The Pennsylvania State University

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STUDY OF PALLADIUM/GALLIUM ANTIMONIDE REACTIONS AND OHMIC CONTACTS TO N-TYPE GALLIUM ANTIMONIDE

A Thesis in

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by

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ABSTRACT

Antimonide-based compound semiconductors show great promise for optoelectronic and high speed electronic devices. GaSb, and related ternary and quaternary alloys, have emerged as critical materials for infrared lasers, thermophotovoltaic devices, solar cells, and transistors. To ensure device reliability and performance, ohmic contacts with low specific contact resistance, good thermal stability, and excellent surface and interfacial morphology are required. In recent years a move from traditional Au-based contacts to Pd-based contacts has improved thermal and morphological stability of contacts to Sb-based semiconductors. The characterization and understanding of how a Pd thin film interacts with GaSb is essential to further improve contacts to n-GaSb. Research presented in this thesis yields phase formation and reaction morphologies important for Pd-based contacts to n-GaSb. A Pd/GaSb thin film study identifies phase formation necessary for the solid phase regrowth mechanism for ohmic contact formation and the ohmic behavior of a Pd (50 nm)/GaSb contact. A subsequent study of the Pd-rich region of the Pd-Ga-Sb phase diagram verifies the existence of several Pd-rich ternary phases observed in the thin film research. Next, research focused on the engineering of Pd-bearing ohmic contacts that include indium. Two low resistance ohmic contacts will be presented that exhibit electrical properties comparable to In-based contacts reported in the literature. However, these contacts improve upon previously reported contacts to n-GaSb by offering improved surface morphology, reduced reaction depth, and improved thermal stability. A Pd₃In₇/WSiN/Au contact presented here exhibits unmatched thermal stability and ultra-shallow reaction depths.

Finally, the effect of surface treatments will be presented as a means to reduce the specific contact resistance, improve reaction uniformity, and understand Sb-based semiconductor passivation. It will be shown that by replacing a conventional surface treatment that includes a deionized water rinse with a dilute ammonium sulfide solution rinse, it is possible to rid the surface of any contamination layers, reduce the specific contact resistance of ohmic contacts to n-GaSb, and improve reaction uniformity.

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Chapter 1

Introduction and Gallium Antimonide

1.1 Introduction

Gallium antimonide (GaSb) based epitaxial structures have shown great potential for applications in laser diodes with low threshold voltages, photodetectors with high quantum efficiency, high frequency devices, superlattices with tailored optical and transport characteristics, and booster cells in tandem solar cell arrangements.[1] Applications of GaSb in thermophotovoltaic (TPV) devices has also recently gained interest. [2] Thermophotovoltaics are the close relative to photovoltaics; TPVs convert infared radiation into electricity and ultimately one can integrate such devices into heating elements for the home, etc. [2] GaSb based devices are also promising candidates for a variety of military and civil applications in the 2-5 and 8-14 µm wavelength regimes, including infrared imaging sensors for missile and surveillance systems, fire detection, and environmental pollution monitors. Ohmic contacts are a factor that significantly affect the III-V semiconductor device characteristics, [3] and the metal-semiconductor interfaces of ohmic contacts are critical in the engineering of these devices. [4] However, forming ohmic contacts to n-GaSb is a difficult task for three reasons: the surface of GaSb is easily oxidized, there is Fermi level pinning at the

surface of GaSb, and it is difficult to heavily dope n-type GaSb. The goal of this thesis work is to fundamentally understand how Pd interacts with GaSb and to use this knowledge to engineer low resistance, thermally stable contacts to n-GaSb. The remainder of Ch. 1 is focused on the properties of GaSb. Chapter 2 provides background on many aspects of metal/semiconductor interfacial reactions and physics. Chapter 3 gives detailed experimental procedures and data analysis necessary to accomplish the research presented in Ch. 4 – 7. The thesis research presented in the following chapters focuses on understanding the reaction between Pd and GaSb in the thin film (Ch. 4) and bulk (Ch. 5) form and the engineering of Pd-bearing contacts to n-GaSb (Ch. 6 and 7).

1.2 Gallium Antimonide

Gallium antimonide (GaSb) is a narrow band gap, III-V compound semiconductor with a lattice parameter of 6.095Å. [1] This lattice matches solid solutions of various ternary and quaternary III-V compounds with band gaps covering a wide spectral range of ~0.3 to 1.58 eV (.8 - 4.3 µm) as depicted in Fig. 1.1. Some important properties of GaSb are listed in Table 1-1. Undoped GaSb is always p-type in nature regardless of the growth technique and conditions, with a residual acceptor concentration of $\geq 10^{17}$ cm⁻³ associated with gallium vacancies and gallium antisite defects.[1] Standard dopants for n-type GaSb are Te, Se, and S, while p-type GaSb is generally doped with Zn, Ge, or Si.[1]



Figure 1.1: Band gap as a function of lattice constant for III-V compounds and their ternary and quaternary alloys.

Table 1-1: Properties of GaSb[1]

Lattice Constant	6.0959 Å
Density	5.6137 g/cm ⁻³
Melting Point	985 K
Direct Band Gap at 300 K	0.725 eV
Direct Band Gap at 0 K	0.822 eV
Electron Affinity (χ_s)	4.02 eV
Crystal Structure	Zinc-Blende

1.2.1 Oxidation of GaSb

GaSb has a highly reactive surface and a variety of reactions lead to the formation of thick surface oxides at room temperature.[5] The formation of native oxides on the GaSb surface at low temperature proceeds by the reaction:[5][6]

$$2GaSb_{(s)} + 3O_{2(g)} \rightarrow Ga_2O_{3(s)} + Sb_2O_{3(s)}.$$
(1.1)

Further studies of the native oxide indicate that the resistivity of the oxide is approximately $10^{10} \Omega$ -cm, [7] and during oxidation there is a pile-up of Sb at the semiconductor surface due to the disparity in oxidation rates of Ga and Sb.[7] Since the GaSb surface is highly reactive, resulting in an oxide thickness of approximately 1 nm after 1 min in open air, [8] surface preparation treatments must be employed to minimize surface oxidation immediately prior to metallization, which benefits the metal/semiconductor interface resistance. It has been reported that the ideal surface treatment for minimizing surface oxides after degreasing is an HCl soak for 5 min followed by a 2-propanol rinse.[9] The propanol rinse results in a 1 – 2 nm oxide layer on the surface, while rinsing with H₂O yields a 2–3 nm oxide layer, and simply degreasing the surface leads to a 3 – 5 nm oxide layer.[9] It will later be shown, however, that even the presence of a 2 – 3 nm dielectric layer, such as an oxide or sulfide, is capable of inhibiting or even prohibiting metal/semiconductor reaction.

1.2.2 GaSb Fermi Level Pinning

A second reason ohmic contacts to n-GaSb are difficult to achieve is because GaSb exhibits Fermi-level pinning at the semiconductor surface near the valence band.[10][11][12] When a metal and semiconductor make intimate contact the Fermi levels of each material must be coincident at thermal equilibrium.[13] For certain III-V

semiconductors (i.e. GaSb) the Fermi level position (and ultimately the barrier to electron transport) at the surface of the semiconductor is independent of the metal that contacts it, and is said to be "pinned." [13] The specifics of this phenomenon are discussed in Section 2.2.4. Fermi level pinning in GaSb may be a result of several mechanisms. As mentioned before (Section 1.2), Ga vacancies are present at the semiconductor surface, and these vacancies may result in the pinning of the Fermi level (E_F) near the valence band. [14] However, it has also been reported that the surface states that pin the Fermi level are due the addition of adatoms on the GaSb surface.[10] Spicer *et al.*[10] studied the Fermi level pinning of GaSb and other materials using photoemission electron spectroscopy (PES). Two key results came from this study: 1) The final pinning position is obtained with low coverage of deposited atoms – at most 15% of one monolayer, and 2) the Schottky barrier height is essentially independent of the adatom. Following this study it was pointed out that the ability to follow the $E_{\rm F}$ as a function of metal coverage in the low coverage regime is very difficult using surface sensitive techniques such as PES. [15] Photoemission electron spectroscopy averages over a large area compared to the metallic island formation and thus using such a surface science approach to follow the $E_{\rm F}$ will average over clean and metal-covered semiconductor surface. As a result, the mechanism for intermediate pinning of the E_F claimed by Spicer et al. [10] must be read with caution as they did not take into account this short coming of the PES technique.

The exact mechanism that results in the pinning of the E_F in GaSb may not be known, but it is well established that the E_F is pinned near the valence band. Figure **1.2(a)** is a compilation of data from several studies

5

showing the approach of the E_F to its final position as a function of adatom coverage for a variety of elements.[10][11][12] Analysis of this data must take into account the growth kinetics of the metal film on the GaSb surface, but it gives a good indication of the final resting place of the E_F . Figure 1.2(b) is an examination of the E_F as a function of indium coverage on n- and p-type GaSb at room temperature (RT) and low temperature (LT) (35 K).[11]

Data presented in Fig. 1.2(b) clearly shows the growth kinetics of In on GaSb is much different at the two temperatures. At room temperature the E_F remains very different on n and p-type GaSb up to high coverage as a result of island formation. At LT the E_F movements are modified in several ways. Strong band bending of the p-GaSb occurs at very low coverage before converging on the valance band maximum (VBM) around 1 Å of metal coverage. The band bending of n-GaSb is not as severe initially at LT compared to RT; however, with ~ 0.15 Å of In coverage, there is a sharp convergence of the E_F toward the VBM. Within 2 Å of In coverage the Fermi levels have converged to their final pinning levels, below the VBM, indicating complete metal coverage of the semiconductor.



Figure 1.2: A summary of several studies (a) comparing Fermi level position as a function of coverage of various metals and (b) a comparison of In coverage at room temperature (RT) and low temperature (LT) indicating that the growth kinetics of the In film is dependent on temperature.

1.2.3 Growth and doping of n-GaSb epitaxial layers

A third reason ohmic contacts to n-GaSb are difficult to form stems from the inability to heavily dope n-GaSb epitaxial layers. The ability to increase the electron concentration levels to very high values ($n \ge 10^{19}$ cm⁻³) would shrink the thickness of the barrier to electron transport at the M/S interface and allow for low resistance contacts to be formed with relative ease. Doping high quality n-GaSb epitaxial layers, to date, has been difficult to achieve above ~ 1-2 x 10¹⁸ cm⁻³.[16]-[24] Un-doped GaSb is always p-type in nature as a result of the native defects in GaSb.[25] During molecular beam epitaxial (MBE) crystal growth, Sb exhibits a low surface mobility resulting in clustering and Sb precipitates. This clustering leaves Sb sites within the crystal vacant for other atoms to occupy and results in Ga antisite defects. Because Ga has fewer electrons than Sb, the ensuing crystal is p-type.

To improve the quality of the GaSb epilayers, MBE researchers have turned to Sb-rich environments. It has been reported that an Sb₄/Ga ratio of approximately 2:1 leads to the highest quality Te-doped GaSb epilayers, [19][26] while others have found little variation in background acceptor concentration and mobility for Sb₄/Ga ratios between 3:1 and 10:1.[20] Longenbach and Wang[26] also report that substrate orientation plays an important role in the GaSb epilayer quality. Typically GaSb epilayer growth is on a (100) substrate. The (111) orientation exhibits fewer Sb dangling bonds, and thus, yields lower Ga antisite defects. This advantage, however, is offset by poor surface morphology during growth and, as a result, the (100) orientation is preferred. Longenbach and Wang[26] combine the benefits of both the (100) and (111) orientations by growing epilayers on a (311) oriented substrate. They justify the growth on such a substrate by showing it is equally weighted between the (100) and (111)-like components. Growth on such an orientation yields excellent morphology and a reduced intrinsic defect density.

Dopants often used during the growth of n-GaSb come from column VI of the periodic table. These elements include Se, Te, and S, and as a result, have an extra electron per atom compared to Sb to "donate" to the GaSb crystal. To date, Te has been the element of choice for doping n-GaSb,[16]- [26] with some work including S and Se as the preferred dopant.[27][28][29] The drawback to using elemental Te as a dopant is its high vapor pressure. The use of Te alone can result in memory effects, crosstalk, and reaction with Ga at the semiconductor surface resulting in poor crystal quality.[30] The solution to this problem is to incorporate Te as a dopant via compounds such as PbTe,[16] GaTe,[20][22][24] Sb₂Te₃,[23] Ga₂Te₃, and SnTe.[21][31]

A Czech Republic group has doped GaSb bulk crystals with Te as high as $5 \ge 10^{20}$ cm⁻³, with theoretical limits being $8 \ge 10^{21}$ cm⁻³. [32][33][34] They claim that doping of GaSb single crystals grown via the Czochralski method in a hydrogen atmosphere is easily achieved, and the resultant crystals have very low dislocation densities. The limiting factor for doping bulk crystals above $5 \ge 10^{20}$ cm⁻³ is that the pull rate of the crystal is too slow for practical utilization. The high doping density claimed by Sestak *et al.*[33][34] is only the atomic concentration of Te in the GaSb; there is no mention of carrier concentration in the bulk crystal growth. The maximum carrier concentration for high quality n-GaSb epitaxial layers via MBE, metal-organic vapor phase epitaxy (MOVPE), and metal-organic chemical vapor deposition (MOCVD) are orders of magnitude lower than those reported for bulk crystal growth. Donor levels are found to be proportional to the arrival rate of the Te dopant up to approximately $1 - 3 \ge 10^{18}$ cm⁻³, beyond which the carrier concentration begins to saturate and mobility is drastically reduced.[16][19][20][21] Figure 1.3 illustrates the free carrier saturation at approximately $3 \ge 10^{18}$ cm⁻³, as well as a decrease in mobility as carrier concentration approaches 10^{18} cm⁻³. Similar results to Fig. 1.3 are also reported by Subbanna *et al.*[16] and Baraldi *et al.*,[31] with saturation occurring at approximately $2 \ge 10^{18}$ cm⁻³. The decrease in mobility is attributed to, as mentioned previously, the saturation of GaSb with Te resulting in Te-Ga compound formation, as well as a degradation of crystallinity.[31]



Figure 1.3: Carrier concentration vs. electron mobility for Te-doped n-GaSb

Until now discussion has focused on MBE growth of n-GaSb epilayers. Other methods such as MOVPE and MOCVD are also used to grow high quality epilayers.[23][24][35] These methods yield similar results to MBE with maximum carrier concentrations occurring at approximately 10^{18} cm⁻³. Above this concentration, mobility and crystal degradation occur. Nakamura *et al.*[24] studied the doping of n-GaSb using Se and Te during MOCVD growth and found a linear relationship between atomic and electron concentration up to $1 \ge 10^{18}$ cm⁻³; above this the carrier concentration decreased with increasing atomic concentration. They attribute this relationship to the formation of complexes between the dopant atoms (Se or Te) and Ga. It was also reported that electron mobility and concentration is higher when GaSb epilayers are grown on GaSb substrates as compared to GaAs substrates.[35]

Chapter 2

Background: The Metallurgy and Physics of Metal/Semiconductor Contacts

Experimental work presented in this thesis requires knowledge of phase diagrams and metal/semiconductor interfaces. Knowledge of the interfacial reaction and electron transport at the metal/semiconductor interface is an important aspect of metal/semiconductor contacts. As a result, it is instructive to explore the metallurgical and physical properties of metal/semiconductor contacts.

2.1 Phase Diagrams in Contact Metallurgy

Equilibrium phase diagrams are used as a tool for choosing elements or compounds that will be in equilibrium with each other. Ternary phase diagrams have proven to be an important tool for identifying reactions that may occur when metal overlayers (M) are in contact with III-V compound semiconductors.[37][38] Through the use of phase diagrams and thermodynamics, choosing thermally stable metallizations is possible; and as a result, improved contact metallizations may be engineered. Ternary phase diagrams consist of three initial components (A, B, and C). To construct a ternary phase diagram, a third composition axis is added to a binary phase diagram. This yields a pyramid whose sides (and bottom) are composed of binary phase diagrams. [39][40] Often, ternary phase diagrams are displayed as compositional diagrams at a fixed temperature (isothermal phase

diagrams). This is simply an isothermal slice of the three-dimensional phase diagram. Figure 2.1 is a hypothetical isothermal ternary phase diagram with compounds A_3C_7 , AB, and B_6C_4 labeled along the axes. Ternary phase diagrams are arranged with the initial constituents (usually pure elements) in the corners of the diagram. Consider the A-C axis in Fig. **2.1**. As one moves from C to A, each marker along the axis constitutes a 10% change in composition from C to A. A₃C₇ is located three tick-marks from C, indicating that the compound is 70% C and 30 % A. Similarly, the compound AB is halfway between A and B, and B₆C₄ is located four tick-marks from B, indicating that 60 % of the compound is B. The most common equilibrium conditions encountered in ternary phase diagrams are illustrated in Fig. 2.1. Four phase equilibrium is also possible at a specific pressure, temperature, and composition. Two phase equilibrium is indicated by the thick black lines connecting the compounds. One three phase equilibrium is depicted by the grey, shaded region encompassed by three of the two phase equilibrium lines. Within the grey shaded area all three phases are in equilibrium with each other. There is also the case where all three elements may react to form a phase that contains some of each element within the ternary phase diagram. This is illustrated in Fig. 2.1 as the compound $A_6B_2C_2$, and is referred to as a ternary phase.

When choosing metallizations that will be stable when in contact with the underlying semiconductor, one often looks for elements (or compounds) that are in equilibrium with the semiconductor. This is indicated by the presence of a tie-line between the metal and the semiconductor. Stable metallizations, however, do not necessarily yield the desired electrical properties one looks for in metal/semiconductor contacts. This is discussed later in the chapter.



Figure 2.1: Hypothetical A-B-C isothermal ternary phase diagram with compounds AB, A_3C_7 , and B_6C_4 in equilibrium with each other.

Beyers *et al.*[**37**] identified a classification scheme, based on key features in the diagrams, for M-III-V phase equilibria. This classification scheme was developed from M-Ga-As phase diagram studies and considers seven specific types of diagrams. Fig. **2.2** illustrates four diagrams that do not involve a ternary phase. The remaining three are simply a variation on the original four and will not be discussed further.



Figure **2.2**: Four basic types of M-III-V ternary phase diagrams as described by Beyers *et al.*

The classification scheme shown in Fig. 2.2 can be explained as follows. *Type I* is III-V dominant and features a tie line between the M and III-V semiconductor, indicating thermal stability between the metal and compound semiconductor. *Type II* is M-III dominant with a key feature being the tie line between a M-III phase and the group V element. As a result of this tie line, a M-IIIV tie line cannot exist, indicating that M is not stable when in contact with III-V. *Type III* is simply the complement to *Type II* and exhibits the same M-IIIV instability. Finally, *Type IV* has no dominant phase in the diagram. The key feature of *Type IV* diagrams is the lack of a tie line between the compounds and elements denoting no phase stability between the compound and elemental phases. Important phase diagrams related to this thesis include the Pd-In-Sb and Pd-Ga-Sb diagrams. The Pd-In-Sb is considered to be *Type IV*, based on the complexity of the diagram that has no dominant phase.[**41**] Although the Pd-Ga-Sb diagram has been studied by Richter and Ipser,[**42**] as well as Liu and Mohney,[**43**] it is incomplete. The Pd-rich region of the diagram has not been studied; however, it has been reported that the ternary phase Pd_{73.5}(GaSb)_{26.5} exists.[**45**] According to Richter and Ipser,[**42**] the GaSb-rich portion of the phase diagram matches the *Type II* diagram. The Pd-rich region of the Pd-Ga-Sb phase diagram will be discussed in some detail later (Chapter 5).

2.2 Metal/Semiconductor Interfaces

2.2.1 Interfacial Reactions

When studying metal-III-V systems, the interfacial reactions are of interest because they control electrical and morphological properties. When depositing metals in microelectronics, one often desires an abrupt, thermally stable interface, but this may difficult to achieve.[46] Atom migration occurs to establish equilibrium, resulting in a net decrease in free energy, due to concentration gradients, negative free energies of reaction for the formation of new phases, electric fields, and strain gradients.[47] Figure 2.3 illustrates five interfacial processes that occur due to the drive for free energy reduction.

Figure 2.3: Interfacial reactions with arrows indicating diffusion direction

The abrupt interface (Fig. 2.3(a)) is characterized by a change from film to substrate within an atomic spacing (1-3 Å).[48] Abrupt interfaces can arise from thermodynamic equilibrium between the film and substrate or as a result of a lack of reaction and low solid-state interdiffusion rates.[48] The extent of reaction is difficult to predict because it is determined by the rate of solid-state diffusion and phase transformations. Solid-state diffusion rates in polycrystalline materials can vary with microstructure, while in epitaxial materials, diffusion rates are dictated by lattice diffusion and defects within the lattice.[48]

Reactions to form new phases between the film and substrate, including self-limiting reactions, can lead to structures similar to that shown in Fig. 2.3(d). Initially, phase formation is interface reaction controlled; however, as these new phases grow the flux of atoms across the interface will slow. At some point the solid-state reactions become limited by diffusion of the elements through the reacted or compound region, [48] either due to an increase in layer thickness of the interfacial region or the formation of an impermeable barrier. [48] The latter is a self-limiting process with the reaction halting when the impermeable barrier is formed. There is also the possibility of a disparity in diffusion rates of species in the film and substrate through the reacted region, [48]
which leads to void formation. In the case of Fig. **2.3(e)**, the substrate species diffusion rate is higher than that of the film, resulting in voids in the substrate.

