the doping density of the epilayer and the other is to reduce the thickness of the layer of sulfur. When the doping density increases, this results in both the width barrier and height barrier decrease. The barrier width decreases according to equation 3, while the barrier height is reduced by the image force. By decreasing the thickness of the sulfur layer is expected that less damage to the morphology of the metal-semiconductor interface is caused.

• A process for cleaning and passivation of surface was specified to GaInAsSb epilayers. In this case, hydrochloric acid (HCl) was not included in the cleaning process and the treatment time with acids was reduced to 2 min.

4.5 Further work

The research is a continuous activity and unlimited time. During this work, important steps have been taken, but there are many others to give. The following suggestions do not go beyond those of the ways that this research has opened and the implementation of these activities will open new ways probably. From this point,
the optimization of the procedures is the constant goal. The next steps are listed below:

- To get the Auger sputtering profiles of each sample and thus have extra tools that help to explain the results and to characterize the contacts.
- To corroborate the results with other electrical measurement techniques.
- To carry out experiments in order to reduce the thickness of the sulfur layer.
- To study the effects on the contact parameters of the thickness of the metal layers deposited.
- To increase the slope of the cooling ramp during thermal annealing procedures in the RTP.
- To experiment with other metals for obtaining a linear current-voltage characteristic in the GaInAsSb epilayers.
REFERENCES