The diffused interface (Fig. 2.3(b)) is characterized by a gradual change in composition from film to substrate.[48] Solubility between the film and substrate may precede the formation of interfacial compounds,[48] resulting in a planar interface region as in Fig. 2.3(b). However, solubility asymmetry between the film and substrate may result in pitted interfaces as in Fig. 2.3(c). Grain boundaries profoundly affect the diffusion rate of atoms in thin films. In polycrystalline thin films, diffusion is dominated by lattice diffusion at high temperatures because the grain boundary volume fraction is very small. As the temperature is lowered, the contribution from grain boundary diffusion increases as a result of the lower activation energy for grain boundary diffusion (compared to the bulk lattice).[50]

From a metallurgical perspective, materials to be used in ohmic contacts to III-V compound semiconductors should ideally meet several criteria: 1) The deposited metal reacts with the III-V semiconductor to promote adhesion, and reactions should occur in the solid state to best control contact morphology.[51] 2) The metal and semiconductor should react in such a way as to minimize void formation (net elemental diffusion is zero). [51] 3) The reaction should result in a thin film ternary alloy, rich in the III-V elements.[51] The advantage of such a contact is that the interfacial accumulation or segregation of group III or V elements does not dictate the electrical and morphological properties.[51]

2.2.2 Solid State Amorphization Reaction (SSAR)

Reaction between thin films may result in the formation of an amorphous phase. This phenomenon occurs in some metal/semiconductor contacts and is discussed here as a point of interest. Research presented in this thesis on the reaction between a Pd thin film and GaSb substrate has shown that there is a nanocrystalline reacted region at low temperatures that behaves in a manner similar to reported amorphous phase formation at thin film interfaces. Discussion on metastable amorphous phase formation has been discussed in depth by Gösele and Tu,[52][53] whose analysis of a metastable amorphous phase is based on kinetic stability analysis[54] used to determine the critical thickness of a first growing phase. The reader is encouraged to explore the literature presented by Gösele and Tu for a complete explanation of SSAR.

The formation of an amorphous phase at a metal/metal (M/M) or metal/semiconductor (M/S) interface was first discussed by Schwartz and Johnson,[55] and it has since been referred to as the "solid state amorphization reaction" (SSAR). In order for SSAR to occur, a series of requirements must be met:[56]

- 1. A large negative heat of mixing must exist between the metals in the amorphous state.
- 2. The diffusivities of the metals must be very different in each other and in the newly formed amorphous phase that forms at the interface.
- The system must not have a stable crystalline phase from which a sublattice of the larger atom can be derived by a diffusionless transformation.

The first requirement ensures that there is a high rate of diffusion and a thermodynamic driving force for the formation of the amorphous phase. The second requirement ensures the formation of an amorphous phase over that of a more stable crystalline phase. The fast diffusing element in the couple allows for elemental mixing, while the slower, essentially immobile, diffusing element hinders structural change in the lattice that would allow for the formation of an equilibrium phase. The third and last requirement implies that there is no intermetallic phase in the binary system that is formed via the diffusion of the smaller atom in the lattice of the larger one, the manner in which SSAR proceeds.

The nucleation, growth, and lifetime of metastable phases has been studied in depth and reviewed by various authors in previous decades. [56] - [62] SSAR results in a metastable amorphous phase. The lifetime of this phase is ultimately limited by the nucleation and growth of a more stable intermetallic. The formation of a metastable amorphous phase is often the result of a low temperature reaction between bilayer or multilayer thin films. The metastable phase has a small nucleation barrier, favoring its formation, and leads to a reduction in free energy, even though its formation does not bring the system to a global minimum in free energy. Although phase selection based on kinetic barriers and maximum degradation of free energy favors the formation of a metastable phase (M), the phase will not continue to grow beyond a certain thickness. The growth rate of M will eventually slow due to diffusion-controlled processes. As diffusion slows the growth of the metastable phase, the equilibrium phase (E) nucleates and grows. In the initial stages, the equilibrium phase experiences interface-controlled growth and grows much faster than M. It is at this point that the metastable phase is at a

maximum thickness. It is subsequently consumed or transformed into the more stable, equilibrium phase.

2.2.3 Diffusion Barriers

Diffusion barriers are thin films used to separate materials from one another and to prevent reaction between the materials.[48] The best diffusion barriers exhibit no thermodynamic driving force for reaction with adjacent elements or compounds, good microstructural integrity, high melting temperature (to favor low diffusivities), and good electrical conductivity (for microelectronics).[46] These properties are important for contacts to III-V compound semiconductors where Au capping layers are often required for wire bonding and to reduce metal sheet resistance. Gold has been shown to react severely with Sb-based compound semiconductors, reducing device reliability; as a result, it is imperative to identify high quality diffusion barriers to minimize the possibility of Au/III-V reactions.[49] This is the case for all contact studies presented in this thesis; as a result, it is of interest to explore some of the properties of useful diffusion barriers.

Diffusion rates on free surfaces are generally the highest, followed by diffusion along grain boundaries and disclocations, with diffusion in the bulk lattice being the slowest.[36] Although surface diffusion rates are highest, these are not considered to be problematic in this research. This is based on the knowledge that the percentage of free surface where elements of interest exist is minimal. Using knowledge based on diffusion rates, an epitaxial or single crystal material is preferred as a diffusion

barrier; however, this is impractical given that these barriers are difficult to fabricate. [50] Practically, one then considers large grained polycrystalline and amorphous films. Three types of barriers are described by Nicolet: [64] stuffed barriers, passive compound barriers, and sacrificial barriers. All three barriers are illustrated in Fig. 2.4. Stuffed barriers rely on the segregation of impurities along fast diffusion, paths such as grain boundaries, to block further atomic diffusion along these paths. In essence the grain boundaries have been "stuffed" with impurity atoms (such as argon, nitrogen, or oxygen) inhibiting diffusion along these routes. Passive compound barriers exhibit chemical inertness, negligible solubility, and negligible diffusivity of A and B into the barrier. Sacrificial barriers maintain the separation of A and B only for a limited time. Sacrificial barriers exploit reactions between the barrier and A and B to form AX and BX compounds that continue to be separated by a narrowing barrier X. This barrier is effective only as long as the barrier is present and the conductivity of AX and BX remain high. Stuffed barriers are often utilized in metal-aluminide and metal-silicide microelectronic systems. One must be aware that diffusion barriers do not eliminate the driving force for diffusion; they merely reduce the rate of interdiffusion by presenting a region of reduced mobility for atomic migration. [50]



Barrier effectiveness lasts as long as AX and BX are separated

Figure **2.4**: Diffusion barriers as categorized by Nicolet.[64] Stuffed barriers are often used in metal/aluminide and metal/silicide contacts.

2.2.4 Metal/Semiconductor Band Alignment

The reaction at the interface of two materials has been explored in 2.2.1 - 2.2.3. It is also useful to consider the physics of a M/S interface. When a metal makes contact with a semiconductor, the Fermi levels in the two materials must be coincident at thermal equilibrium, which results in a potential barrier at the metal-semiconductor interface.[13] For an n-type semiconductor with a work function less than that of the metal, the energy diagram may resemble either case presented in Fig. 2.5.[13] The first case, known as the Schottky-Mott limit, is illustrated along the top in Fig. 2.5. The second case, referred to as the Bardeen limit, is illustrated along the bottom of Fig. **2.5**. These cases are the limiting cases for metal/semiconductor contacts.[**13**]



Figure **2.5**: Energy-band diagram of metal semiconductor contacts for intimate contact without (Schottky-Mott - shown above) and with (Bardeen - shown below)surface states.

Before proceeding, it is useful to define several terms shown in Fig. 2.5. The Fermi level (E_F) is defined as the energy level where electrons have a 50% probability of occupying an energy state (above absolute zero). [13] The metal work function (Φ_m) is the amount of energy required to raise an electron from the E_F to the vacuum level (VL), the energy level of an electron at rest outside the metal surface.[65] Likewise, the semiconductor electron affinity (χ_s) describes the amount of energy required to raise an electron from the semiconductor conduction band (E_c) to the VL. When the metal and semiconductor are brought into contact, a barrier (Φ_B) to electron transport is formed. The depletion region width (W) is the region within the semiconductor that is absent of charge carriers. Finally, for the Bardeen limit, the charge neutrality level (Φ_o) is set by the semiconductor surface (interface) states and is the position that the E_F must assume to ensure charge neutrality at the semiconductor surface. [65].

2.2.4.1 The Schottky–Mott Limit

Initially the metal and semiconductor are separated by a vacuum, and the bands are flat, as shown in Fig. 2.5 (top). As the metal and semiconductor are brought closer, the Fermi level must be constant throughout the system to maintain equilibrium. This results in the flow of electrons from the semiconductor to the lower energy states of the metal.[13] An increasing negative charge is built up on the metal surface, which is counterbalanced by the positively charged donor atoms that remain in the semiconductor. Charge transfer is necessary at the M/S interface to maintain overall charge neutrality of the system. This results in the formation of an electric field at the M/S interface as well as band bending at the semiconductor surface. In the case referred to as the Schottky-Mott limit, the barrier to electron transport (Φ_B) from the semiconductor to the metal, measured relative to the Fermi energy, is given by: [13]

$$\Phi_{\rm B} = \Phi_{\rm m} - \chi_{\rm s}. \tag{2.1}$$

Here it is assumed that the surface dipole contributions, Φ_m and χ_s , do not change when the metal and semiconductor are brought into contact, that there are no localized states on the semiconductor surface, and that there is perfect contact between the metal and semiconductor.[65] This situation is illustrated as the last M/S configuration in the Schottky-Mott limit in Fig. 2.5. In practice, Eq. 2.1 is not obeyed for many semiconductors because there is often a thin insulating oxide and/or surface states on the semiconductor surface.

2.2.4.2 The Bardeen Limit

Often the barrier height (Φ_B) has little dependence on the metal work function (Φ_m) due to a phenomenon known as Fermi level pinning. [66] An explanation of this phenomenon for many semiconductors was set forth by Bardeen in 1947,[66] who suggested that the discrepancy was due to the effects of surface states on the semiconductor.

As in the Schottky-Mott limit, initially the metal and semiconductor are separated by a vacuum and there is no interaction between them. However, now there is a continuous distribution of energy states at the semiconductor surface characterized by a neutral level, Φ_0 . The presence of surface energy states induces a charge (Q_{ss}) on the semiconductor surface that is dependent on the type of surface state. As the metal and semiconductor are brought closer together, illustrated in Fig. 2.5 as the bottom row, there is again a flow of electrons from the semiconductor to the metal. The charge transfer, however, has little effect on the band bending within the semiconductor as a result of the preexisting surface states, which fill or empty with exchange of charge between the metal and semiconductor. The surface states are also known as interface states when contact is made between the metal and semiconductor. Intimate contact typically is not achieved for III-V compound semiconductor such as GaAs, GaSb, and InP because of the rapid growing oxides on the semiconductor surface.[6][7] As a result, the Bardeen model is often depicted (and originally proposed) with an intervening dielectric layer at the M/S interface.

In the absence of surface states, the negative charge (Q_m) on the metal surface must be equal an opposite that of the positive charge created by uncompensated donors (Q_d) within the semiconductor because the M/S junction must be electrically neutral overall.[65] The same is true when interface states are present. The neutrality condition is now described as

$$Q_m + Q_d + Q_{ss} = 0,$$
 (2.2)

where Q_{ss} is the charge introduced by the interface states.[65] The presence of Q_{ss} influences the depletion region width (W) as well as Φ_B at the M/S interface. If Φ_o is above the Fermi level there is a net positive charge on the interface states and Q_d must be smaller than if no interface states were present. [65] This results in a shrinking of W and Φ_B . There is also a shifting the Fermi level towards Φ_o , decreasing the positive charge in the surface states. On the other hand, if Φ_o is below the Fermi level, as shown in Fig. 2.5, there is a net negative charge on the interface states and Q_d must be greater than if no interface states were present. Thus, to satisfy neutrality conditions, E_F is pushed down towards Φ_o and the barrier to electron transport is increased. In the presence of interface states, the Fermi level will always be shifted toward Φ_o , a requirement necessary to meet charge neutrality and equilibrium conditions. It is usual to measure Φ_o from the top of the valence band, in which case the barrier height is now given by:

$$\Phi_{\rm B} = E_{\rm g} - \Phi_{\rm o}. \tag{2.3}$$

Equation 2.3 is known as the Bardeen limit. The barrier height and E_F at the interface is said to be pinned by the density and charge of surface states.

As previously mentioned in Ch. 1, the GaSb surface consists of native oxides and Ga vacancies that contribute to Fermi-level pinning near the valence band. This situation is similar that that illustrated in Fig. 2.5 as the Bardeen limit, where the barrier height is independent of the metal. As a result, the Bardeen model is better suited for describing the Schottky barrier at the metal/GaSb interface.

2.2.5 Current Transport at the M/S interface

There are four basic processes, under forward bias (current flowing from the semiconductor to the metal), by which current is transported through a metal-semiconductor contact.[13] These processes are: (A) transport of electrons from the semiconductor over the potential barrier into the metal (thermionic emission), (B) quantum mechanical tunneling of electrons through the barrier (field emission), (C) recombination of electrons and holes in the space charge region, and (D) recombination of electrons and hole in the neutral region (hole injection). All four processes are illustrated in Fig. 2.6. In addition to the four processes illustrated in Fig. 2.6, there is also the possibility of defect assisted tunneling and recombination.



Figure **2.6**: Current transport processes at the M/S interface under forward bias.

Thermionic-emission dominates for contacts to semiconductors with lower doping concentrations (A in Fig. 2.6). Current transport in semiconductors that are heavily doped is dominated by field emission (B in Fig. 2.6).[13] Intermediate cases often result in a combination of thermionic and field emission. The basic transport equation at a M/S interface is given by:[68]

$$J = J_{SM} - J_{MS}, (2.4)$$

where J is the total current density, J_{SM} is the current density flowing from the semiconductor to the metal, and J_{MS} is the current density flowing from the metal to the semiconductor. When studying M/S contacts in forward bias, it is useful to explore J_{SM} for thermionic and field emission. The term J_{SM} , at a bias voltage V, is written as:[13][68]

$$J_{SM}(V) = \frac{A^*T}{k} \int_0^\infty P(\xi) e^{-\frac{q\Phi_{Bn} - qV + \zeta}{kT}} d\xi + \frac{A^*T}{k} \int_0^{q(V_{Bo} - V - \Delta\Phi)} F_s P(\eta) (1 - F_m) d\eta , \quad (2.5)$$

where A* is known as Richardson's constant and is dependent on the electron effective mass. F_s and F_m are the Fermi-Dirac distribution functions in the semiconductor and metal, respectively. $P(\xi)$ and $P(\eta)$ are the quantum transmission functions of the electrons above and below the barrier maximum, respectively. The first term on the right hand side of Eq. 2.5 represents the contribution from thermionic emission of electrons over the barrier, and the second term represents field emission of electrons through the barrier.[13] The magnitude of thermionic emission and tunneling current are related to barrier height, doping, and temperature, all of which are in the electron transmission functions.

2.2.5.1 Thermionic Emission

In thermionic emission, the current is controlled by the transfer of electrons over the M/S barrier, and transport of electrons through the barrier is considered negligible.[67] This being the case, the second term in Eq. 2.5 may be neglected. The total current density (J) due to thermionic emission of electrons over the barrier is written as: [13] [67]

$$J = A * T^{2} e^{\frac{-q\Phi_{Bn}}{kT}} \left[e^{\frac{qV}{kT}} - 1 \right],$$
 (2.6)

which indicates that there is an exponentially increasing current in forward bias (V). Equation **2.6** also indicates there is an exponential dependence of the current density with inverse temperature when the semiconductor is lightly doped.

2.2.5.2 Field Emission (Tunneling)

As doping in the semiconductor is increased the width of the depletion region decreases, making tunneling of electrons through the barrier possible. For heavily doped semiconductors the barrier may be thin enough that appreciable tunneling can occur and thermionic emission of electrons over the barrier may be negligible. [13][68] As a result, the first term in Eq. 2.5 can be neglected. At very high doping (or low temperatures) the current density is written as: [67]

$$J \approx J_F e^{\frac{q_V}{E_{00}}},\tag{2.7}$$

where

$$E_{00} = \frac{h}{4\pi} \sqrt{\frac{N_D}{\varepsilon_s m^*}}, \qquad (2.8)$$

and

$$J_{F} = \frac{\pi A * T}{kC_{1} \sin(\pi k T C_{1})} e^{-\frac{q \Phi_{B}}{E_{00}}}.$$
 (2.9)

 E_{00} is a reference energy that depends only on doping (N_D), semiconductor permittivity (ϵ_s), and electron effective mass (m*); and C₁ is inversely proportional to ln(V/E₀₀). From Eqs. **2.7** – **2.9** it is clear that as doping is increased, current density dependence on temperature decreases. The current density (J) exhibits only a weak dependence on temperature through J_F, and E₀₀ is independent of temperature.[**67**]

2.2.5.3 Thermionic-Field Emission

There is also the possibility of thermionic and field emission contributing equally (or nearly equally) to the current density at the M/S interface. This occurs in moderately doped semiconductors as well as at moderate temperatures where $E_{00} \sim kT$.[67] The current density is then written as:

$$J \approx J_{TF} e^{\frac{qV}{E_0}}, \qquad (2.10)$$

where

$$J_{TF} = \frac{A * T \sqrt{\pi E_{00} q(\Phi_B - V - \xi)}}{k \cosh\left(\frac{E_{00}}{kT}\right)} \cdot \exp\left(-\frac{q\xi}{kT} - \frac{q}{E_0}(\Phi_B - \xi)\right), \quad (2.11)$$

and

$$E_0 = E_{00} \operatorname{coth} \left(\frac{E_{00}}{kT} \right). \tag{2.12}$$

From Eq. 2.10 – Eq. 2.12, it should be noted that there is a dependence on temperature and doping through J_{TF} .

2.2.5.4 Recombination within the Space Charge Region

Recombination of holes and electrons within the space charge region usually takes place via localized states within the band gap.[65] Theory explaining current due to recombination is similar to that for p-n junction and is written as:[65]

$$J = \frac{qn_{i}W}{2\tau} e^{\frac{qV}{2kT}} \left[1 - e^{\frac{-qV}{kT}} \right],$$
 (2.13)

where n_i is the intrinsic carrier concentration, W is the depletion region width, and τ is the carrier lifetime within the depletion region.

Comparing the ratio of thermionic emission current to recombination current, it has been shown that the recombination current is likely to be more important when dealing with semiconductors with large Schottky barriers at the M/S interface.[65] Also evident from Eq. 2.13, recombination becomes more important as carrier lifetime, band gap, and forward bias are increased. As a result, it is hypothesized that recombination current plays a less important role for contacts to n-GaSb than that of n-GaAs or Si as these semiconductors exhibit higher Φ_B values.[67]

2.2.5.5 Hole Injection

When the Schottky barrier for a metal contact to an n-type semiconductor is large, the region of the semiconductor directly adjacent to the contact will contain a high density of holes. [65] As a result, there is a possibility that these carriers will drift into the space charge region of the semiconductor, resulting in the injection of holes into the neutral region of the semiconductor. Assuming that the Fermi level of the holes coincides with that of the metal and remains flat throughout the space charge region, the hole injection current density is written as:[65]

$$J_{h} = \frac{qD_{p}p_{o}}{L} \left[e^{\frac{qV}{kT}} - 1 \right], \qquad (2.14)$$

where p_o is the equilibrium hole concentration (= n_i^2/N_D) at the edge of the space charge region; and D_p and L are the diffusion constant of holes in the semiconductor and neutral region thickness, respectively.[65] The hole injection current increases with Φ_B , which is a result of the decrease in the electron current density as Φ_B increases.[65] Also, evident from Eq. 2.14, J_h is inversely proportional to semiconductor doping levels since p_o and N_D are inversely proportional.

2.3 Ohmic Contacts and Specific Contact Resistance

An ohmic contact is defined as a metal-semiconductor contact having negligible resistance relative to the bulk or spreading resistance of the semiconductor. [13] The specific contact resistance (ρ_c) describes the current transport characteristics of a M/S contact, and is in part a measure of the quality of the contact. A high quality ohmic contact is required to have values of ρ_c sufficiently small enough so that the observed linear current-voltage curve is mainly due to the series resistance of the semiconductor material near the contact at zero bias (V).[68] The specific contact resistance is defined as the reciprocal of the derivative of current density with respect to voltage, that is: [68]

$$\rho_c = \left(\frac{\delta J}{\delta V}\right)_{V=0}^{-1}.$$
(2.15)

High doping concentration, low barrier height, or a combination of both, are required to obtain low values of ρ_c, and approaches to accomplish these situations are used in forming most ohmic contacts.[**13**] As discussed earlier, thermionic-emission (A in Fig. **2.6**) dominates for contacts to semiconductors with lower doping concentrations, and field emission (B in Fig. **2.6**) dominates for contacts with high doping concentrations. The current density (J) varies according to temperature and doping; and as a result, so will the specific contact resistance.

The specific contact resistance for lightly doped semiconductors (thermionic emission) is found by differentiating Eq. **2.6** with respect to voltage, and then taking the inverse. By doing so, one acquires:[**67**]

$$\rho_c = \frac{k}{qA^*T} e^{\frac{q\Phi_B}{kT}},\tag{2.16}$$

and from Eq. 2.16 it is clear that with increasing temperature and decreasing barrier height ρ_c will decrease exponentially. It should also be noted that ρ_c is inversely proportional to A^{*}, which means that as the effective mass of the electron is increased, ρ_c will decrease, although at a much slower rate.

As doping is increased, thermionic emission over the barrier gives way to the tunneling of electrons through the barrier. This leads to another set of equations, as previously described, and by taking the inverse of the derivative of Eq. 2.7 with respect to voltage we arrive at:[67]

$$\rho_{c} = \left[\frac{A * T \pi q}{k Sin(\pi C_{1} kT)} \exp\left(\frac{-\phi_{B}}{E_{oo}}\right) - \frac{A * q}{C_{1} k^{2}} \exp\left(-\left(\frac{\phi_{B}}{E_{oo}}\right) + (C_{1} \xi)\right)\right]^{-1}, \quad (2.17)$$

where

$$C_{1} = \frac{Log\left(-4\phi_{B}/\xi\right)}{2E_{oo}}$$
(2.18)

and

$$\xi = E_c - E_F \,. \tag{2.19}$$

Highly doped semiconductors, evident from Eq. 2.17, exhibit only a small temperature dependence of the specific contact resistance; however, ρ_c is highly dependent on the doping levels (N_D) of the semiconductor. By measuring the specific contact resistance as a function of temperature, we are able to determine if there is temperature dependence and ultimately the current transport mechanism at the M/S interface.

There is also the possibility, as described above, that no one transport mechanism dominates. Thermionic-field emission is a combination of electrons going over and through the barrier. The specific contact resistance of a metal/semiconductor contact is then described by differentiating Eq. **2.11** according to Eq. **2.15**, which yields:

$$\rho_{c} = \frac{k^{2} Cosh\left(\frac{E_{oo}}{kT}\right)}{qA^{*} \left[\pi q(\phi_{B} + \xi)E_{oo}\right]^{1/2}} \left[Coth\left(\frac{E_{oo}}{kT}\right)\right]^{1/2} \exp\left[\left(\frac{(\phi_{B} - \xi)}{E_{o}}\right) + \frac{\xi}{kT}\right]$$
(2.20)

Ohmic contacts play an important role as the medium by which current passes to and from the active regions of devices and circuits. Often there are several layers of metallization, but the most important interface is the metal/semiconductor interface, [69] where the current transport characteristics are determined. Due to the proximity of the metal/semiconductor interface to the active regions of semiconductor structures, one must consider reactions, interdiffusion, mechanical properties, and electromigration at the metal-semiconductor interface because these issues are critical for stable contacts. [69]

2.4 Ohmic Contact Formation Mechanisms

Forming ohmic contacts to compound semiconductors, such as GaSb, may be accomplished in several different manners. Techniques include diffusion and ion implantation to incorporate atoms in the semiconductor forming an n⁺ or p⁺ region at the semiconductor surface; epitaxially growing heavily doped or compositionally graded capping layers on the semiconductor surface; and alloying deposited metals with the semiconductor.[**67**]

For GaAs, the most common method used in contacts to GaAs is the alloy regrowth method.[67] This method requires that deposited metallizations liquefy and dissolve some GaAs upon annealing, forming an alloy containing a dopant (or impurity) atom in high concentration as well as Ga and As. Upon cooling, the dopant or impurity atom is incorporated into the semiconductor during epitaxial regrowth of the semiconductor. [67]

The alloy regrowth method utilizes liquid phase formation at the metal/semiconductor interface.[67] The formation of such phases reduces reaction uniformity at the interface as well as reproducibility of electrical properties. An alternative to the liquid regrowth method is the incorporation of dopant or impurity atoms using solid-state reactions.[67] Sintered metal contacts offer the advantage of increased reaction uniformity and reproducible electrical properties. Two important solid-state reaction mechanisms for the incorporation of impurity atoms that reduce the barrier height in n-GaAs are the solid-state regrowth mechanism[70] and the exchange mechanism.[73] In metal/GaAs systems these mechanisms are sometimes used for the incorporation of

group III elements in place of Ga. As a result, it is also hypothesized in this thesis work that these methods might be favored for the incorporation of group III elements, such as In, in n-GaSb for barrier reduction.

2.4.1 The Solid Phase Regrowth Mechanism

The solid phase regrowth mechanism, illustrated in Fig. 2.7, was first proposed by Sands *et al.*[70] based on Pd/Si contacts to GaAs. Sands *et al.* [70] proposed a scheme where two elements, M and M', are deposited on a semiconductor substrate, AB. The film in contact with the substrate, consisting of M, reacts at low temperatures to form a ternary phase M_xAB :

$$xM + AB \rightarrow M_xAB.$$
 (2.21)

M may also react with M', but only to a limited extent. The second element, M', is chosen such that its reaction product with M is more thermodynamically stable than M_xAB, so M' reacts with the ternary phase M_xAB to form a compound MM'_y upon annealing at higher temperatures:

$$xyM' + M_xAB \rightarrow AB(M') + xMM'_y.$$
 (2.22)

The AB semiconductor substrate is close enough to the reacted interface that the regrowth of AB(M') is epitaxial with M' incorporated, as indicated in Eq. **2.22** by AB(M') and in Fig. **2.7** by AB:M'.



Figure 2.7: Illustration of the regrowth mechanism (From Sands *et al.*)

The regrowth mechanism has been reported for Pd-In ohmic contacts to GaAs via the formation of $In_xGa_{1-x}As$ at the metal/GaAs interface.[71] A (Pd/In)/Pd/GaAs metallization was employed, and during low temperature annealing (~100 °C) the following reactions occurred: [71]

$$4Pd + GaAs \rightarrow Pd_4GaAs, \qquad (2.23)$$

and

$$3Pd + 7In \rightarrow Pd_3In_7.$$
 (2.24)

Upon annealing at higher temperatures, the subsequent reaction:

$$Pd_4GaAs + Pd_3In_7 \rightarrow 7PdIn_xGa_{1-x} + In_yGa_{1-y}As$$
 (2.25)

occurred, where x and y relate by the mass balance: 7x + y = 7. This reaction sequence is illustrated in Fig. 2.8.

The incorporation of In into the GaAs substrate results in the formation of a ternary alloy (InGaAs) with properties dependent on the amount of In incorporated into the substrate. As larger fractions of In are incorporated into the GaAs the resulting semiconductor exhibits properties of an alloy of GaAs and InAs. This is advantageous for ohmic contact because InAs has a smaller band gap than GaAs (0.42 eV versus 1.42 eV),[72] and the barrier to electron transport at the M/S interface decreases with an increase in In concentration, allowing for additional thermionic emission of electrons over the barrier.



Figure **2.8**: Schematic of regrowth mechanism implemented for a (Pd/In)/Pd/GaAs contact reported by Wang *et al.*[71]

2.4.2 The Exchange Mechanism

A second reaction mechanism utilized to control the electrical characteristics of a metal/semiconductor interface in the solid-state is the exchange mechanism, [73] depicted in Fig. 2.9. Swenson *et al.*[73] present an extensive study on the thermodynamics and kinetics of the exchange mechanism and this study is the basis for further discussion of this mechanism. The exchange mechanism is the solid state exchange of a group III element between a metallic compound (TIII') and compound semiconductor (IIIV); where T is the transition metal, III and III' are two different group III elements, and V is the group V element. No new phases

form during the exchange process, only a shift in composition of the original phases is involved.



Figure **2.9**: Illustration of the exchange mechanism (a) before and (b) following group III exchange.

As shown in Fig. 2.9(b), the exchange of the group III element between TIII' and the semiconductor IIIV leads to the formation of a ternary semiconductor alloy $III'_{x}III_{1-x}V$ and a ternary metallic alloy $TIII'_{y}III_{1-y}$, where x and y denote composition of III'V and TIII' within the ternary alloys, respectively. The resulting electrical contact properties correspond to those of a contact to the semiconductor alloy. This is similar to the solid phase regrowth mechanism example where the incorporation of In into GaAs formed a ternary InGaAs semiconductor alloy with a reduced band gap and smaller barrier to electron transport. While the exchange mechanism is conceptually straightforward, a metallization must meet stringent criteria to be capable of participating in an exchange reaction.

Thermodynamic considerations must be taken into account in order for the exchange mechanism to be operative. There must be no new phase formation favored at the metal/semiconductor interface, according to the quaternary T-III-III'-V phase diagram. Figure 2.10 illustrates a T-V-III-III' system in which an exchange reaction is favored. The quaternary diagram depicted in Fig. 2.10 consists of four ternary diagrams: V-III-III', T-III-III', V-III'-T, and V-III-T. The IIIV and III'V semiconductors form a solid solution (III'_xIII_{1-x}V), and TIII and TIII' form a complete solid solution (TIII'yIII_{1-y}). The quaternary phase diagram indicates that TIII' and III'V are in equilibrium with each other, as are TIII and IIIV. As a result equilibrium exists between the semiconductor $(III'_xIII_{1-x}V)$ and intermetallic $(TIII'_yIII_{1-y})$ alloys. This equilibrium is depicted in Fig. 2.10 as the shaded region in the diagram. The quaternary isotherm shaded in Fig. 2.10 emulates a ternary system rather than a quaternary system; thus, the quaternary system is known as a reciprocal system. A system as depicted above fulfills all thermodynamic requirements for the exchange mechanism to be probable. Mass balance requirements dictate the overall composition lies along the dashed line connecting IIIV and TIII' within the shaded region in Fig. 2.10, satisfying the requirement that no new phases form at the metal/semiconductor interface. Taking into account kinetic considerations, a complete reciprocal system is not absolutely necessary for the exchange mechanism to be feasible. Rather, what is important is that the

compositional plane defined by the reciprocal system resembles a reciprocal system in the III'-rich region of the diagram.



Figure **2.10**: T-V-III-III' quaternary phase diagram with compounds pertinent to the exchange mechanism.

Chapter 3

Experimental Procedures and Data Analysis

The following chapter presents a detailed summary of the experimental procedures that were followed during thesis research. There are three major sections that outline the steps followed during experimental work. Each section describes sample preparation and materials characterization procedures, as well as data analysis for each research project.

3.1 Pd/GaSb Thin Film Reactions

3.1.1 Sample Preparation

To analyze the initial reaction stages of the Pd/GaSb reaction, samples were prepared using moderately doped n-GaSb (n = $2 - 6 \ge 10^{17}$ cm⁻³) wafer substrates. Prior to wafer preparation and metal deposition, samples were cleaved to an appropriate size according to the characterization technique used. Samples that were characterized using transmission electron microscopy (TEM) were initially cleaved into $2 \ge 5$ mm pieces, and those used in x-ray diffraction (XRD) analysis were cleaved into $7 \ge 9$ mm pieces. To rid the surface of organic contaminants, the samples were next soaked in acetone and methanol for 5 min each followed by a deionized (DI) water rinse before they were blown dry with N₂. To minimize the amount of native oxides on the GaSb surface, samples were subjected to an 18.5 % HCl etch for 30 s followed by a DI water rinse and N₂ blow dry immediately before they were loaded into a sputter deposition vacuum chamber. The vacuum chamber was then pumped to a base pressure of ~ 1×10^{-7} Torr, and 50 nm of Pd was sputter deposited at a rate of ~1 Å/s. Following metal deposition, samples were sealed in evacuated quartz ampoules (~ 5 x 10^{-3} Torr) and annealed at various temperatures and times according to Table **3-1**.

Temperature	Time (min)	
As-deposited	NA	
100 °C	90	
	180	
	360	
200 °C	10	
	30	
	45	
300 °C	10	
	30	
350 °C	10	
	30	

Table **3-1**: Annealing conditions of Pd (50 nm)/GaSb

Following annealing, samples were prepared according to the particular technique used for analysis. Samples analyzed by XRD did not require any further preparation prior to characterization. Samples analyzed via TEM were bonded face-to-face using MBOND 600. Samples were then sliced into 500 µm thick specimens using a diamond cutoff wheel and polished on one side. Next the samples were mounted onto a TEM copper grid using MBOND 200 and polished to a thickness of approximately 15 µm before being placed in a Fischione 1010 low angle milling and polishing system to achieve electron transparency.

3.1.2 Pd/GaSb Materials Characterization

Samples were analyzed using grazing incidence x-ray diffraction (GIXD) or TEM. Transmission electron microscopy was performed on cross-section specimens using a JEOL 2010F field emission electron microscope. Samples analyzed using TEM were characterized via nanobeam diffraction (NBD), scanning TEM (STEM), and energy dispersive xray spectroscopy (EDX). X-ray diffraction patterns were acquired using a Philips (now PanAnalytical, Inc.) X'PERT MRD x-ray diffractometer and were compared to known Pd, Pd-Ga, Pd-Sb, Pd-Ga-Sb, and GaSb diffraction patterns from the literature for phase identification. [80][81][82][83]

3.1.2.1 Quantitative Energy Dispersive X-ray Spectroscopy

In order to quantify data acquired via EDX, the Cliff-Lorimer ratio technique was employed.[84][85] This technique requires that standards with known compositions be used as a reference to identify the composition of unknown samples. Two samples of known composition were made: PdGa and GaSb. Initially a 5g ingot of PdGa was made as a target for pulsed-laser deposition (PLD) of a 100 nm PdGa film for TEM analysis. The ingot was prepared using Pd foil (99.99 %) cut into ~ 3 x 3 mm pieces and Ga shot (99.999 %) 4 mm in diameter. The material was

weighed to within ± 0.1 mg of the calculated value, and sealed in a 1 cm quartz ampoule under medium vacuum (7 mTorr). The sample was then heated to 1100 °C, 55 °C above the congruent melting point of PdGa, [39] at a rate of \sim 5 °C /min and then held at 1100 °C for 45 min to ensure complete melting. The sample was next cooled to 900 °C and held for 24 h, and then cooled to 800 °C and held for an additional 24 h, after which the sample was quenched to room temperature. Following the heat treatment, the ingot was polished on one side to a mirror finish and mounted on a PLD target stub for deposition of 100 nm of PdGa on a salt crystal. Following deposition, the salt crystal was cleaved into 2 x 2 mm pieces and several pieces were placed in DI water to dissolve the salt and leave the PdGa film floating on the surface. The PdGa thin foil specimens were then collected from the water using a TEM specimen grid with a cross-hatch pattern in the center, after which the samples were ready for analysis. GaSb specimens were prepared from a GaSb wafer. The specimens were prepared using the same technique described above for the Pd/GaSb specimens.

Five to ten EDX spectra were collected from each sample. Each spectra was collected for 100 s to ensure a high signal-to-noise ratio. Integrated peak intensities of the Ga K-lines (9.03 - 10.43 and 10.04 - 10.5 keV), Sb L-lines (3.48 - 4.25 keV), and Pd L-lines (2.38 - 3.41 keV) were calculated using Emispec System's ES Vision 4.0 software. Using the integrated peak intensities of EDX spectra collected from the PdGa and GaSb samples, we are able calculate the relationship between peak intensity and concentration for Ga-Pd, Sb-Pd, and Ga-Sb according to:[84]

$$\frac{I_A}{I_B} = k_{AB} \frac{C_A}{C_B}, \qquad (3.1)$$

where I_A and I_B are the integrated peak intensities of two elements in a given spectra, and C_A and C_B are the atomic concentrations of the same elements. The constant k_{AB} is known as the k-factor, which relates concentration and integrated peak intensity in an EDX spectra. The experimental k-factors k_{GaPd} , k_{SbPd} , and k_{GaSb} for the JEOL 2010 F TEM used in this study, given in Table **3–2**, are used to calculate quantitative compositions of phases in any Pd/GaSb thin film sample. This is accomplished by acquiring EDX spectra under the same TEM conditions (acquisition time, beam energy) as spectra collected for the standard PdGa and GaSb samples.

k _{AB}	Experimental value	Error
k _{GaSb}	0.719	0.043
k_{GaPd}	0.317	0.021
k_{SbPd}	0.447	0.029

Table **3-2**: Experimental k-factors for the Pd-Ga-Sb system

Error propagation is important when attempting to quantify elemental composition. As a result, it is pertinent to discuss the method in which experimental error was calculated during data quantification. Each spectrum was analyzed using Emispec System's ES Vision 4.0. This software has the ability to calculate integrated peak intensities (I_A and I_B) for a given energy range that may be chosen automatically or specified by the user. Integration is accomplished by the software via a polynomial fit of the energy peaks. Following peak integration the software outputs the integrated intensity (I_x) and an associated uncertainty (δI_x) for the integration. Each k-factor in Table **3-2** is calculated from a standard sample with known concentration and the integrated peak intensity according to:

$$k_{AB} = \frac{I_A C_B}{I_B C_A}.$$
(3.2)

 C_A and C_B are well known with error values < 1 at.%, and I_A and I_B have associated error values of δI_A and δI_B . The error associated with I_A and I_B are large enough (≥ 5 at.%), that the error in C_A and C_B are taken to be negligible. The error calculated in k_{AB} is then: [86]

$$\frac{\partial k_{AB}}{\left|k_{AB}\right|} = \sqrt{\left(\frac{\partial I_A}{I_A}\right)^2 + \left(\frac{\partial I_B}{I_B}\right)^2} . \tag{3.3}$$

From Eq. 3.1 and Eq. 3.3, the concentration ratio (C_A/C_B) with error can be calculated according to: [86]

$$\frac{C_A}{C_B} \pm \delta \left(\frac{C_A}{C_B}\right) = \frac{I_B}{k_{AB}I_A} \pm \sqrt{\left[\frac{\delta k_{AB}}{k_{AB}}\right]^2 + \left[\frac{\delta I_A}{I_A}\right]^2 + \left[\frac{\delta I_B}{I_B}\right]^2}$$
(3.4)

Using Eq. 3.4, and spectra from the PdGa and GaSb standards, we are able to calculate the Sb:Ga ratio (C_{Sb}/C_{Ga}) and Ga:Pd ratio (C_{Ga}/C_{Pd}) with associated errors in unknown samples. From this we may calculate the Sb:Pd ratio according to:

$$\frac{C_{Sb}}{C_{Pd}} \pm \delta\left(\frac{C_{Sb}}{C_{Pd}}\right) = \frac{C_{Sb}}{C_{Ga}} \frac{C_{Ga}}{C_{Pd}} \pm \sqrt{\left(\frac{\delta\left(\frac{C_{Sb}}{C_{Ga}}\right)}{\frac{C_{Sb}}{C_{Ga}}}\right)^2 + \left(\frac{\delta\left(\frac{C_{Ga}}{C_{Pd}}\right)}{\frac{C_{Ga}}{C_{Pd}}}\right)^2}$$
(3.5)

Once C_{Sb}/C_{Pd} and C_{Ga}/C_{Pd} are calculated, the concentrations of Ga and Sb are calculated based on the Pd concentration:

50

$$C_{Pd} \pm \delta(C_{Pd}) = C_{Pd} \pm \sqrt{\left(\frac{\delta(I_{Pd})}{I_{Pd}}\right)^2}$$
(3.6)

$$C_{Ga} \pm \delta(C_{Ga}) = \left(\frac{C_{Ga}}{C_{Pd}}\right) C_{Pd} \pm \sqrt{\left(\frac{\delta(C_{Pd})}{C_{Pd}}\right)^2 + \left(\frac{\delta\left(\frac{C_{Ga}}{C_{Pd}}\right)}{\frac{C_{Ga}}{C_{Pd}}}\right)^2}$$
(3.7)

$$C_{Sb} \pm \delta(C_{Sb}) = \left(\frac{C_{Sb}}{C_{Pd}}\right) C_{Pd} \pm \sqrt{\left(\frac{\delta(C_{Pd})}{C_{Pd}}\right)^2 + \left(\frac{\delta\left(\frac{C_{Sb}}{C_{Pd}}\right)}{\frac{C_{Sb}}{C_{Pd}}}\right)^2}$$
(3.8)

$$C_{Pd} + C_{Ga} + C_{Sb} = 1 \tag{3.9}$$

where the Pd concentration (C_{Pd}) is chosen such that Eq. **3.9** is satisfied, yielding C_{Ga} and C_{Sb} . Following analysis of each individual spectra, an average of the ten spectra is calculated. Energy dispersive x-ray spectroscopy data reported in the following pages are averaged values of approximately ten individual spectra acquired for each sample. Error associated with each value is also an average of the individual spectra error. It should be noted that during EDX quantification the thin film approximation was assumed. This assumption circumvents the problem of x-ray absorption within a sample by acquiring EDX scans in a region of the sample that is thin enough to neglect the absorption effect. Assuming

absorption is negligible may lead to large errors in the quantification process if the film is not thin enough; as a result, it is useful to verify that absorption can be neglected for this thesis research.

According to Horita *et al.*[87] absorption correction is calculated according to:

$$\frac{I_B}{I_A} = \left(\frac{I_A}{I_B}\right)_O \left[\frac{\binom{\mu}{\rho}_A}{\binom{\mu}{\rho}_B}\right] \left[\frac{1 - \exp\left(-\binom{\mu}{\rho}_B \rho \tau * Csc(\alpha)\right)}{1 - \exp\left(-\binom{\mu}{\rho}_A \rho \tau * Csc(\alpha)\right)}\right]$$
(3.10)

Where I_B/I_A is the measured intensity ratio of element B and A, $(I_B/I_A)_O$ is the absorption-corrected intensity ratio, (μ/ρ) is the mass absorption coefficient of element A or B in specimen AB, ρ is the specimen density, τ is the specimen thickness, and α is the x-ray take-off angle. By assuming that all the x-rays are generated at one-half the thickness of the specimen, Eq. **3.10** can be simplified to:

$$\frac{I_B}{I_A} = \left(\frac{I_A}{I_B}\right)_O \exp\left(-\left(\left(\frac{\mu}{\rho}\right)_B - \left(\frac{\mu}{\rho}\right)_A\right) * \rho \frac{\tau}{2} * Csc(\alpha)\right)$$
(3.11)

Using a weighted average mass absorption coefficient, according to photon energy,[88] an absorption-corrected intensity ratio can be calculated for various Pd-Ga, Pd-Sb, and Ga-Sb ratios according to specimen thickness. Figure 3.1 illustrates the variation in absorption as a function of specimen thickness for GaSb and Ga₂Pd₅ using a take-off angle (α) of 20°. The weighted mass absorption coefficient for Ga and Sb in GaSb is 30.0 cm²/g and 160.1 cm²/g, respectively. The weighted mass absorption coefficient for Ga and Pd in Ga₂Pd₅ is 28.9 cm²/g and 225.2 cm²/g, respectively. Based on Eq. 3.11, the absorption correction for these compounds is < 10% up to a specimen thickness of 350 nm. For the purpose of simulation the absorption-corrected intensity was assumed to be 1. Figure **3.1** indicates that the quantitative EDX analysis presented in this thesis should not be affected by more than \pm 5 % as a result of thickness variations across the specimen, within the range of typical EDX quantification capabilities.



Figure 3.1: Adjusted I_B/I_A for two compounds studied in the current thesis work. Both specimens exhibit only minor absorption throughout the thickness range tested.

3.1.2.2 Nano-beam Electron Diffraction and Phase Identification

Phase identification via GIXD is not always possible when characterizing low symmetry phases such as those found in the Pd-Ga and Pd-Sb binary systems.[**39**][**81**] This is due to severe peak overlap in the XRD patterns between phases in the Pd-rich portions of the Pd-Ga and Pd-Sb binary phase diagrams.[**39**][**81**] As a result, nanobeam diffraction (NBD) may be useful in assisting with phase identification. The NBD function on the JEOL 2010F allows the operator to form an electron probe 1.9 Å in diameter. As a result, the JEOL 2010F is capable of acquiring electron diffraction patterns from areas only a few nanometers in diameter, allowing for the identification of individual grains within the Pd/GaSb reacted region. During electron diffraction there is some beam spread as a result of sample thickness. This, however, does not effect materials characterization in this study because grain sizes are a minimum of 15 nm in diameter, large enough to ensure that diffraction patterns come from single grains even with beam spread.

Acquired NBD patterns are used to calculate the d-spacings of planes within the given phase, as well as angles between those planes. The d-spacings are calculated according to:[**89**]

$$Rd = \lambda L, \qquad (3.12)$$

where R is the distance from the central beam to a diffracted spot on the electron diffraction pattern, d is the d-spacing of the plane associated with that diffracted spot, λ is the electron wavelength (0.0251 Å at 200 keV), and L is the camera length of the microscope. Camera lengths of 25 and 40 cm were used during phase identification via NBD; these camera lengths were calibrated by a TEM technician to be 26.77 (± 0.80) and 42.57 (± 1.27) cm, respectively, using a Si standard.

Angles between planes are next acquired by measuring the angles between adjacent spots on the NBD pattern. These angles are then matched, along with d-spacing, to known x-ray diffraction pattern angles from Pd-Ga and Pd-Sb binary phases.[80] The indexed x-ray diffraction patterns contain planes that correspond to a given d-spacing. Angles
between given planes, however, had to be calculated from (hkl) values given in the literature in order to identify phases in the Pd/GaSb reacted region. Hexagonal and orthorhombic phases are found in the Pd-Ga-Sb system, and are important to this particular study. Plane spacing are calculated according to:[90]

Hexagonal:
$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2},$$
 (3.13)

and

Orthorhombic:
$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$
. (3.14)

Interplanar angles are calculated according to: [90]

Hexagonal:
$$\cos\phi = \frac{h_1h_2 + k_1k_2 + \frac{1}{2}(h_1k_2 + h_2k_1) + \frac{3a^2}{4c^2}l_1l_2}{\sqrt{\left(h_1^2 + k_1^2 + h_1k_1 + \frac{3a^2}{4c^2}l_1^2\right)\left(h_2^2 + k_2^2 + h_2k_2 + \frac{3a^2}{4c^2}l_2^2\right)}},$$
 (3.15)

and

Orthorhombic:
$$\cos\phi = \frac{\frac{h_1h_2}{a^2} + \frac{k_1k_2}{b^2} + \frac{l_1l_2}{c^2}}{\sqrt{\left(\frac{h_1^2}{a^2} + \frac{k_1^2}{b^2} + \frac{l_1^2}{c^2}\right)\left(\frac{h_2^2}{a^2} + \frac{k_2^2}{b^2} + \frac{l_2^2}{c^2}\right)}},$$
 (3.16)

where h, k, and l are the Miller indices of a particular plane; a, b, and c are the lattice parameters for that crystal; and ϕ is the angle between (h₁k₁l₁) and (h₂k₂l₂). The (hkl) and lattice parameter values were taken from the literature for each phase. Other crystal structures in the Pd-Ga and Pd-Sb binary systems include rhombohedral and cubic; however, no NBD patterns matched phases with either crystal structure. For this reason, equations pertaining to the d-spacing and angle calculation of these phases are not included, but can be found in Cullity.[90] Measured d-spacing and angles from the NBD patterns were matched to calculated ones from the literature according to Eq. 3.12 – Eq. 3.16. A match was considered to be made when the measured and calculated d-spacing were within the measured experimental error and the interplanar angles matched within \pm 5 degrees of the calculated values.

3.2 Pd-Ga-Sb Phase Diagram Procedures

Phase diagram samples were prepared using Pd powder (99.99%, 325 mesh), Sb powder (99.999%, 200 mesh), Ga splatter (99.999%, metals basis, 2 - 4mm pieces), and GaSb powder (ground from semiconductor grade GaSb chunks to ~ 200 mesh). Samples were weighed to yield a total mass of 0.80 g using a Mettler AE240 balance. Initial compositions are not listed here, but are given in Table 5-1, Table 5-2, and Table 5-4 to facilitate discussion of the experimental results. Table 5-1, Table 5-2, and Table 5-4 summarize the initial atomic percent and calculated weights of the starting materials for samples to be annealed at 500, 600, and 700 °C, respectively. For samples containing elemental Ga, the powder elements (Pd, GaSb, and Sb) were pressed into pellets prior to being annealed with elemental Ga. Samples were then sealed in an evacuated quartz tube ($\sim 7 \times 10^{-3}$ torr) and placed into a box furnace to be annealed. Samples were initially annealed for 1 week at 500°C to ensure mixing of the pressed powder pellets and Ga. Following the initial anneal all samples were ground into a powder and re-pressed into pellets. Samples not containing elemental Ga were weighed, intimately mixed, and pressed

into 7 mm diameter pellets. The pressed powders were then sealed in an evacuated quartz tube ($\sim 7 \times 10^{-3}$ torr) and placed into a furnace to be annealed at 500, 600, or 700 °C. Similar to samples containing elemental Ga, the samples were annealed for 1 week and were then quenched in cold water, ground into powders, pressed into pellets, and resealed in evacuated quartz tubes to assist in the intermixing of the elements. All samples were then annealed for an additional 12 weeks (a total of 13 weeks), at the designated temperature, to promote equilibribration of he samples.

Following the final anneal, samples were quenched in water. They were subsequently cut in half using a diamond cutoff wheel. Half of the sample was then mounted in 1-inch diameter polishing mounts using Lecoset 7000 cold-curing resin, and mechanically polished to a mirror finish. The other half of the sample was ground into a powder for XRD structure analysis. Polished samples were next carbon coated and loaded into an electron probe x-ray microanalysis (EPMA) vacuum chamber for compositional elemental analysis.

Electron probe x-ray microanalysis also utilizes standards to accurately identify weight and atomic concentrations of elements in a given sample. Palladium metal (99.99%) and a GaSb wafer substrate were used to calibrate the EPMA for the phase diagram work. The EPMA was calibrated by a technician prior to each experiment. According to equipment specifications provided by the manufacturer, when properly calibrated, the EPMA yields atomic concentration values with errors of ~1%.

All diffraction patterns acquired from the powder samples were compared to known Pd-Ga, Pd-Sb, and Pd-Ga-Sb phases diffraction patterns to verify phase identification.[80] Unidentified peaks were then presumed to be due to the presence of a ternary phase identified via EPMA.

3.3 Ohmic Contacts to n-GaSb

3.3.1 Sample Preparation, Metallizations, and Current-Voltage Measurements

All contacts were prepared on a 770 nm thick Te-doped n-type GaSb epilayer (n $\cong 2 \ge 10^{18} \text{ cm}^{-3}$) grown on a 770 nm thick p-type GaSb (p = 1 $\ge 10^{17} \text{ cm}^{-3}$) epilayer. Both epilayers were grown on a Zn-doped ptype GaSb substrate. Samples were soaked in acetone and methanol for 1 min each, rinsed in deionized water (DI) to remove organic contamination and finally blown dry with compressed N₂. Photolithography was performed to prepare patterns for measuring the specific contact resistance by the circular transfer length method (CTLM), as described by Marlow and Das,[75] Ahmad and Arora,[76] and Wang *et al.*.[77] The CTLM pattern setup is illustrated in Fig. 3.2. It should be noted that the CTLM mask presented in Fig. 3.2 is only an illustration of the mask layout, and it is not to scale. A center contact pad 80 µm in diameter with gap spacings of 4, 8, 14, 20, 30, 50, and 75 µm were used for extracting electrical data that was later plotted as resistance versus gap spacing. This process is discussed in greater detail in the next section.



Figure **3.2**: CTLM ring pattern used for measuring the specific contact resistance of contact metallizations. Gap spacings measure 4, 8, 14, 20, 30, 50, and 75 μm, respectively. (Not to scale)

Prior to deposition of *evaporated* metallizations, samples were subjected to an 18.5% HCl solution for 30 s to remove surface oxides, rinsed in DI water, and blown dry with N₂ .[**78**] During a semiconductor passivation experiment (described in Ch. 7) it was found that replacing the DI water rinse with a 2.1% (NH₄)₂S rinse for 3 – 5 s following the HCl etch results in more intimate contact between the metal and semiconductor, and ultimately reduces the specific contact resistance of the contacts. This result is discussed later, and is used as the preferred surface treatment (referred to as the sulfide rinse) for the remainder of the contact experiments, which included only *sputtered* metallizations. Following the surface treatment, samples were promptly loaded into a vacuum chamber and pumped to a base pressure of $< 2x10^{-7}$ Torr, and films were deposited by electron beam evaporation or sputter deposition. Evaporated metallizations included Pd/In/Pd, Pd/Pt/Au, and Pd/In/Pd/Pt/Au. Sputtered metallizations included Pd₃In₇/Pt/Au, Pd₃In₇/W/Au, Pd₃In₇/TiN/Au, Pd₃In₇/WSi₂/Au, and Pd₃In₇/WSiN/Au. They are illustrated in Fig. **3.3**.



Figure **3.3**: Metallization schemes for (a and b) evaporated and (c) sputtered contacts. Initial metallizations for evaporated contacts did not include Au or a diffusion barrier.

Following deposition, samples were soaked in acetone with ultrasonic agitation to remove the photoresist, then rinsed with methanol and DI water, and blown dry with compressed N₂. Current-voltage (I-V)characteristics were measured after deposition and after annealing using a Keithley 236 source-measure unit in current sweep mode with four probes, two sourcing current and two measuring voltage. Anneals were performed in a tube furnace under N₂ gas flowing at a rate of 100 cm³/min or in a rapid thermal anneal furnace (RTA), depending on the time required for the anneal. Gap spacings were measured using a scanning electron microscope (SEM).

Following electrical characterization of the contacts, materials characterization was carried out using a variety of techniques. Surface morphology was investigated using a SEM and atomic force microscope (AFM), and the reaction depth of each contact was studied by performing TEM and Auger electron spectroscopy (AES). Samples examined by TEM were blanket layer samples deposited at the same time the contact metallization was deposited. Cross-sectional TEM specimens were ground to ~15 µm thick, and ion milled in a Fischione 1010 ion mill to achieve electron transparency.

3.3.2 Measuring the Specific Contact Resistance of Metal/Semiconductor Contacts

Metal/semiconductor contacts can be found in at least two geometries:[79] vertical and horizontal (lateral) contacts. Contacts in this thesis are lateral contacts because current flow is confined to a region near the semiconductor surface and between laterally spaced contacts. Commonly in lateral contacts the linear transfer length method (TLM) is used for measuring the resistance at a metal/semiconductor interface; however, the use of such a technique requires special care to isolate the current flow between contacts. For III–V semiconductors, this is typically accomplished by etching the area around the contact to form a mesa structure.[79] Another method used to measure the resistance at a metal/semiconductor interface is the circular transfer length method (CTLM). There is one main advantage to using the CTLM test structure like that pictured in Fig. 3.2. Unlike TLM, the current for the CTLM is always confined between the contacts, even without etching mesas.[79] The only possible path current is able to flow is radially between the inner to outer contacts, which eliminates the possibility of unconfined current flow between the contacts that could cause spreading resistance.

In this thesis, the total resistance for a pair of contacts is measured using four probes. Two probes are placed on the metal pads inside the gap and two are placed on the surrounding metal layer illustrated in Fig. 3.2. Current is then forced between one probe on a pad and one on the surrounding metal while the remaining two probes measure the change in voltage across the metal gap as the current is swept from - 10 mA to + 10 mA. For ohmic contacts, the relationship between voltage (V) and current (I) is linear, thus, the total resistance (R) of the metal contact for a given metal gap spacing can be taken as the reciprocal of the slope of the current-voltage curve. The measured resistance is a combination of the resistance from the metal contacts (r_c) as well as the resistance of the semiconductor that separates the contacts (r_s) . The contact resistance (r_c) depends not only on the resistance at the metal/semiconductor interface, but also on the size of the contact itself. As a result, to directly compare resistance values between different metallizations that may have various sized contact pads, it is useful to obtain a resistance measurement that is contact size independent.

The majority of the current transferred between contacts is at the contact edge, and decreases exponentially as one moves away from the edge.[76] The length over which most of the current is transferred is known as the transfer length (L_t).[76] The transfer length is a relation between the specific contact resistance and the semiconductor sheet resistance (R_s), written as:[76]

$$L_t = \sqrt{\frac{\rho_c}{R_s}} \,. \tag{3.17}$$

Normalizing the contact resistance by multiplying the contact resistance and the active region of the contact yields an area independent resistance value – the specific contact resistance (ρ_c).

The specific contact resistance was introduced in Ch. 2 as part of the discussion on current transport at a metal/semiconductor interface. It is a measure of the resistance at the metal/semiconductor interface that does not involve the size of the metal contact. This measurement takes into account a portion of the metal directly above and the semiconductor directly below the interface, as well as any interfacial layers that may be present.[79]

To extract ρ_c from the total resistance measured during the I-V sweeps one must take into account several variables that affect the resistance measurements in the CTLM. The following discussion is based on Fig. **3.4**. As mentioned earlier, contacts utilizing the CTLM to measure ρ_c are lateral contacts. This means current is confined to a region near the surface of the semiconductor and flows between adjacent metal pads as shown in Fig. **3.4(a and b)**. The total resistance between two contacts separated by a gap (x_2 - x_1) is a function of several parameters that include the sheet resistance of the metal film (R_{sm}), sheet resistance of the semiconductor epitaxial layer beneath and between the contacts (R_s and R_{ss}), and the specific contact resistance (ρ_c). Each of these parameters is illustrated in Fig. **3.4(c)**.[75][76][77][79]



Figure 3.4: A top view (a) and cross-sectional schematic (b) of two metal contacts separated by a gap and the equivalent two-dimensional circuit (c) for the circular transfer length method.

Assuming that the metal sheet resistance in Fig. 3.4(b) is zero ($R_{sm} \approx 0$) or negligibly small, the total resistance measured between the contacts is:[77]

$$R = \frac{1}{2\pi} \left[R_s L_t \left(\frac{1}{x} \frac{I_0 \binom{x_1}{L_t}}{I_1 \binom{x_1}{L_t}} + \frac{1}{x_1} \frac{K_0 \binom{x_2}{L_t}}{K_1 \binom{x_2}{L_t}} \right) + R_{ss} \ln \left(\frac{x_2}{x_1} \right) \right]$$
(3.18)

where I_0 , I_1 , K_0 , and K_1 are Bessel functions describing the current transport at the interface. Assuming that $R_{ss} = R_s$, Eq. **3.18** can be approximated using a series expansion to yield the measured total resistance (R) in more manageable terms:

$$R = \frac{R_s}{2\pi} \left\{ \ln\left(1 + \frac{x_2 - x_1}{x_1}\right) + \frac{1 + \frac{L_t}{8x_1} + \frac{9L_t^2}{128x_1^2}}{\frac{x_1}{L_t} - \frac{3}{8} - \frac{15L_t}{128x_1}} + \frac{1 - \frac{L_t}{8(x_1 + (x_2 - x_1))} + \frac{9L_t^2}{128(x_1 + (x_2 - x_1))^2}}{\frac{x_1 + (x_2 - x_1)}{L_t} + \frac{3}{8} + \frac{15L_t}{128(x_1 + (x_2 - x_1))}} \right\}.$$
 (3.19)

The total resistance (R) in Eq. 3.19, as well as the geometrical factors x_1 and x_2 in Fig. 3.4 and Eq. 3.19, are measurable quantities. Plotting the total resistance (R) as a function of gap spacing (x_2 - x_1), one can extract R_s and L_t . This is accomplished by fitting the total resistance versus gap spacing data to Eq. 3.19, as illustrated in Fig. 3.5. The specific contact resistance (ρ_c) is then calculated from Eq. 3.17.



Figure 3.5: Plot of total resistance (R) as a function of gap spacing (x_1-x) between metal contacts in the circular transfer length model.

The metal sheet resistance is not always negligibly small, and as a result, the calculation of ρ_c becomes much more involved. [76][77] It has also been shown that by neglecting a non-zero R_{sm} in the CTLM measurements, the measured ρ_c can be off by several orders of magnitude. [76][77] This is a result of an artificially high measured total resistance (R) which leads to artificially high ρ_c values. Therefore, it is imperative to choose a top metal layer (such as Au) which will reduce R_{sm} to values that are small enough as not effect the measurement of ρ_c .

3.3.3 Sample Preparation for Sulfur Passivation Studies

To identify the role a dielectric layer plays in reaction morphology and specific contact resistance, a study on surface passivation was

devised. Gallium antimonide wafer substrates were utilized for materials characterization studies of sulfur passivated samples. Samples for electrical measurements were prepared from the same epilayer described in **3.3.1**. Samples were cleaved into 2 x 8 mm pieces and soaked in acetone and methanol for 1 min each to remove organic contamination, rinsed in deionized water (DI), and finally blown dry with compressed N₂. They were next prepared using one of several surface treatments described here in Table 3-3 and again in Table 7-1. For Treatments 1 - 6 that included HCl, the samples were next rinsed in deionized (DI) water for 3 – 5 s and blown dry with compressed N_2 before sulfur passivation. After samples were treated with 21% (NH₄)₂S, they were simply blown dry using compressed N₂. Treatment 7 excluded the rinse in DI water following the HCl etch. The samples were then promptly loaded into a vacuum chamber and pumped to a base pressure of 10^{-7} Torr, after which blanket layers of TaN (50 nm) or Pd/In/Pd (4/40.3/5.7 nm) films were deposited by sputtering or electron beam evaporation, respectively.

Samples that included TaN as the metallization were studied both in the as-deposited state and following a 20 min anneal at 500 °C. TaN is expected to be stable when in contact with the passivated semiconductor and therefore is not expected to react with or consume any superficial layer that may form on the semiconductor surface during passivation. For this reason, a TaN layer was used to assist in the measurement of the superficial layer thickness via TEM. Samples that included Pd/In/Pd as the metallization were utilized to identify the effect of an interfacial layer on the reaction at the M/S interface. To test the effect of surface passivation on the resistance of the ohmic contacts, Pd/In/Pd/Pt/Au and Pd₃In₇/WSiN/Au contacts were fabricated in the same fashion as described in Section **3.3.1**.

Treatment	Solution	Time (s)		
1	$21\% (NH_4)_2S$	300		
2	18.5% HCI	30		
		2 – 5		
	$DI \Pi_2 O$	5 - 5		
	$21\% (NH_4)_2S$	60		
3	21% (NH ₄) ₂ S	60		
4	18.5% HCl	30		
	DI H ₂ O	3 - 5		
5	$21\% (NH_4)_2S$	10		
C		0.0		
6	18.5% HCI	30		
	DI H ₂ O	3 - 5		
	21% (NH ₄) ₂ S	10		
7	18.5% HCl	30		
	$2.1\% (NH_4)_2S$	5		

Table **3-3**: GaSb surface treatments

Chapter 4

Initial stages of the Pd/GaSb thin film reaction

4.1 Introduction

Knowledge of the interaction of a metal and semiconductor, both in bulk and thin film form, is often used to engineer contacts to compound semiconductors. Initially, one may identify possible metallizations that will be in equilibrium with the underlying semiconductor using equilibrium phase diagrams.[38][42][43][92] This is the basis for engineering thermally stable contacts to compound semiconductors. To fully understand kinetic and thermodynamic properties of M/S contact, however, it is also important to investigate the interaction between the thin metal film and semiconductor in the early stages of the reaction. Such reactions may be essential for engineering electrical properties of the contacts.

Ohmic contacts can significantly affect semiconductor device characteristics.[3] Highly resistive contacts are capable of limiting device performance, and uniform reactions with limited semiconductor consumption is vital for devices with shallow active regions. Palladiumbearing contacts to GaSb have provided specific contact resistances on the order of $10^{-6} \Omega$ -cm² or lower,[93][94] and palladium is known to disperse the native oxide on GaAs[98] and GaSb.[99] To date, researchers often refer to the behavior of Pd/GaAs for an understanding of Pd/GaSb reactions.[100][101][102][103] There has been only limited correlation between the electrical properties of Pd and Pd-based contacts to GaSb and interfacial reactions that take place. [99][101][104]

Research on the interaction between Pd and GaSb, until now, has been limited. Su *et al.* [104] first reported the effects of heat treatment on the electrical properties of Pd/GaSb Schottky diodes. Palladium Schottky contacts (500 nm) were examined and found to be rectifying up to 300 °C for 30 min, but as the annealing temperature was increased to 450 °C for 30 min, the contacts became ohmic. They attributed the degradation of the Pd Schottky contacts to the formation of complex phases at the Pd/GaSb interface. Using Rutherford backscattering spectroscopy and xray diffraction, Su *et al.* identified reaction products to be Ga₅Pd at 300 °C, and Pd₂Sb, Ga₅Pd, Pd₈Sb₃, and Ga₂Pd₅ at 450 °C, with Ga₅Pd being the dominant phase. The formation of Ga₅Pd was spectulated to be the major factor in causing the ohmic behavior. Varblianska *et al.* [101] later studied a Pd (100 nm) ohmic contact to n-GaSb and also found rectifying behavior up to temperatures of 300 °C with ohmic behavior at 350 °C. Upon annealing the contacts at higher temperatures, an increase in the contact resistance occurred. Based on the work of Su et al., Varblianska et al. [101] attribute the ohmic behavior to the formation of Ga_5Pd , with the formation of Pd-Sb binary phases above 350 °C leading to contact degradation. Vogt et al. [99] examined the interfacial reaction between Pd and GaSb at room temperature as part of a Pd/Au contact (30/80 nm) to p-GaSb. They report, based on transmission electron microscopy, that asdeposited Pd films appear to disperse the native oxide on GaSb and form a homogeneous interfacial reaction region. Vogt et al.[99] also reported that Pd is more reactive than other metals, such as Pt and Ti, based on the formation of compounds at the Pd/GaSb interface. Finally, Vogt *et al.* [100] discuss a Pd/S/Pd contact to n-GaSb. They investigate the microstructure of the Pd/S/Pd contact following a 3 h anneal at 200 °C. The reacted region consists of three layers. The top layer is identified to be PdS₂ via electron diffraction. The middle and bottom layers of the reacted region are identified via EDX to be $Pd_y(GaSb)_{1-y}$ and $Pd_x(GaSb)_{1-x}$, respectively, with y > x.[100] While this is the first known report of $Pd_x(GaSb)_{1-x}$ being formed at a Pd/GaSb interface, no further investigation of the microstructure was presented.[100]

In this study, we explore the interaction between a 50 nm layer of Pd and a GaSb substrate annealed in the temperature range of 100 - 350 °C for 10 - 360 min. We report on the formation of Pd-rich ternary phases at temperatures below 200 °C and Pd-Ga and Pd-Sb binary phases above 300 °C. Identification of reaction products will be discussed, and a description of interfacial morphologies will be provided. We will also comment on the suitability of Pd to participate in the regrowth mechanism often used for ohmic contact formation to compound semiconductors.[70]

4.2 Results and Discussion

4.2.1 As-Deposited Pd/GaSb

Following deposition of 50 nm of Pd, as seen in Fig. **4.1**, a reacted region (RR) with an average thickness of 13 (± 1) nm has formed. Following the HCl surface treatment and metal deposition, approximately 2 - 3 nm of oxide remains on the semiconductor surface, shown in Fig. **4.1** as the light region at the Pd/RR interface. The oxide is non-uniform with regions of the interface exhibiting no oxide. From the TEM micrograph, it is noted that reaction between Pd and GaSb does not appear to be hindered by the presence of an oxide. Nano-beam electron diffraction (NBD) indicates that the reaction region is nano-crystalline. The grain size of the RR is estimated to be on the order of only a few nanometers based on TEM imaging of the specimen.





Figure 4.1: (a) 50 nm Pd on GaSb prior to annealing accompanied by (b) NBD pattern of the reaction region indicating it is nano-crystalline.

According to NBD, a single, highly structured ring around the center spot (Fig. 4.1(b)) corresponds to a d-spacing of 2.3 (\pm 0.1) Å for the reacted region. Glancing angle x-ray diffraction was also preformed on as-deposited samples to identify additional phase formation on a larger scale. X-ray diffraction analysis yielded only those peaks associated with FCC Pd. Additional investigation using NBD indicates that there may be a structural relationship between the RR and FCC Pd. Figure 4.2 illustrates typical NBD patterns at the RR/GaSb (Fig. 4.2(a)) and RR/Pd (Fig. 4.2(b)) interface. Figure 4.2(a) reveals that the reacted region does not match the spot pattern of the GaSb substrate; however, it does match exactly with the broken ring pattern from several Pd grains in Fig. 4.2(b). This suggests that the crystal structure of the RR may resemble a FCC structure with the lattice constant approximately equal to Pd. [80] Nanobeam diffraction also indicates the presence of two additional rings further from the central spot. The rings have a finite width of ~ 0.2 cm when taken using a camera length of 40 cm. Each outer ring, with respective width, is indicated by an arrow in Fig. 4.2(b). The second and third ring correspond to d-spacings of 1.3 (\pm 0.2) Å and 0.9 (\pm 0.1) Å, respectively. These d-spacings match closely to the smaller d-spacings of Pd when taking into account ring width. This indicates that Pd may initially be capable of forming a solid solution with Ga and Sb as the reaction proceeds, while maintaining the FCC structure.



Figure 4.2: Nanobeam diffraction patterns from the interface of the nanocrystalline region and (a) GaSb and (b) Pd film.

Further investigation of the reaction region using STEM and EDX indicates the reaction region is rich in Pd. As shown in Table 4-1, throughout the reaction region the concentrations of Ga and Sb remain relatively constant; however, Ga may be slightly more concentrated at the Pd/reacted region (RR) interface. Quantitative EDX reveals the reaction region to be approximately 67% Pd, with the remainder being equal parts Ga and Sb. This composition corresponds to a nominal chemistry of Pd₄GaSb. Combining this with the information gained from NBD suggests that Pd may be able to dissolve up to 33 % Ga_{0.5}Sb_{0.5} and still be able to maintain, at least on the nanometer scale, it structure prior to annealing.

Pd/RR interface			RR/GaSb interface			
	Atomic %	error		Atomic %	error	
Pd	67.9	4.5	Pd	65	4.3	
Ga	18.5	3.9	Ga	16.6	3.8	
Sb	14.6	3.3	Sb	18.5	4.3	

Table **4-1**: Approximate atomic concentrations of Pd, Ga, and Sb in the reacted region prior to annealing.

As deposited Pd is capable of reacting through the non-uniform native oxide that is present on the GaSb surface to produce a Pd-rich ternary phase resembling the FCC structure of Pd. The ability to do so is important when considering Pd as part of a contact metallization to GaSb that utilizes the solid phase regrowth method as the ohmic contact formation mechanism. Similar to Pd/GaSb, an intervening oxide is present for as-deposited Pd/GaAs; however, Pd and GaAs react to form a polycrystalline ternary compound, Pd₅(GaAs)₂, prior to annealing.[105] The reaction results in a highly textured hexagonal phase with grains approximately 6 nm in thickness.[105] This differs from the present study in which Pd/GaSb forms a Pd-rich nanocrystalline reacted region 13 (\pm 1) nm in thickness.

4.2.2 Pd/GaSb annealed at 100 °C

Annealing Pd/GaSb at 100 °C for 90 min results in a uniform RR that is 19 (± 1) nm thick, as shown in Fig. **4.3**. The oxide at the Pd/RR interface has remained even after annealing at 100 °C for 90 min. However, it does not appear to affect reaction uniformity between the Pd and GaSb. Nanobeam diffraction (NBD), shown in Fig. **4.3(b)**, of the reaction region reveals that the region is again nanocrystalline. The measured d-spacing corresponding to the first ring from the reacted region remains the same at 2.3 (±0.1) Å.



(a)



Figure 4.3: (a) Pd/GaSb annealed at 100 °C for 90 min accompanied by a (b) NBD pattern of the reaction region indicating it is nanocrystalline following this mild anneal.

Scanning TEM and EDX indicates that the reaction region has the same nominal Pd concentration following annealing at 100 °C as that found prior to annealing. Two EDX line scans were taken, the first at a location where the oxide remained between the Pd and GaSb. This scan indicates that the reaction region is uniformly rich in Pd with approximately 70% Pd. However, a second scan in a region where there is intimate contact between the Pd and GaSb reveals a graded Pd concentration ranging from approximately 80% to 70% Pd. The majority of the Pd/RR interface exhibits residual oxides even after mild annealing. The presence of this oxide, based on the EDX discussion above, is likely to be an influential factor affecting interdiffusion of Pd and GaSb at lower temperatures. Random EDX spot scans of the reaction region at the Pd/RR interface and RR/GaSb interface indicate that the reaction region, even with the presence of a non-uniform oxide, is uniformly rich in Pd. As shown in Table **4-2**, the Pd concentration is approximately 69% throughout the RR following a 90 min anneal at 100 °C.

Samples were next annealed at 100 °C for 180 min. The entire RR is uniform with an approximate thickness of 30 (\pm 3) nm, as seen in Fig. **4.4**. The oxide at the Pd/RR interface is still present following the annealing treatment, but is now largely discontinuous. This illustrates the ability of Pd to gradually disperse the native oxides on GaSb at relatively low annealing temperatures, which is useful when forming ohmic contacts to GaSb. During the annealing process, the RR begins to crystallize resulting in the formation of a bilayer RR within 180 min. The overall composition of the reacted region is essentially the same as the samples annealed for 90 min at 100 °C with an average Pd concentration of approximately 69 %. This suggests that the Pd₄GaSb phase persists even after annealing at 100 °C for 180 min. As shown in Table **4–2**, compositional analysis indicates only a slight variation in atomic concentration of Pd between the two layers, with the Ga:Sb ratio remaining close to one in both cases. Nanobeam diffraction reveals that the bottom layer of the RR remains nanocrystalline. The bottom layer in the reaction region is similar to that found in the as-deposited case, and upon indexing the first ring in the NBD pattern, a d-spacing of 2.3 (± 0.1) Å was recorded.



(a)



Figure 4.4: (a) Pd/GaSb annealed at 100 °C for 180 min with (b) accompanying NBD pattern of the bottom layer in the reaction region.

Nano-beam diffraction indicates that the top layer is polycrystalline. As seen in Fig. 4.4, the top of the RR consists of grains approximately 36 (± 3) nm in width and 11 (± 2) nm in thickness. For a better statistical analysis of possible orientations from the top layer of the RR, glancing angle x-ray diffraction (GIXD) was used to examine the samples. Glancing angle x-ray diffraction confirms the presence of Pd, as well as four unidentified peaks. The four peaks, corresponding to 1.843, 1.807, 1.664, and 1.243 Å, are attributed to the polycrystalline layer that has formed in the top layer of the RR. This is based on previous analysis that the nanocrystalline region maintains an FCC structure with a \approx Pd. The dspacing ratios of the four XRD peaks do not correlate with a cubic structure.

Table **4-2**: Atomic concentrations of Pd, Ga, and Sb within the reacted region following anneals at 100 °C for various times.

	Approximate Atomic %					
Sample	Pd	error	Ga	error	Sb	error
100 °C - 90 min						
Pd/reacted region	68.9	4.6	17.1	4.2	13.9	3.6
Reacted region/GaSb	68.7	4.6	16.5	3.7	14.8	3.4
100 °C - 180 min						
Polycrystalline layer	70.4	4.6	14.6	3.8	16.4	4.1
Nanocrystalline layer	67.1	4.3	16.5	4.1	18.3	4.4
100 °C - 360 min						
Polycrystalline layer	78.1	5.2	10.5	3.4	11.4	3.6
Nanocrystalline layer	78.6	5.2	9.9	3.0	11.1	2.7

Doubling the annealing time at 100 °C from 180 min to 360 min yields similar results. As shown in Fig. **4.5**, a two layer reacted region 33 (± 2) nm thick is present with the top layer consisting of grains ranging from 20 to 50 nm across with an average width of ~ 32 nm. The grain thickness (measured along y-axis in Fig. **4.5**) is 14 (± 2) nm. No oxide is visible at the Pd/RR interface; however, voids are present at the Pd/RR interface and within the Pd grains. The formation of voids within the Pd film confirms that Pd is the major diffusing species in the Pd/GaSb thin film couple.



Figure 4.5: Pd/GaSb annealed at 100 °C for 360 min.

Nano-beam diffraction again indicates similar results as those samples annealed at 100 °C for 180 min. The bottom layer is nanocrystalline with a strong ring corresponding to 2.3 (\pm 0.1) Å, and the top layer is polycrystalline. Glancing angle x-ray diffraction reveals the presence of Pd as well as three unidentified peaks corresponding to dspacings of 1.838, 1.828, 1.245 Å. These peaks are attributed to the polycrystalline phase at the top of the RR. The peaks are similar to those in the samples annealed for 180 min; however, the weak peak at 1.664 Å ($2\theta = 55.15$) is no longer measured. Figure **4.6** is a comparison of the GIXD patterns for samples annealed at 100 °C for 180 and 360 min. The patterns are almost identical with only minor variation in peak location.



Figure **4.6**: X-ray diffraction pattern of Pd/GaSb samples annealed at 100 °C for 180 and 360 min. Unlabeled peaks correspond to a Pd-rich, polycrystalline ternary phase within the Pd/GaSb reacted region.

Annealing Pd/GaSb at 100 °C for 360 min results in intimate contact between Pd and the RR. As shown in Table **4–2**, EDX analysis also indicates that the reaction region is now approximately 78 % Pd, corresponding to a nominal composition of Pd₇GaSb. The atomic concentration of Pd in the RR has increased by 10 % over that of the samples annealed for shorter times at 100 °C, while the structure of the layers remain relatively unchanged. As with previous annealing conditions, analysis of the d-spacing ratio of the unidentified peaks indicates that the polycrystalline phase is not cubic.

In summary, mild annealing of Pd/GaSb at 100 °C results in a gradual dispersion of the native oxides on GaSb and the formation of Pdrich ternary phases. The initial reaction is nanocrystalline with associated d-spacings of 2.3 (\pm 0.1), 1.3 (\pm 0.2), and 0.9 (\pm 0.1) Å, similar to FCC Pd. As the reaction continues, a bilayer is formed consisting of a polycrystalline and nanocrystalline layer, with the nanocrystalline layer remaining the same thickness throughout the RR (~ 19 nm). Even though the polycrystalline layer increases in Pd concentration from Pd₄GaSb to Pd₇GaSb the crystal structure is preserved. Nano-beam diffraction and GIXD do not yield enough information to definitively identify the crystal structure of the polycrystalline region; however, GIXD suggests that it is of lower symmetry than cubic.

The reacted phase in contact with GaSb as-deposited and after annealing at 100 °C appears to have a critical thickness associated with the growth of a second, polycrystalline phase. The initial thickness of the nanocrystalline region is 13 nm in the as-deposited state. As a result of annealing at 100 °C, the nanocrystalline layer increases to and maintains an approximate thickness of 19 nm. Any increase in thickness of the reacted region is a result of the growth of a second phase. Samples annealed at 100 °C all exhibit a nanocrystalline phase that is 19 - 20 nm in thickness, regardless of the annealing time. The overall reacted region increases from 20 to 33 nm while annealing at 100 °C; however, this is due to the nucleation and growth of a second, polycrystalline phase at the Pd/RR interface.

This phenomenon may be closely related to the solid state amorphization reaction (SSAR) first reported by Schwartz and Johnson, [55] in which an amorphous phase exhibits a critical thickness at which point a second (equilibrium) phase nucleates and grows. [54] The preference to form a metastable phase, such as the nanocrystalline phase in Pd/GaSb, is due to a much smaller nucleation barrier compared to that for the equilibrium phase. [54] [53] The metastability of the phase can be expected to last as long as its growth rate is interfacecontrolled. [54] [53] By analogy, once the transport rate of Pd through the RR to the GaSb substrate slows and becomes diffusion-controlled, the nucleation and growth of the second phase is possible and ultimately results in the decomposition or transformation of the metastable phase. The transition from interface to diffusion-controlled growth appears to occur after 90 min at 100°C for Pd/GaSb, as indicated by the formation of the polycrystalline phase. Following the formation of the polycrystalline phase, both layers of the RR increase in Pd concentration up to approximately 80 % Pd for samples annealed at 100 °C. The observed phases are considered metastable based on Pd-Ga-Sb phase diagram work which confirms the presence of Pd-rich ternary phases with Pd concentrations greater than that found in the nanocrystalline reacted layer. This is discussed later in Ch. 5.

4.2.3 Pd/GaSb annealed at 200 °C

Next, Pd (50 nm)/GaSb samples annealed at 200 °C were studied. Samples were annealed for 10, 30, and 45 min and analyzed using TEM and GIXD to identify reaction products and morphology. The reactions that occur at 200 °C require considerable explanation. As a result, to facilitate the reader, this portion of the Pd/GaSb study is broken into individual sections based on annealing time.

4.2.3.1 Pd/GaSb annealed at 200°C for 10 min

Samples annealed for 10 min at 200 °C form a three-layer RR. As shown in Fig. 4.7, the total reaction thickness is 37 (\pm 2) nm. The top, middle, and bottom layers measure 11 (\pm 1), 13 (\pm 2), and 9 (\pm 2) nm, respectively. Following the anneal, there is approximately 37 nm of unreacted Pd remaining at the surface; however, large voids are now visible at the Pd/RR interface indicating a large disparity in diffusion fluxes between Pd and GaSb.



Figure **4.7**: Pd/GaSb annealed at 200 °C for 10 min. The RR consists of three distinct layers.

Elemental analysis using STEM and EDX reveals that the top (nanocrystalline) layer, as shown in Table **4-3**, remains ~ 70% Pd, similar to samples annealed at 100 °C. The reacted layer is no longer uniform in thickness or composition, indicated by a decrease in Pd concentration in the second and third layers compared to the first. Energy dispersive xray spectroscopy also indicates segregation of Ga and Sb within the second and third layers. Figure **4.8** is an EDX scan within the second (Fig. **4.8(a)** and third (Fig. **4.8(b)**) layer of the reacted region. As indicated in Table **4-3** and Fig. **4.8**, the third layer is non-uniform with parts of the layer missing all together. The EDX scan of the bottom layer in Fig. **4.8(b)** also indicates a nominal grain width of approximately 10 - 15 nm.



Figure 4.8: Horizontal EDX line scans across the middle (A) and bottom (B) layer in the reacted region of samples annealed at 200 °C for 10 min.

According to NBD, the top layer next to the Pd film has remained nanocrystalline with a d-spacing of 2.3 (\pm 0.1) Å, while the second and third layers are polycrystalline. The NBD patterns acquired from the bottom layers within the RR do not match a cubic structure or the only identified ternary Pd-Ga-Sb phase in the literature, Pd₂₅(GaSb)_{4.5}.[**45**] Glancing incidence x-ray diffraction verifies the presence of Pd, and the pattern exhibits several unidentified peaks. There are a total of five new x-ray diffraction peaks associated with the RR. The nanocrystalline (top) layer was previously identified to follow the Pd structure closely, as a result, these new peaks are associated with the bottom two layers of the RR. Unidentified peaks correspond to d-spacings of 2.091, 1.805, 1.652, 1.635, and 1.248 Å. Energy dispersive x-ray spectroscopy analysis suggests that the majority of the third layer consists of Pd-rich binary phases. This leads to the possibility of phase identification of the bottom layer via peak comparison to the reported Pd-Ga and Pd-Sb binary phases. Peaks for Pd and five Pd-rich binary phases have been identified to match several of the GIXD peaks. These phases include Ga₃Pd₇, Ga₂Pd₅, Pd₅Sb₂, Pd₂Sb, and Pd₈Sb₂, all of which are identified in Fig. **4.9**. Three of the five peaks that are not associated with Pd can be matched to the previously mentioned phases; however, as indicated from Fig. **4.9**, unambiguous phase identification is quite difficult as a result of peak overlap among the Pd-rich Pd-Ga and Pd-Sb phases. Along with the aforementioned binary phases, peaks associated with the $Pd_x(GaSb)_{1-x}$ ternary phase identified at 100 °C are marked in Fig. **4.9**. The nominal composition of the phase, as discussed earlier, is Pd₄GaSb.

	Approximate Atomic %					
Sample	Pd	error	Ga	error	Sb	error
200 °C - 10 min						
Top layer	73.0	4.8	15.3	7.4	12.0	6.8
Middle layer	59.1	4.4	varies		varies	
Bottom layer	44.5	29.5	varies		varies	
200 °C - 30 min						
Polycrystalline layer	76.3	5.1	12.8	4.9	11.0	4.5
Nanocrystalline layer	65.7	4.4	18.7	6.6	15.6	5.8
Middle layer	65.3	4.3	varies		varies	
Bottom layer	55.6	3.7	varies		varies	
200 °C - 45 min						
Top layer	82.8	5.5	8.7	3.5	8.5	3.2
Bottom layer	68.2	4.5	varies va		ries	

Table 4-3: Pd/GaSb elemental composition within the reaction region for samples annealed at 200 °C



(N¥) siunoo Figure 4.9: X-ray diffraction data of Pd/GaSb samples annealed at 200 °C.

4.2.3.2 Pd/GaSb annealed at 200°C for 30 min

When the annealing time is increased to 30 min at 200 °C, the reaction is no longer uniform. There are regions of complete Pd consumption and others where the reaction mimics that found in samples annealed for 10 min. Fig. **4.10(a)** illustrates the reaction morphology at 200 °C for 30 min. The reacted region clearly has two distinct thicknesses associated with the amount of Pd consumed. Those regions that exhibit only partial consumption of the Pd have a RR thickness of 47 (\pm 5) nm. The RR thickness increases to 62 (\pm 3) nm where the Pd is mostly (< 10 nm remaining) or completely consumed.

Before proceeding further, it is useful to put into context the term "non-uniform." A "non-uniform" reaction, as described here, is considered to occur when the reacted region thickness (or Pd consumption) varies by more than 15 nm, or the composition of the reacted region varies laterally. It should be understood that in many devices the majority of metal contacts to semiconductors vary on length scales much larger (> 100 nm) than what is considered non-uniform here. [93] [100][103] On the other hand, some Sb-based heterojunction bipolar transistors (HBTs) use Pd as the ohmic contact and require minimal consumption of semiconductor, as well as reaction uniformity on the nanometer scale.[Bibliography][77] For this reason, it is chosen here to describe non-uniform reactions are those exhibiting at least a 15 nm disparity in either reaction thickness or Pd consumption.

The majority of the RR consists of three layers; however, according to TEM a transformation of the top layer occurs during Pd consumption. Nanobeam electron diffraction of the top layer shows that the film is nanocrystalline when only limited amounts of Pd are consumed, as illustrated in Fig. 4.10(b). As one moves to regions on the sample where the Pd is completely consumed this top layer is transformed into a polycrystalline layer. The transition of the top layer from nanocrystalline to polycrystalline is shown in Fig. 4.10(c). White dots on the TEM micrograph are present to assist the reader in following the transition. On the left side of the micrograph in Fig. 4.10(c) there are 4 layers visible. The top layer is polycrystalline and the second layer is the nanocrystalline phase. As one moves to the right, the nanocrystalline region is completely transformed into the polycrystalline phase. Prior to the formation of the polycrystalline phase, the nanocrystalline layer is 16 (\pm 2) nm thick. The nanocrystalline layer appears to "swell" to 20 (± 2) nm before the phase transforms to polycrystalline, which is approximately 24 nm thick. The bottom two layers remain relatively unchanged at 15 (\pm 3) and 19 (\pm 2) nm for the middle and bottom layer, respectively. While the middle layer is similar to samples annealed for 10 min, the bottom layer has more than doubled in thickness, as indicated by the vertical growth of the binary phase layer into the semiconductor substrate.


Figure 4.10: TEM micrographs of Pd/GaSb annealed at 200 °C for 30 min illustrating the (a) non-uniform reaction between Pd and GaSb, (b) the presence of a nanocrystalline layer where limited Pd is consumed, and (c) transition of the top layer from a nanocrystalline to polycrystalline phase.

Samples annealed at 200 °C for 30 min exhibit a nanocrystalline layer within the reacted region similar to samples annealed at 100 °C. Patterns taken from the polycrystalline region could not be matched to any binary phases in the literature, [80] and the ratio of d-spacings indicate that the phase is similar to those found for the long annealing times at 100 °C. These phases are lower in symmetry than cubic. Electron diffraction patterns from the middle and bottom region also indicate that these layers are polycrystalline.

Scanning TEM and EDX analyses of samples annealed at 200 °C for 30 min indicate a gradual tapering of the Pd concentration from top to bottom with the top polycrystalline layer containing approximately 76% Pd and the bottom layer containing 56% Pd as indicated in Table **4-3**. When the top layer is nanocrystalline, the Pd concentration is about 10 % less than that of the polycrystalline layer, indicating a saturation point for the nanocrystalline phase between 65 and 75 % Pd for samples annealed at 200 °C. Several EDX scans were performed on each layer of the RR and indicate that both the nanocrystalline and polycrystalline layers are uniform in Pd concentration. The middle and bottom layer, similar to the 10 min anneal, exhibit binary phase formation.

Glancing angle x-ray diffraction of samples annealed for 30 min (Fig. 4.9) indicates no change in the structure of the reacted region phases compared to samples annealed at 200 °C for 10 min (or even shorter times). Transmission electron microscopy did not indicate the presence of a polycrystalline ternary phase layer next to the Pd film in samples annealed at 200 °C for 10 min (Fig. 4.7). The lack of the phase identification via TEM is contradicted by GIXD. Several unidentified peaks in the GIXD scan, for samples annealed at 200 °C, appear to be a result of the formation of the ternary polycrystalline top layer regardless of annealing time.

4.2.3.3 Pd/GaSb annealed 200°C for 45 min

When the annealing time is increased to 45 min at 200 °C, the Pd film is completely consumed, and growth of the vertical grains has occurred at the RR/GaSb interface. The reacted region consists of three layers, as shown in Fig. 4.11, with a total thickness of 82 (\pm 2) nm. The top and middle layers measure 28 (\pm 2) and 5 - 20 nm, respectively. This is within experimental error of the thicknesses measured from samples annealed for 30 min; however, the middle layer is much less uniform. The bottom layer has increased in thickness to 38 (\pm 2) nm, more than double that of samples annealed for 30 min, and grains now measure ~ 15 - 20 nm in width.



Figure 4.11: Pd/GaSb annealed at 200 °C for 45 min. The Pd film is completely consumed and vertical grains are evident at the RR/GaSb interface.

Analysis using STEM and EDX reveals that the top polycrystalline layer is a uniform ternary phase containing ~ 83 % Pd, slightly higher in concentration compared to previous samples annealed at 200 °C. Energy dispersive x-ray spectroscopy again confirms the presence of Pd-rich binary phase formation within the middle and bottom layers with an approximate Pd concentration of 70%. Energy dispersive x-ray spectroscopy also indicates an increase in the Pd concentration over that of the previously analyzed samples annealed at 200 °C. Further investigation using NBD indicated the possible presence of Ga₂Pd₅, Pd₅Sb₂, and Pd₂Sb. This is supported by NBD patterns that match, within experimental error, the d-spacings and angles between planes of these phases. Only two patterns were successfully indexed due to difficulty deconvoluting the patterns. The first pattern indexed matched that of Ga₂Pd₅ and Pd₂Sb (both orthorhombic), and the second pattern matched Pd₅Sb₂. As a result of the spot patterns matching more than one phase, conclusive evidence of the presence of these phases is not possible. The d-spacings corresponding to these phases and other Pd-rich binary phases are indicated in the x-ray diffraction pattern in Fig. **4.9**.

4.2.3.4 Interfacial Layers and Reaction Morphology at 200 °C

Palladium is capable of dispersing the native oxides on GaAs when annealed at 220 °C; however, it has been shown here that the native oxide of GaSb is still present for short annealing times. There is a possibility that the non-uniform reaction occurring at 200 °C (10 and 30 min) may be the result of the presence of the non-uniform oxide.

Until now, all samples have been treated with a HCl acid etch and DI rinse. This surface treatment is known to result in a 2 - 3 nm residual oxide, [9] which is confirmed here for as-deposited Pd/GaSb samples. It has also been demonstrated earlier in this study that this oxide is non-uniform prior to annealing. Samples annealed at 100 °C appeared to be only slightly influenced by the presence of the oxide and exhibit very uniform RR. Although it is not possible to tell from TEM micrographs alone, the accompanying EDX analysis indicates a Pd concentration gradient from 80 to 70 % where the oxide is not present, and no such gradient in regions where it is present. When the temperature is increased to 200 °C, however, the oxide appears to influence the microstructure much more severely. To test the hypothesis that the oxide influences the RR composition and morphology, samples were next prepared with a modified surface treatment that has been shown to reduce the dielectric

layer thickness at a metal/semiconductor interface and is discussed later in Ch. 7. This treatment included an HCl etch (30 s) and 2.1% (NH₄)₂S rinse (3 - 5 s). As expected, samples annealed at 100 °C for 360 min exhibited no discernable change compared to those prepared using the conventional HCl etch and DI rinse, shown in Fig. **4.12**. This indicates that at 100 °C the oxide may play a very minor role on the resultant microstructure uniformity, if any.



Figure **4.12**: Pd/GaSb prepared using the modified surface treatment and subsequently annealed at 100 °C for 360 min.

Samples subjected to the modified surface treatment were also annealed at 200°C for 10 min to identify if the oxide plays a role at intermediate annealing temperatures. Two samples were analyzed and it was found that there was little difference between the uniformity of conventionally prepared samples and those prepared using the sulfide rinse. The reaction, however, for the sulfide rinse samples was much more severe than those samples rinsed in DI water, as indicated by Fig. **4.13**. Following the annealing of the sulfide rinse samples the surface of the metal film also appeared to be non-uniform under a light microscope. This lead to the hypothesis that samples were laterally nonuniform on a larger scale and further investigation using a scanning electron microscope (SEM) was completed.



Figure **4.13**: Pd/GaSb prepared using the modified surface treatment and subsequently annealed at 200°C for 10 min.



Figure 4.14: Scanning electron micrograph of the Pd/GaSb surface prepared using the modified surface treatment and annealed at 200°C for 10 min. The surface is very non-uniform, indicating a laterally non-uniform reaction between Pd and GaSb.

Imaging samples in the SEM revealed that prior to annealing the sample surface is smooth with no identifiable features. Following the anneal at 200°C for 10 min, however, the sample surface was laterally non-uniform on the micron scale. Figure **4.14** is an SEM micrograph of the Pd/GaSb surface following the heat treatment. It is clear from the micrograph that the reaction between Pd and GaSb is laterally non-uniform, giving good indication that the reaction between Pd and GaSb is generally non-uniform on the nanometer scale at an annealing temperature of 200°C. The surface treatment does not seem to affect the resultant microstructure between Pd and GaSb.

4.2.3.5 Discussion of Pd/GaSb annealed at 200 °C

Samples annealed at 200 °C exhibit a tri-layer RR that continually increases in Pd concentration for up to 45 min. Increasing the annealing temperature to 200 °C results in a higher mobility of Ga and Sb at the RR/GaSb interface and has allowed for the segregation of Ga and Sb, leading to the formation of Pd-rich binary phases not found at 100 °C. Samples annealed at this moderate temperature (200 °C) also exhibit nonuniform reactions between the Pd film and GaSb substrate. This is most evident in samples annealed for 30 min; however, it is also believed to occur in samples annealed for shorted times as indicated by GIXD data. The reaction morphology does not appear to be affected by the presence of a dielectric layer at the M/S interface.

Some samples exhibit a similar microstructure to that presented by Vogt *et al.*[100] after annealing a Pd/S/Pd contact at 200 °C for 3h. Transmission electron microscopy micrographs presented by Vogt *et al.*[100] of the layer formation between the Pd/S/Pd contact and GaSb match, almost exactly, the micrographs presented here for samples annealed at 200 °C for 45 min. Aside from the presence of S in the top layer of the annealed Pd/S/Pd contact, the middle and bottom layers of the RR appear to have the same 3 layered characteristic, with vertical grains forming at the RR/GaSb interface. However, contrary to Vogt *et al.*,[100] phase identification of the Pd/GaSb RR here indicates that the bottom layer consists of binary Pd–Ga and Pd–Sb phases, not the suggested $Pd_x(GaSb)_{1-x}$ ternary phase.

It is useful to note that Pd/GaAs undergoes a very similar reaction when annealed between 220 and 275 °C for 10 min.[70] Annealing at 220 °C results in void formation within the Pd film at the Pd/RR interface, much like that for Pd/GaSb at 200 °C (Fig. 4.7). Upon increasing the annealing temperature to 275 °C, Pd/GaAs undergoes a laterally nonuniform reaction. The majority of the reaction consists of the hexagonal Pd₅(GaAs)₂ phase accompanied by a surface layer of unreacted Pd; however, there are localized areas where the Pd is completely consumed. In these areas a second hexagonal phase is formed that is more rich in Pd (Pd₄GaAs). The RR in such locations on the GaAs also appears to be twice the thickness compared to regions where the Pd remains.

4.2.4 Pd/GaSb annealed at 300 °C

Increasing the annealing temperature to 300 °C results in the total consumption of Pd within 10 min, as well as the formation of a

polycrystalline reacted region. Samples annealed for 10 min at 300 °C exhibit two distinct microstructural layers. The layered characteristic is very similar to samples annealed at 200 °C for 45 min. Fig. **4.15** shows the typical morphology of samples annealed at 300 °C for 10 min. The total reacted layer thickness has increased to an average of 129 (\pm 8) nm, and a bilayer (based on grain size) is evident in the TEM micrograph. The bilayer is the result of vertical grain growth at the RR/GaSb interface, and a decomposition of the Pd_xGaSb_{1-x} ternary phase at the top of the RR. The decomposition of Pd_xGaSb_{1-x} yields smaller disoriented Pd–Ga and Pd–Sb grains that are rich in Pd. The top layer consists of smaller grains, while the bottom layer consists of grains approximately 69 (\pm 5) nm long by 28 (\pm 4) nm wide. The vertical grains in the bottom layer resemble those found in samples annealed at 200 °C for 45 min.



Figure 4.15: Pd/GaSb annealed at 300 °C for 10 min. The Pd layer is totally consumed and the reacted region is now completely polycrystalline.

Nano-beam diffraction in the TEM was not possible due to the thickness of the TEM specimens analyzed. The electron diffraction patterns consisted of many grains, and identifying single phases from the patterns was not possible. X-ray diffraction was also performed on the samples annealed at 300 °C for 10 min. Similar to samples annealed at 200 °C for 45 min, the patterns match many phases in the binary Pd-Ga and Pd-Sb phase diagrams.[80] This made it impossible to identify the true phases present in the reaction product from the GIXD pattern.

Scanning TEM and EDX indicate the presence of binary, and possibly ternary, phases. Energy dispersive x-ray spectroscopy suggests that all phases present are rich in Pd and consist mainly of Pd-Ga and Pd-Sb compounds. It should be noted that due to specimen thickness and compositional variation from grain to grain, the true elemental composition of individual grains is difficult to verify. This is because Pd-Ga grains may sit below Pd-Sb grains and vice-versa, convoluting the EDX data. Data analysis using STEM and EDX suggest that there is a random mixture of Pd-Ga and Pd-Sb phases, with no preferential splitting of phases within the bilayer reaction region when samples are annealed at 300 °C for 10 min.

Increasing the annealing time of Pd/GaSb to 30 min at 300 °C yields larger diameter grains and a reaction region that is approximately 105 (\pm 10) nm in thickness. This thickness is somewhat less than samples annealed for 10 min, which may be a result of the consumption of the top layer in the RR, as well as grain coalescence; but it is more likely that the Pd thickness across the sample was not truly uniform. Figure **4.16** illustrates the typical reaction morphology of samples annealed for 30 min. The grain size varies from ~ 10 nm to over 50 nm in diameter, and the bilayer structure seen in previous samples is not as apparent.



Figure **4.16**: Reaction morphology of Pd/GaSb samples annealed at 300 °C for 30 min.

Scanning TEM and EDX analysis indicate a mix of Pd-Ga and Pd-Sb grains once again throughout the thickness of the film. Elemental analysis of the samples indicate that the layers are rich in Pd with varying composition dependent on the presence of Ga or Sb. Figure 4.17(a) and (b) are two scans across the reacted region in Fig. 4.16 from left to right. Figure 4.17(a) is a scan at the top of the RR, and Figure 4.17(b) is a scan at the bottom of the RR. These scans show a mixture of Pd-rich Pd-Ga and Pd-Sb phases and indicate that there may be a larger quantity of Pd-Sb grains in the RR. The values given for atomic percent have an average error of 10 %. For this reason they are considered only approximate and are used to assist in the identification of phases present through NBD and GIXD.



Figure 4.17: Elemental analysis of a Pd/GaSb sample annealed at 300 °C for 30 min. EDX line scan across the (a) top and (b) bottom of the reacted region indicate a mixture of Pd-Ga and Pd-Sb phases.

Next, NBD was performed on the samples and approximately 15 electron diffraction patterns were acquired. These patterns were then analyzed for d-spacing values and angles between planes as described earlier. The values were then correlated with known powder diffraction files for Pd-rich binary phases in the PCPDF.[**80**] For those phases that did not have an experimental powder diffraction file, but with a known crystal structure, the diffraction pattern was calculated using data from Pearson's Handbook of Crystallography and the software program *PowderCell*TM.[**81**] Using NBD three phases were identified in the reacted region. These phases are Ga₂Pd₅, Pd₅Sb₂, and Pd₂Sb. Fig. **4.18** shows three NBD patterns with labeled diffraction planes from these phases. Of the patterns taken, an equal number of patterns indicated the presence of Ga₂Pd₅ and Pd₅Sb₂, but Pd₂Sb was identified from only two patterns, indicating that Pd₂Sb may be present to a lesser extent. Each pattern is marked with an arrow to indicate the central diffracting beam from which all other spots were indexed.



Figure **4.18**: Nano-beam diffraction patterns of identified phases when Pd/GaSb is annealed at 300 °C for 30 min. According to NBD, resulting reaction produces (a) Ga₂Pd₅, (b) Pd₅Sb₂, and (c) Pd₂Sb.

Following NBD characterization of samples annealed at 300 °C for 30 min, GIXD was performed to verify the presence of Ga_2Pd_5 , Pd_5Sb_2 , and Pd_2Sb . The diffraction pattern obtained for samples annealed at 300 °C for 30 min is the same as those annealed for 10 min. This allowed for identification of the phases present in those samples as well. Fig. **4.19** shows the XRD patterns for samples annealed at 300 °C. All peaks up to

2θ = 80° are labeled; peaks above this are associated with d-spacings smaller than those found in the literature so matching these peaks was not possible. In several cases more than one phase matched the diffraction peaks and are labeled accordingly.

The formation of binary Pd-Ga and Pd-Sb phases at 300 °C indicates, again, that the reactivity of Pd/GaSb is higher than Pd/GaAs. This statement is also supported when comparing the reacted region thicknesses in Pd/GaSb and Pd/GaAs. Annealing Pd/GaAs samples at 275 °C for 10 min results in the growth of the Pd₅(GaAs)₂ formed in the asdeposited state with small regions of a second ternary phase, Pd₄GaAs, exhibiting a well defined orientation with respect to the GaAs. [70] When the annealing temperature is increased to 315°C for 10 min, thinner regions of the film consist of 15-30 nm of Pd₅(GaAs)₂, while thicker regions, spaced about 1 µm apart, consist of Pd₄GaAs, with small amounts of Pd₂Ga and Pd₂As. [70] The reacted region for Pd/GaSb is 105 - 130 nm thick, much thicker than Pd/GaAs, and has completely decomposed to several binary phases. This may be explained by the atomic bonding of GaSb and GaAs. Gallium arsenide is stable up to 1238 °C, above which it congruently melts to for a liquid; GaSb is stable up to only 712 °C.[39] This indicates that the atomic bonding between Ga and As is stronger than that of Ga and Sb; and, as a result, it is no surprise that the Pd/GaSb reaction occurs at a higher rate relative to Pd/GaAs.



Figure **4.19**: X-ray diffraction pattern of Pd/GaSb samples annealed at 300 °C for 10 min (bottom) and 30 min (top). The identified phases Ga₂Pd₅, Pd₅Sb₂, and Pd₂Sb correlate well with those identified via NBD.

4.2.5 Pd/GaSb annealed at 350 °C

Increasing the annealing temperature to 350 °C results in a similar microstructure compared to samples annealed at 300 °C for 30 min. Samples annealed for 30 min were studied using TEM, STEM, EDX, and GIXD; while those samples annealed for 10 min were only studied using GIXD for phase identification. The following discussion is limited to samples annealed for 30 min at 350 °C.

Following heat treatment at 350 °C, the reacted region ranges from 130 and 155 nm with an average thickness of 145 (\pm 8) nm. As seen in Fig. **4.20**, the grain size within the RR has increased compared to previous annealing condition with some grains measuring the length of the RR. According to TEM analysis, the reacted region is now a mixed layer of Pd-Ga and Pd-Sb grains.



Figure 4.20: Pd/GaSb annealed at 350 °C for 30 min.

Scanning TEM and EDX indicate Pd-rich binary phases, similar to those samples annealed at 300 °C for 30 min. EDX analysis did indicate

some segregation of grains according to composition. Scanning across the top of the RR revealed the majority of grains to be a Pd-Ga phase, while scanning across the bottom of the RR indicated an equal presence of Pd-Ga and Pd-Sb grains. Fig. **4.21** shows two EDX scans in the RR. Fig. **4.21** (a) is a scan across the top of the reaction region and Fig. **4.21(b)** is a scan across the bottom of the reaction region, both indicating some segregation of phases.



Figure 4.21: EDX scans of the RR following annealing Pd/GaSb at 350 °C for 30 min. Scans across the (a) top and (b) bottom of the reaction region indicate some segregation of Pd-Ga and Pd-Sb phases.

Following STEM and EDX analysis, NBD was performed on the samples for phase identification in the same manner as described earlier. Approximately ten unique patterns were acquired, and the phases were identified according to d-spacing and angles between planes. Ga_2Pd_5 , Pd_5Sb_2 , and Pd_2Sb were identified via NBD. Representative patterns of these phases are illustrated in Fig. **4.22** with identified diffraction planes and corresponding indicies. Arrows in Fig. **4.22(a) - (c)** indicate the

central diffracting plane from which all other planes are referenced. The Pd₂Sb phase was identified from only one pattern, indicating only a minimal amount of this phase.



Figure **4.22**: Nano-beam diffraction patterns of Pd/GaSb samples annealed at 350 °C for 30 min. Identified phases were (a) Ga₂Pd₅, (b) Pd₅Sb₂, and (c) Pd₂Sb.

The presence of Ga_2Pd_5 , Pd_5Sb_2 , and Pd_2Sb was verified via GIXD and the resulting pattern was similar to those for the samples annealed at 300 °C for 30 min. Samples annealed at 350 °C for 10 min were also studied via GIXD. These samples again yield a similar XRD pattern to those annealed at 300 °C. Fig. **4.23** shows the XRD patterns for samples annealed at 350 °C. All peaks below 80° are matched to the three phases identified via NBD.



Figure **4.23**: X-ray diffraction patterns of samples annealed at 350 °C for 10 min (bottom) and 30 min (top). The patterns verify the presence of Ga₂Pd₅, Pd₅Sb₂, and Pd₂Sb identified via NBD.

At moderately high annealing temperatures (300 - 350 °C) the uniform ternary phases present as the top layer of the RR in samples annealed at 200 °C give way to Pd-rich binary phases. These phases are shown to be stable for at least 30 min at 350 °C. The initial transition from the uniform ternary phases at lower temperatures begins to occur at 200 °C, even during the shortest annealing time of 5 min, suggesting an instability of the ternary phase in the Pd/GaSb couple at and above 200 °C. For this reason, the incorporation of Pd as part of a contact metallization dependent on solid phase regrowth requires annealing temperature below 200 °C to ensure the formation of binary Pd-Ga and Pd-Sb phases does not occur. The formation of binary phases results in the consumption of the GaSb substrate and will ultimately preclude regrowth of the semiconductor. Phase identification of samples annealed at 300 and 350 °C is also similar to the likely binary phases identified in samples annealed at 200 °C (Ga₂Pd₅, Pd₂Sb₅, and Pd₂Sb).

It is apparent that there is an increase in the Ga₂Pd₅ phase compared to the other phases when the annealing time and temperature are increased from 300 °C to 350 °C and 10 to 30 min, respectively. This is supported by EDX, NBD, and GIXD analysis. Analysis of the EDX line scans performed on samples annealed at 300 °C indicate a larger number of the grains are Sb-based (Pd₅Sb₂ and Pd₂Sb). As the time and temperature is increased to 350 °C and 30 min, the EDX scans show a shift toward Ga-bearing phases. The EDX scans are also supported by GIXD data. The Pd₅Sb₂ peak at ~ 47° and the Ga₂Pd₅ peak at ~ 77° in Fig. **4.19** and Fig. **4.23** are of particular interest. By increasing the time annealed at 300 °C, the Ga₂Pd₅ peak is found to decrease while the Pd₅Sb₂ peak remains relatively constant. When the temperature is increased to

350 °C, initially the Ga₂Pd₅ peak is minor; however, when the annealing time is increased to 30 min, it becomes the dominant peak in the pattern. The shift toward a Ga-based binary phase with increasing temperature is supported by the work of Su *et al.*; [104] however, our Ga-bearing phase is rich in Pd, it is not Ga₅Pd as reported by Su *et al*. We also report a roughly equal, if not greater, presence of Sb-bearing phases at 300 °C, where Su *et al.* suggest only the Ga_5Pd phase as a reaction product at 300 °C. The discrepancy between the phases currently reported and those by Su *et al.* may be a result of a difference in experimental conditions. In the present study samples were annealed in an evacuated quartz tube, limiting Sb loss during annealing. Su *et al.* report annealing samples in a N₂ atmosphere. There is no indication that the samples were sealed in a N₂ atmosphere to reduce Sb loss. Antimony has a high vapor pressure, [106] as a result there is likely to be significant Sb volatilization during the annealing process if GaSb is annealed in a dynamic atmosphere. Su *et al.* also report the presence of Pd-Ga and Pd-Sb phases based on one or two peaks in the diffraction pattern. We have shown here that no such identification is possible since there are many peak overlaps between most Pd-Ga and Pd-Sb phases.

The present study is also in partial agreement with Vogt *et al.* [99] We have verified that Pd does react with GaSb at room temperature; however, there is no evidence that Pd successfully rids the interface of the interfacial oxide layer prior to annealing. In their study, Vogt *et al.* used electron beam evaporation to deposit Pd on GaSb; however, it is very difficult to verify the phase formation between Pd and GaSb in the TEM micrograph presented in Vogt's study. To address the discrepancy, samples were prepared using e-beam evaporation as the deposition technique. As seen in Fig. 4.24, there is no discernable difference between samples that use sputtering or electron beam evaporation prior to annealing. The RR is 15 (\pm 1) nm thick and exhibits the same nanocrystalline structure as sputtered samples, with a dominant NBD ring corresponding to 2.3 (\pm 0.1) Å. To the best of our knowledge Pd is capable of completely dispersing the native oxides on GaSb, but only after mild annealing.



Figure **4.24**: As deposited Pd/GaSb using electron beam evaporation as the deposition technique. The reaction is the same as samples that were sputtered.

4.3 Conclusions

The early stages of reaction in a metal/semiconductor thin film couple is of great importance when engineering low resistance ohmic contacts and stable Schottky barriers. In this work, the evolution of the Pd/GaSb reaction has been explored with emphasis on the reactions important to contact formation of Pd-bearing contacts. The reaction at the Pd/GaSb interface begins as a nanocrystalline ternary phase with an approximate composition of Pd4GaSb and becomes more rich in Pd when annealed. Ternary Pd_xGaSb grains are formed following annealing at 100 °C for 180 min and are shown to be stable for a minimum of 360 min at this same temperature. When the annealing temperature is increased to 200 °C, the reaction is accelerated and becomes non-uniform, with regions of complete Pd consumption. The microstructure at 200 °C appears to be dependent on the amount of Pd consumed and more directly on the Pd concentration within the RR. The nanocrystalline region appears remain with approximately 65 to 75% Pd, above which it transforms into a polycrystalline phase. Also at 200 °C, a transition from the ternary phases to binary Pd-Ga and Pd-Sb phases is initiated at the RR/GaSb interface. Following 10 min at 300 °C, all evidence of the ternary phases disappears with the formation of a mixed reaction layer consisting of Ga_2Pd_5 , Pd₅Sb₂, and Pd₂Sb. These binary phases are shown to be stable up to 350 °C for a minimum of 30 min.

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Chapter 5

The Pd-rich portion of the Pd-Ga-Sb phase diagram

The development of thermally stable ohmic contacts to GaSb is a challenging process. As we have seen, in order to understand reactions at the metal/semiconductor interface it is instructive to turn to binary and ternary phase diagrams. These diagrams allow one to know the equilibrium phases that form upon heat treatment. The Pd-Ga-Sb ternary phase diagram is helpful for predicting final phase formation between a Pd ohmic or Schottky contact and a GaSb substrate at a fixed temperature. This diagram has been determined at 500 °C up to 50% Pd [42] and is presented in Fig. **5.1(a)**. According to Fig. **5.1(a)**, if a Pd contact is annealed at 500 °C and allowed to equilibrate with the GaSb substrate, the equilibrium phases will be PdGa, GaSb, and Sb. PdGa is in equilibrium with GaSb according to the Pd-Ga-Sb phase diagram, making it a possible candidate for a stable metallization to GaSb. Work completed by Liu, Fig. **5.1(b)**, also indicates the possibility of Pd₃Ga₇ and PdGa₅ as stable compounds in contact with GaSb at room temperature (25 °C).[43][44]



Figure 5.1: Pd-Ga-Sb phase diagram as presented by Richter and Ipser (a) and Liu (b). The phase diagram has been experimentally determined by Richter and Ipser up to 50 at% Pd at 500 °C, and is predicted by Liu at 25 °C.

The Pd/GaSb thin film studies presented in Ch. 4 indicate Pd-rich ternary phases exist with varying Pd compositions of 65 - 83%. The structure and exact composition of the ternary phases discussed in Ch. 4 could not be established; as a result, it is interesting to explore the Pdrich portion of the Pd-Ga-Sb phase diagram using bulk analysis techniques such as electron probe x-ray microanalysis (EPMA) and XRD.

5.1 The Pd-Ga-Sb phase diagram at 500 and 600 °C

Initial phase diagram experiments, based on the literature, were focused on annealing samples at 500 °C.[42] Initial sample compositions are listed in Table **5-1**. These samples did not equilibrate even after annealing for 12 weeks. This was indicated by the presence of more than three phases in each sample; however, the samples did give insight into possible ternary phases present in the Pd-rich region of the diagram. Phases of the composition Pd₇₅(GaSb)₂₅ and Pd₆₇Ga₁₆Sb₁₇ were present in three samples annealed at 500 °C, and are similar in concentration to phases found in the thin film studies presented in Ch. 4. New samples were prepared, with initial compositions listed in Table **5-2**, and annealed at 600 °C. An increase of 100 °C in annealing temperature was made to increase the reaction kinetics and further promote equilibrium. Results of EPMA analysis are listed in Table **5-3**.

Sample	Starting material composition		
	Pd	GaSb	
Pd _{0.6} (GaSb) _{0.4}			
Atomic Percent	60	40	
Mass (g)	0.5000	0.3000	
Pd _{0.66} (GaSb) _{0.34}			
Atomic Percent	66	34	
Mass (g)	0.5466	0.2534	
Pd _{0.8} (GaSb) _{0.2}			
Atomic Percent	80	20	
Mass (g)	0.6531	0.1469	
Pd _{0.735} (GaSb) _{0.265}			
Atomic Percent	73.5	26.5	
Mass (g)	0.6043	0.1957	

Table 5-1: Initial sample compositions for samples annealed at 500 $^{\circ}\mathrm{C}$

Sample	Starting material composition			
	Pd	GaSb	Ga	Sb
Pd _{0.67} Ga _{0.094} Sb _{0.166}				
Atomic Percent	67.0	9.4	0.0	7.2
Mass (g)	0.5970	0.1365	0.0	0.0665
Pd _{0.67} Ga _{0.16} Sb _{0.17}				
Atomic Percent	67.0	16.0	0.0	1.0
Mass (g)	0.5529	0.2376	0.0	0.0094
$Pd_{0.6}Ga_{0.05}Sb_{0.35}$				
Atomic Percent	60.0	5.0	0.0	35.0
Mass (g)	0.4646	0.0697	0.0	0.2658
$Pd_{0.75}Ga_{0.05}Sb_{0.2}$				
Atomic Percent	75.0	5.0	0.0	15.0
Mass (g)	0.5931	0.0712	0.0	0.1357
Pd _{0.7} (GaSb) _{0.3}				
Atomic Percent	70.0	30.0	0.0	0.0
Mass (g)	0.5774	0.2226	0.0	0.0
Pd _{0.75} (GaSb) _{0.25}				
Atomic Percent	75.0	25.0	0.0	0.0
Mass (g)	0.6154	0.1846	0.0	0.0
Pd _{0.8} (GaSb) _{0.2}				
Atomic Percent	80.0	20.0	0.0	0.0
Mass (g)	0.6531	0.1469	0.0	0.0
Pd _{0.9} (GaSb) _{0.1}				
Atomic Percent	90.0	10.0	0.0	0.0
Mass (g)	0.7273	0.0727	0.0	0.0

Table 5-2: Initial sample compositions for samples annealed at 600 $^{\circ}\mathrm{C}$

	At % after anneal			
Initial Composition	Pd	Ga	Sb	Final Phase
Pd ₆₇ Ga ₁₆ Sb ₁₇	66.8	15.8	17.4	Pd ₆₇ Ga ₁₆ Sb ₁₇
	67.0	24.7	8.3	Pd ₆₇ Ga ₂₅ Sb ₈
	51.1	47.5	1.5	PdGa
	74.4	2.7	22.9	Pd ₅ Sb ₂ or Pd ₈ Sb ₃
$Pd_{90}(GaSb)_{10}$	81.3	5.9	12.8	$Pd_{81}Ga_6Sb_{13}$
	72.0	26.5	1.4	Pd ₁₃ Ga ₅ or Ga ₂ Pd ₅
$Pd_{60}Ga_5Sb_{35}$	68.1	19.2	12.7	Pd ₆₈ Ga ₁₉ Sb ₁₃
	67.1	11.0	21.9	$Pd_{67}Ga_{11}Sb_{22}$
	74.5	2.6	22.9	Pd ₅ Sb ₂ or Pd ₈ Sb ₃
$Pd_{80}(GaSb)_{20}$	83.8	3.3	12.9	$Pd_{84}Ga_3Sb_{13}$
	73.1	25.9	1.0	$Pd_{13}Ga_5$ or Ga_2Pd_5
	74.4	1.8	23.8	Pd ₅ Sb ₂ or Pd ₈ Sb ₃
$Pd_{74}Ga_{9.4}Sb_{16.6}$	73.7	9.1	17.1	$Pd_{74}Ga_9Sb_{17}$
	75.2	12.7	12.1	Pd ₇₅ (GaSb) ₂₅
$Pd_{75}Ga_5Sb_{20}$	74.3	2.1	23.7	Pd ₅ Sb ₂ or Pd ₈ Sb ₃
	75.3	12.7	12.0	Pd ₇₅ (GaSb) ₂₅
Pd ₇₅ (GaSb) ₂₅	74.4	1.0	24.6	Pd ₅ Sb ₂ or Pd ₈ Sb ₃
	75.7	12.1	12.1	Pd ₇₅ (GaSb) ₂₅
Pd ₇₀ (GaSb) ₃₀	66.6	31.0	2.4	Pd ₂ Ga
	72.7	3.7	23.6	Pd ₅ Sb ₂ or Pd ₈ Sb ₃

Table **5-3**: EPMA results of 600 °C Pd-Ga-Sb ternary phase diagram samples

Ternary compositions detected at 500 °C were also present in samples annealed at 600 °C. All samples equilibrated according to the phase rule; however, the there was a lack of mass balance in some of the samples. The most obvious disparity in mass balance is seen in the $Pd_{90}(GaSb)_{10}$ sample in Table 5-3. The final phases only account for approximately 76% Pd, leaving a 14% disparity between initial composition and final phases. Four other samples yielded the same results. These samples contained volume fractions of phases that did not match that of expected fractions for a given initial composition. One such example is illustrated in the Pd₆₇Ga₁₆Sb₁₇ sample, which contained large regions of Pd₆₇Ga₂₅Sb₈.

One possible reason for the mass balance discrepancy is a volatilization of Sb during the long term anneal, but pressed pellets were reweighed after annealing with mass changes of less than 1%, making this unlikely. It is more likely that samples did not equilibrate and other regions within the phase diagram sample contain more than three phases, which would account for the mass balance discrepancies. As a result of the mass balance discrepancy, XRD of samples annealed at 600 °C was not performed. Although samples may not have completely equilibrated, verification of more Pd-rich ternary phases was accomplished. Three Pd-rich ternary phases, similar in composition to measured compositions in the Pd/GaSb thin film study, were successfully identified using EPMA. The final phases that closely matched Pd_x(GaSb)_{1-x} at 600 °C were Pd₆₇Ga₁₆Sb₁₇, Pd₇₅(GaSb)₂₅, and Pd₆₈Ga₁₉Sb₁₃.

It should be noted that some phase compositions reported throughout this study are identified as either "Pd₅Sb₂ or Pd₈Sb₃" or "Pd₁₃Ga₅ or Ga₂Pd₅." The composition variation between these compounds is ≤ 1 %. This is within the experimental error of the EPMA technique, and as a result, it is too difficult to successfully identify the phase present merely using EPMA. Each binary phase identified in the samples annealed at 600 °C appears to have some solid solubility of the third element as well. According to EPMA, the Pd–Ga binaries have a solid solubility of approximately 1 – 2.4 % Sb, and the Pd–Sb binaries are able to dissolve an average of 2% Ga into the lattice.

5.2 The Pd-Ga-Sb phase diagram at 700 °C

Following some success at 500 and 600 °C, samples were next prepared according to Table **5-4**. These samples were annealed at 700 °C to facilitate the formation of equilibrium phases. EPMA and XRD were utilized to identify the composition of these phases. According to EPMA, all samples equilibrated with no apparent mass balance discrepancies. Compositional data for each sample is summarized in Table **5-5**.

Sample	Starting material composition			
	Pd	GaSb	Ga	Sb
Pd _{0.6} Ga _{0.35} Sb _{0.05}				
Atomic Percent	60.0	0.0	35.0	5.0
Mass (g)	0.5414	0.0	0.2070	0.0516
Pd _{0.67} Ga _{0.11} Sb _{0.22}				
Atomic Percent	67.0	11.0	0.0	11.0
Mass (g)	0.5393	0.1593	0.0	0.1013
Pd _{0.67} Ga _{0.16} Sb _{0.17}				
Atomic Percent	67.0	16.0	0.0	1.0
Mass (g)	0.5529	0.2376	0.0	0.0094
Pd _{0.67} Ga _{0.25} Sb _{0.08}				
Atomic Percent	67.0	0.0	25.0	8.0
Mass (g)	0.5792	0.0	0.1416	0.0791
Pd _{0.737} Ga _{0.099} Sb _{0.171}				
Atomic Percent	73.7	9.2	0.0	7.9
Mass (g)	0.5923	0.1343	0.0	0.0733
$Pd_{0.75}Ga_{0.20}Sb_{0.05}$				
Atomic Percent	75.0	0.0	20.0	5.0
Mass (g)	0.6394	0.0	0.1117	0.0488
Pd _{0.75} (GaSb) _{0.25}				
Atomic Percent	75.0	25.0	0.0	0.0
Mass (g)	0.6154	0.1846	0.0	0.0

Table 5-4: Initial sample compositions for samples annealed at 700 °C

	Atomic	Percent		
Initial composition	Pd	Ga	Sb	Final phase
Pd _{73.7} Ga _{9.9} Sb _{17.1}	74.3	2.8	23.0	Pd ₅ Sb ₂ or Pd ₈ Sb ₃
	75.5	12.3	12.2	$Pd_{75}(GaSb)_{25}$
	73.8	9.0	17.1	$\mathrm{Pd}_{74}\mathrm{Ga}_9\mathrm{Sb}_{17}$
Pd ₆₇ Ga ₁₆ Sb ₁₇	73.3	0.8	25.9	Pd ₅ Sb ₂ or Pd ₈ Sb ₃
	67.3	15.0	17.8	$Pd_{67.3}Ga_{15}Sb_{17.8}$
	67.3	24.3	8.4	Pd _{67.3} Ga _{24.3} Sb _{8.4}
$Pd_{67}Ga_{25}Sb_8$	66.8	29.6	3.6	Pd_2Ga
	72.8	2.6	24.6	Pd ₅ Sb ₂ or Pd ₈ Sb ₃
	70.7	13.7	15.7	$Pd_{70.7}Ga_{14}Sb_{16}$
Pd ₇₅ (GaSb) ₂₅	72.5	25.9	1.6	Pd ₁₃ Ga ₅ or Ga ₂ Pd ₅
	74.2	8.9	17.0	$Pd_{74}Ga_9Sb_{17}$
	75.6	12.2	12.1	Pd ₇₅ (GaSb) ₂₅
$Pd_{67}Ga_{11}Sb_{22}$	72.1	0.4	27.5	Pd ₅ Sb ₂ or Pd ₈ Sb ₃
	12.7	20.1	67.1	$Pd_{67}Ga_{13}Sb_{20}$
$Pd_{60}Ga_{35}Sb_5$	66.7	26.6	6.7	Pd ₆₇ Ga _{26.5} Sb _{6.5}
	50.6	48.2	1.2	PdGa
$Pd_{75}Ga_{20}Sb_5$	83.3	9.1	7.6	Pd _{83.3} Ga _{9.1} Sb _{7.6}
	72.7	26.3	1.0	Pd ₁₃ Ga ₅ or Ga ₂ Pd ₅

Table **5-5**: EPMA results of 700 °C Pd-Ga-Sb ternary phase diagram samples

Four samples equilibrated to form at least one ternary phase of the composition $Pd_x(GaSb)_{1-x}$, closely matching the identified phases in the Pd/GaSb thin film experiments. These include $Pd_{75}(GaSb)_{25}$, $Pd_{67.3}Ga_{15}Sb_{17.8}$, $Pd_{70.7}Ga_{14}Sb_{16}$, and $Pd_{83.3}Ga_{9.1}Sb_{7.6}$. Three samples annealed at 700 °C equilibrated such that only 2 phases were present upon EPMA analysis. All samples were next investigated using x-ray powder diffraction, except $Pd_{75}Ga_{20}Sb_5$. This sample exhibited metallic-like ductility and was too difficult to grind into a powder.

The Pd₆₀Ga₃₅Sb₅ sample was first investigated and, according to EPMA, equilibrated to form Pd₆₇Ga_{26.5}Sb_{6.5} and PdGa. X-ray powder diffraction yielded approximately 52 peaks, with 9 matching PdGa.

Figure 5.2 is the XRD pattern for the equilibrated $Pd_{60}Ga_{35}Sb_5$ sample. Peaks matching the PdGa phase are identified with a "•," and all unidentified peaks are presumed to be from the ternary phase. Given the complexity of the pattern, structure analysis was not attempted. The 20 values and d-spacings of the unidentified peaks are summarized in Appendix A, Table A-1. It is apparent from Fig. 5.2 that the ternary phase is of low symmetry, based on the large number of peaks associated with the phase. It should also be noted that peak overlaps may occur between the PdGa and Pd₆₇Ga_{26.5}Sb_{6.5} phases.



Figure 5.2: X-ray diffraction pattern of the equilibrated Pd₆₀Ga₃₅Sb₅ ternary phase sample with identified peaks matching the PdGa phase. Unidentified peaks are associated with the ternary phase Pd₆₇Ga_{26.5}Sb_{6.5}.

Next the $Pd_{67}Ga_{11}Sb_{22}$ sample was analyzed. According to EPMA (Table 5-5) the sample contained one binary phase and one ternary phase ($Pd_{67}Ga_{13}Sb_{20}$). The binary composition was close in composition to Pd_5Sb_2 and Pd_8Sb_3 , thus diffraction peaks associated with both phases are identified in the XRD pattern illustrated in Fig. 5.3. It is evident from

Fig. 5.3 that the majority of the identified peaks are associated with at least one of the Pd antimonide phases mentioned above. The possible overlapping of peaks between two possible binary phases *and* the ternary phase makes it impossible to identify all the peaks that are associated with the ternary phase alone. As a result, the XRD pattern with peaks associated with the possible binary phase is given, but the structure of the ternary phase remains unsolved.



Figure 5.3: X-ray diffraction pattern of the equilibrated Pd₆₇Ga₁₁Sb₂₂ sample. The sample has one binary and one ternary phase according to EPMA, however the binary phase is unidentifiable based on XRD and composition alone due to the similar composition of Pd₅Sb₂ and Pd₈Sb₃ and peak overlap.

Next the Pd₆₇Ga₂₅Sb₈ sample was analyzed. According to EPMA the sample is composed of approximately 60 % Pd₂Ga, 30 % Pd_{70.7}Ga₁₄Sb₁₆, and 10 % Pd₅Sb₂ or Pd₈Sb₃. Peaks associated with the binary phases are labeled in Fig. **5.4**. Once again it is not possible to identify the contributing Sb-bearing phase due to the amount of overlap that occurs.

The difficulties of phase identification be a result of the low symmetry phases present in the Pd–Ga and Pd–Sb compounds.[80][81] Although structure analysis has not been successful, EPMA confirms the presence of a $Pd_x(GaSb)_{1-x}$ phase with similar composition as that found in the thin film experiments. The nanocrystalline and polycrystalline ternary phases present in the Pd/GaSb samples annealed at 100 °C are close to $Pd_{70}(GaSb)_{30}$.



Figure **5.4**: X-ray diffraction pattern of the equilibrated Pd₆₇Ga₂₅Sb₈ sample. The sample is composed of Pd₂Ga, Pd_{70.7}Ga₁₄Sb₁₆, and Pd₅Sb₂ or Pd₈Sb₃.

The remaining three samples with initial compositions

Pd_{73.7}Ga_{9.9}Sb_{17.1}, Pd₆₇Ga₁₆Sb₁₇, and Pd₇₅(GaSb)₂₅ were found to contain two ternary phases each. As a result, diffracting peaks may be associated with more than one phase in the samples and these samples are not discussed further. The XRD patterns for all three samples are located in Appendix A (Fig. A.1, Fig. A.2, and Fig. A.3) for the interested reader. Using
compositional information gained from EPMA, diffraction peaks within each pattern presented in Fig. A.1, Fig. A.2, and Fig. A.3 are labeled with the possible contributing phase.

In the previous pages an attempt to identify ternary Pd-Ga-Sb phases was successful; however, any attempt to analyze the crystal structure has been met with little success. This is in part due to the low symmetry phases present in the Pd-Ga and Pd-Sb binary phase diagrams and the difficulty encountered in preparing single phase ternary samples. One particular sample (Pd₆₀Ga₃₅Sb₅) did yield useful information for peak association of the ternary phase Pd₆₇Ga_{26.5}Sb_{6.5}. Beyond this, EPMA analysis does give insight as to what the Pd-Ga-Sb phase diagram at 700 °C may look like in the Pd-rich region, at least in part. Using data obtained from EPMA analysis (Table 5-5), we are able to construct part of the diagram. Figure 5.5 illustrates the experimentally determined equilibrium phases in the Pd-rich region of the Pd-Ga-Sb phase diagram at 700 °C. There are eight identified ternary phases in Fig. 5.5 marked with an "X." Four ternary phases identified in the phase diagram consist of $\sim 67\%$ Pd; however, a solid solution may actually exist between Pd₆₇Ga_{26.5}Sb_{6.5} and Pd_{67.3}Ga_{24.3}Sb_{8.4}, and between Pd_{67.3}Ga₁₅Sb_{17.8} and Pd₆₇Ga₁₃Sb₂₀. It is not thought that one exists between $Pd_{67.3}Ga_{24.3}Sb_{8.4}$ and $Pd_{67.3}Ga_{15}Sb_{17.8}$ because these phases were found to coexist within the same sample as distinct phases. The possible solid solution is illustrated in Fig. 5.5 as the shaded region with a "?" between the ternary phases containing 67% Pd.



Figure 5.5: Tie lines on the incomplete Pd-Ga-Sb phase diagram in the Pd-rich region at 700 °C. Ternary phases are labeled and the location of each phase is marked with an "X."

Recalling EDX data from the Pd/GaSb experiments, the initial composition of the RR was approximately 67% Pd and 23% GaSb. As the reaction progressed with increasing time and/or temperature, the RR ternary phases exhibited an increase in Pd concentration. The Pd concentration of the ternary phases in the thin film reactions ranged from $\sim 67\%$ to 83% while maintaining an approximate 1:1 ratio of Ga:Sb, much like the phases identified in Fig. 5.5. When the temperature of the Pd/GaSb samples was increased above 100 °C, Ga₂Pd₅ and Pd₅Sb₂ with some Pd₂Sb formed. This observation is consistent with the lack of a tie-

line between any of the ternary phases and GaSb. While the phase diagram samples did not yield structural data for individual ternary phases, it has verified the presence of ternary phases within the very complex, Pd-rich, Pd-Ga-Sb phase diagram.

Chapter 6

Indium-based Ohmic Contacts to n-GaSb

6.1 Review of Contacts to n-GaSb

To date ohmic contacts to n-GaSb are primarily Au-based [49] [69][91][107]-[111] and Pd-based.[100]-[103] Gold-based ohmic contacts consistently provide specific contact resistances (ρ_c) less than 10⁻⁴ Ω-cm². Villemain *et al.*[**111**] report a Te/Au (60/340 nm) metallization yielding a specific contact resistance $\approx 1 \times 10^{-6} \Omega$ -cm² (n = 10^{18} cm^{-3}) when annealed at 380 °C for 1 h and then 450 °C for 2 s. While this contact resistance is suitable for some devices, Au-based ohmic contacts are not recommended for GaSb devices based on metallurgical considerations. Piotrowska et al. [49] studied the Au/GaSb interaction, finding that 100 nm of Au(Zn) reacts with GaSb to form a 100 nm reaction layer when annealed at 180 °C for 3 min. The reaction layer advances to 850 nm in depth when the Au/GaSb contact is annealed at 350 °C for 3 min. The consequences of using Au-based ohmic contacts may be device instability and failure because devices can be subjected to temperatures in excess of 180 °C during packaging and less severe but still elevated temperatures for longer times during operation.

Palladium-based contacts that do not include indium provide ρ_c as low as 4.9 x 10⁻⁶ Ω -cm² (n = 9.9 x 10¹⁷ cm⁻³). [103] Palladium disperses

the native oxide on GaAs, [74] and is reported to do the same on GaSb; [99] furthermore, the introduction of Pd may lead to solid phase reactions that minimize surface and interfacial roughening. [71] One trend for Pd-based contacts is to combine Pd with Ge, S, or Te in an attempt to create a heavily doped layer in the semiconductor just beneath the contact. [100]-[103] Vogt *et al.* [103] report a Pd/Ge/Au/Pt/Au metallization with a ρ_c of 4.9 x 10⁻⁶ Ω -cm². The authors believe the first Au layer in the contact promotes diffusion of Ge into the semiconductor. They further argue Ge acts as an n-type dopant in this situation, although Ge is used as a p-type dopant during the growth of p-GaSb.[1] A deviation of 50 °C above 300 °C leads to an order of magnitude increase in specific contact resistance, while lower annealing temperatures do not yield linear current-voltage curves. Based on high resolution TEM, annealing the metallization at 300 °C for 45 s results in spikes of a Pd-Ge compound penetrating into the semiconductor approximately 150 nm. This reaction depth is suitable for some applications but does not provide a sufficiently shallow contact when active regions of devices are on the order of tens of nanometers below the semiconductor surface, and semiconductor consumption must be kept to a minimum.

Although contacts that contain Pd and Ge yield low specific contact resistances, contacts based on amphoteric dopants may be inappropriate for applications that require long-term reliability.[71] An alternate method proposed for forming ohmic contacts to n-GaSb is to lower the Schottky barrier at the metal/semiconductor interface by forming an interfacial layer of $In_xGa_{1-x}Sb$, analogous to the successful In-based contacts to n-GaAs.[71] [96] The dependence of the band gap on the composition of ternary alloys follows the quadratic form:[72]

$$E_{g}(A_{1-x}B_{x}) = (1-x)E_{g}(A) + xE_{g}(B) - x(1-x)C$$
(6.1)

where C is known as the bowing parameter and accounts for deviations from linear interpolation between the two binary semiconductors A and B. $In_xGa_{1-x}Sb$ consists of the compound semiconductors GaSb and InSb. Using the band gaps of GaSb (0.725 eV),[1] InSb (0.18 eV)[13] and the experimentally determined bowing parameter (0.415 eV) [72] we are able to calculate the band gap of $In_xGa_{1-x}Sb$ according to In composition:

$$E_g((GaSb)_{1-x}(InSb)_x) = 0.725(1-x) + 0.18 x - 0.415 x(1-x)$$
 (6.2)

Figure 6.1 is a schematic drawing of the band gap dependence on In composition. As In is incorporated into the GaSb substrate, the band gap decreases. It is also predicted the valence band off-set between InSb and GaSb is neglible for unstrained heterojunctions, yielding a lower Schottky barrier at the metal/semiconductor interface.[112] By decreasing the Schottky barrier at the metal/semiconductor interface through the formation of $In_xGa_{1-x}Sb$, ohmic behavior is more readily achieved.



Figure **6.1**: Predicted band gap as a function of In composition. Complete miscibility occurs above 473 K.

Prior to this study, two papers focused on In-bearing contacts to n-GaSb, providing low ρ_c on the order of $10^{-6} \Omega$ -cm² or less. [93][94] The metallization schemes presented by Yang *et al.* (Pd/Te/Pd/In/Au) [93] and Ikossi *et al.* (Pd/Ge/Pd/In/Pd) [94] use Te or Ge in conjunction with In in an attempt to decrease the barrier height while creating a heavily doped layer at the metal/semiconductor interface. Drawbacks of these previously reported contacts to GaSb include the narrow annealing temperature range over which low ρ_c is achieved,[94] poor surface morphology,[93][94] and deep reaction depth.[93][94] Ikossi *et al.*[94] report a specific contact resistance of $1.4 \times 10^{-6} \Omega$ -cm² (n $\approx 10^{18}$ cm⁻³). This value is achieved after annealing at 350 °C, but deviations in annealing temperature of 25 °C lead to an increase in ρ_c of one order of magnitude. There is also no mention of surface morphology in the as-deposited or annealed states. Yang *et al.* [93] obtain a ρ_c less than $10^{-6} \Omega$ -cm², but the surface

morphology contains indium agglomerations one micron in size or larger, and the reaction depth of the contact is approximately 150 nm.

For the In-bearing ohmic contacts to GaSb presented in this thesis, a Pd:In ratio of 3:7 was chosen based on limited phase diagram data. The complete Ga-In-Pd-Sb phase diagram is not known, but Pd₃In₇ is reported to be in equilibrium with InSb at 300, 450, and 700 °C, [95] and Pd₃Ga₇ is predicted to be in equilibrium with GaSb at 25 °C.[44] Furthermore, Pd₃In₇ and Pd₃Ga₇ share the same crystal structure. [81] They might form a continuous solid solution, and this solution may allow an exchange of Ga and In between the contact and GaSb, without consumption of the semiconductor. Such a reaction could lead to a shallow, low resistance ohmic contact to n-GaSb. A similar Pd and In-bearing ohmic contact to n-GaAs based on this approach has been reported by Chen *et al.* [96] Metallization layer thicknesses in this study were therefore chosen such that a Pd₃(In,Ga)₇ phase could form upon annealing, potentially leading to a Ga_xIn_{1-x}Sb region at the metal/semiconductor interface. However, the use of In alone may lead to surface roughening and liquid phase formation. Indium also does not penetrate the oxide layer on GaAs, [97] and it may not penetrate the native oxide on GaSb. By combining Pd and In in a contact metallization, the oxide layer may be dispersed, and an intermetallic phase may form between the Pd and In, increasing the thermal stability of the contact.

6.2 Evaporated Pd/In contacts

6.2.1 Results and Discussion

The first contacts tested on n-GaSb consisted of Pd/In/Pd/In/Pd (19.4/80.6/9.7/80.6/9.7 nm) layers. Nominal thicknesses have been listed for each layer in parenthesis. The overall atomic ratio of Pd:In was chosen to be 3:7, and alternating Pd/In layers were used to promote intermixing of the metals upon annealing. Specific contact resistances of approximately 3 x $10^{-5} \,\Omega$ -cm² were measured for the Pd-In contact when annealed at 200 °C for 15 min. The specific contact resistance did not improve with increased time or temperature. After annealing, the contacts were patterned again according to Ch 3, and a layer of Au (100 nm) was deposited on the annealed contacts. With no subsequent anneal, the measured specific contact resistance decreased by an order of magnitude. This decrease in the apparent specific contact resistance illustrates that the metal sheet resistance is important in our experiments, and as discussed in greater detail in Section 3.3.2, a thick Au overlayer is important for measuring the true $\rho_{\rm c}$. [76] [77] On the other hand, adding Au to the contact could lead to unwanted reactions between the Au and GaSb.[49] To reduce the Au/GaSb interaction, a layer of Pt was added as a convenient barrier between the Pd/In layers and the Au cap.

Initial experiments on multilayer contacts containing Pt and Au were performed with Pd/In/Pd/In/Pd/Pt/Au (19.4/80.6/9.7/80.6/9.7/50/150 nm) layers, providing a ρ_c of 3.4 x 10⁻⁶ Ω -cm² for samples annealed at 300 °C for 10 min. A simplified Pd/In/Pd/Pt/Au (4/40.3/5.7/50/100 nm) contact was subsequently studied. As discussed below, the simplified contacts provide an important advantage of improved morphology over the first set of thicker contacts. Linear I-V curves were obtained after deposition and again after annealing for all samples studied. As-deposited samples exhibited a ρ_c of 9.2 x 10⁻⁵ Ω -cm². Specific contact resistance values after a single annealing step (referred to as a "single-stage anneal") are plotted in Fig. 6.2.



Figure **6.2**: Specific contact resistance of Pd/In/Pd/Pt/Au (4/40.3/5.7/50/100 nm) contacts following a single-stage anneal.

There is an increase in ρ_c when annealed at 125 °C for 60 min, but the ρ_c continually decreased as the annealing temperature increased, and values as low as $4.1 \times 10^{-6} \ \Omega - cm^2$ were achieved for contacts annealed at 350 °C for 15 min. However, the increased annealing temperatures lead to a degradation of surface morphology, with agglomerations up to 5 µm in size. The surface of the contact also changed from a gold to silver color, and x-ray photoelectron spectroscopy (XPS) surface analysis indicates an outdiffusion of Ga, Sb, and In, along with traces of Pt and Pd. Clearly, the Pt barrier fails for this annealing condition.

To improve the surface morphology, a two-stage annealing scheme was adopted to promote solid phase reactions at temperatures below the melting point of In (156 °C) thus reducing the possibility of liquid phases. The first stage consists of a 60 or 120 min anneal at 125 °C; the second stage leads to a low contact resistance and consists of a 10 min or longer anneal at 300 to 400 °C. The specific contact resistance continually decreased with increasing annealing temperature, as seen in Fig. **6.3**, but the surface morphology began to breakdown above 350 °C, with similar results obtained to the single-stage anneal. The optimal 2-stage anneal at 350 °C. A 60 min anneal at 125 °C followed by a 10 min anneal at 350 °C also yields comparable values. This annealing scheme results in improved surface morphology and ρ_c of 2.4 x 10⁻⁶ Ω -cm².



Figure **6.3**: Specific contact resistance of Pd/In/Pd/Pt/Au (4/40.3/5.7/50/100 nm) contacts using a 2-stage scheme.

The Pd/In/Pd/In/Pd/Pt/Au (19.4/80.6/9.7/80.6/9.7/50/150 nm) contacts contained In agglomerations on the order of $1-2 \mu m$. However, we found that by minimizing the Pd/In layer thicknesses and depositing the In at low rates ($\cong 1 \text{ Å/s}$), the size of the In agglomerations were reduced by an order of magnitude or better. The Pd/In/Pd/Pt/Au (4/40.3/5.7/50/100 nm) layer structure yielded the optimal surface morphology and specific contact resistance after annealing at 125 °C for 60 min followed by 350 °C for 10 min. According to SEM analysis, shown in Fig. 6.4, the agglomerations were reduced to 50-200 nm in diameter in the as-deposited state, Fig. 6.4(a), and agglomerations were not observed after annealing, as shown in Fig. 6.4(b). However, some surface features were still present, suggestive of a non-uniform reaction between the metal and semiconductor. Atomic force microscopy revealed a root mean square (RMS) surface roughness of 10.2 nm for samples in the asdeposited state, and 9.2 nm for samples following the 2-stage annealing scheme: 125 °C for 60 min followed by 350 °C for 10 min, which suggests only minimal improvements following the anneal.



Figure 6.4: SEM image of the (a) as-deposited Pd/In/Pd/Pt/Au contact surface showing agglomerations 50-200 nm in diameter and (b) SEM image of the Pd/In/Pd/Pt/Au surface after annealing at 125 °C for 60 min followed by 350 °C for 10 min.

The metal/semiconductor (M/S) interface was subsequently investigated using TEM, STEM, and EDX. Samples annealed at 125 °C for 60 min and then 350 °C for 10 min were investigated. Figure 6.5(a) and (b) are TEM micrographs of the annealed sample showing the morphology and reaction products at the metal/semiconductor interface. Void formation within the reacted region may be a result of a disparity of elemental diffusion rates at the M/S interface. Recalling the Pd/GaSb study, void formation occurred within the Pd film as a result of Pd indiffusion during heat treatments at 100 and 200 °C. Ultimately, one desires a uniform reaction at the M/S interface, but the reaction between the Pd/In/Pd/Pt/Au and GaSb resulted in a non-uniform reaction region. The reaction layer includes Pd-Ga grains and In_xGa_{1-x}Sb regions that total 135 nm in thickness. It is believed that the use of Pt as a diffusion barrier may be at least partly responsible for the non-uniform reaction between the metal and semiconductor. Platinum serves well as a diffusion barrier to the Au cap layer, but from the Pt-In phase diagram, it is known that many intermetallics form between Pt and In.[113] In fact, Pt and In were found to intermix in our contacts, along with incorporation of lower levels of Ga and Sb in the Pt. Extensive reaction of In with Pt could result in excess Pd at the M/S interface, since the Pd:In ratio was chosen such that the Pd₃In₇ phase would form. The excess Pd could react with the GaSb and consume the semiconductor. Using EDX, Pd-Ga grains were identified at the deepest points of the reacted region, supporting the hypothesis that excess Pd exists at the metal/semiconductor interface, reacting with and consuming the semiconductor.





(b)

Figure 6.5: TEM micrographs of the reaction between the Pd/In/Pd/Pt/Au contact and GaSb substrate showing the (a) non-uniform reaction across the M/S interface and (b) the formation of $In_xGa_{1-x}Sb$.

Scanning TEM imaging and EDX profiling support the hypothesis that $In_xGa_{1-x}Sb$ is formed at the M/S interface after annealing. A region approximately 50 nm thick at the M/S interface has been identified as $In_xGa_{1-x}Sb$, and is labeled in Fig. 4. Until now, it has to our knowledge

only been speculated that In_xGa_{1-x}Sb forms at the M/S interface of Inbearing contacts to n-GaSb.[93][94] The low resistance of this M/S contact is attributed to the formation of the In_xGa_{1-x}Sb at the M/S interface, which provides a lowering of the barrier height at the interface due to a smaller Schottky barrier to n-InSb compared to n-GaSb.

Finally, the electrical properties of three non-In bearing contacts were examined. First a Pd/Pt/Au (12/35/60 nm) contact was studied and was rectifying as deposited, but yielded values on the order of $10^{-5} \,\Omega\text{-cm}^2$ when annealed at or above 300 °C, with the lowest value of 1.7 x 10^{-5} Ω cm² when annealed at 350 °C for 10 min. A previously reported Pd/Ge/Au/Pt/Au (8.7/56/23.3/47.6/105.6 nm) contact was also prepared for direct comparison. [103] Surface preparation steps for the Pd/Ge/Au/Pt/Au contact were followed according to Vogt *et al.* and included a HCl etch (30 s) followed by a DI rinse and annealed at 300 °C for 45 s using a rapid thermal anneal (RTA). [103] This metallization provided a specific contact resistance of 8.3 x $10^{-6} \Omega$ -cm² on our epilayers. The non-indium bearing contact ρ_c values are listed in Table 6-1 along with the values obtained for the Pd/In/Pd/Pt/Au (4/40.3/5.7/50/100 nm) contact for comparison. All values obtained using non-In bearing contacts in this study are higher than the In-bearing contact presented here, confirming the value of In for promoting a lower specific contact resistance. The Pd/In/Pd/Pt/Au contact furthermore does not contain Ge, which may be beneficial for long-term stability given the tendency of Ge to act as an acceptor when incorporated during the growth of GaSb crystals.

Metallization and Annealing Condition	$ ho_{\rm c}$ (x 10 ⁻⁶ Ω -cm ²)
Pd/Pt/Au (12/35/60 nm)	
As Deposited	Non-Ohmic
350 °C, 10 min	$17 (\pm 5)$
Pd/Ge/Au/Pt/Au (8.7/56/23.3/47.6/105.6 nm) 300 °C, 45 s	8.3 (± 0.7)
Pd/In/Pd/Pt/Au (4/40.3/5.7/50/100 nm)	
As Deposited	$9.2 (\pm 0.7)$
125 °C, 60 min & 350 °C, 10 min	$2.6 (\pm 0.3)$
125 °C, 120 min & 350 °C, 10 min	$2.4 (\pm 0.3)$

Table 6-1: Comparison of metal contacts to n-GaSb

6.2.2 Evaporated Pd/In/Pd Conclusions

The Pd/In/Pd/Pt/Au ohmic contact provides a $\rho_c = 2.4 \times 10^{-6} \Omega - cm^2$, and this study demonstrates that In is an important element in the formation of the ohmic contact. Without In, the other contacts tested in this study did not provide such low specific contact resistances. Furthermore, the formation of $In_xGa_{1-x}Sb$ was observed at the contact interface using STEM and EDX, pointing to a reduced barrier height at the M/S interface after annealing. The annealing temperature range over which the specific contact resistance drops to a minimum and a suitable surface morphology is achieved is at least twice as wide as that of previously reported In-bearing contacts. This temperature range is restricted by the contact morphology rather than the ρ_c . The surface morphology of the contact consists of 50 – 200 nm agglomerations with an RMS roughness of 10.2 nm in the as-deposited state, an improvement of an order of magnitude over what has been reported for other In-bearing contacts. Two drawbacks of this contact metallization include the nonuniform reaction at the M/S interface, as well as a reaction region measuring 135 nm thick. The Pd/In/Pd/Pt/Au contact presented in this article has shown potential as a high quality ohmic contact to n-GaSb, but some improvements must be addressed. Improving reaction uniformity and depth is critical for device performance. The thermal stability of the contact must also be addressed if devices are to operate for extended periods of time. These concerns require the exploration of an improved diffusion barrier and thinner contact layers that will minimize semiconductor consumption.

6.3 Sputtered $Pd_3In_7/X/Au$ contacts (X = Pt, W, TiN, WSi₂, or WSiN)

6.3.1 Results and Discussion

Sputtered contacts were next investigated as a means to identify the ohmic formation mechanism (Section 2.4), to improve the diffusion barrier, and to improve surface and reaction morphology. To fabricate the contacts, a pre-alloyed target was purchased from SPI, Inc. with a nominal composition of Pd₃In₇. A pre-alloyed Pd₃In₇ would be unable to participate in the regrowth mechanism because the compound MM', as discussed earlier in the regrowth mechanism, has already formed before reaction with the semiconductor. This precludes the formation of a ternary phase $Pd_x(GaSb)_{1-x}$ necessary for the regrowth mechanism. Thus, if specific contact resistances and phase formation similar to the evaporated contacts can be accomplished, the ohmic formation mechanism might be attributed to the exchange mechanism, provided that the formation of $In_xGa_{1-x}Sb$ still occurs.

Initial experiments focused on Pt and W as a diffusion barrier. Metallization schemes included Pd₃In₇/Pt/Au (10/50/100 nm and 20/50/100 nm) and Pd₃In₇/W/Au (10/50/100 nm, 10/50/140 nm, and 20/50/100 nm). Optimal specific contact resistances are listed in Table **6–2**. Values presented in Table **6–2** correspond to the annealing condition that yields the lowest specific contact resistance for each metallization. As deposited contacts did not yield linear I–V characteristics. In general, as seen from Table **6–2**, the specific contact resistances of the sputtered contacts containing Pt and W as the diffusion barrier are two to three times the ρ_c values obtained with the evaporated contacts. The as-deposited Pd/In/Pd/Pt/Au contacts were ohmic, which indicates that ion bombardment during sputter deposition may introduce damage to the GaSb surface, thus making the contacts non-ohmic. This damage is subsequently relieved upon annealing and ohmic contacts are achieved.

The thickness of the Pd_3In_7 and Au layers were subsequently varied on the $Pd_3In_7/W/Au$ contacts to determine if the initial layer thickness and/or the Au capping layer affected ρ_c . Increasing the Au capping layer from 100 nm to 140 nm (to yield a total contact thickness of 200 nm) did not effect ρ_c ; however, by doubling the Pd_3In_7 thickness from 10 to 20 nm, the measured ρ_c decreased by 20%. The layer thickness was again doubled to 40 nm, but the surface morphology of the contact prior to annealing was no longer smooth. As a result, contacts containing 20 nm of Pd₃In₇ were further studied.

Table 6-2: Minimum specific contact resistances of W and Pt sputtered contacts.

Metallization and Annealing Condition	$ ho_{c}$ (Ω -cm ²)	Error
Pd ₃ In ₇ /Pt/Au (10/50/100 nm)		
As deposited	Not Ohmic	
325 °C - 10 min	$6.7 \ge 10^{-6}$	$3 \ge 10^{-7}$
Pd ₃ In ₇ /Pt/Au (20/50/100 nm)		
As deposited	Not Ohmic	
325 °C - 10 min	Not Ohmic (Sever	e Degradation)
Pd ₃ In ₇ /W/Au (10/50/100 nm)		
As deposited	Not Ohmic	
325 °C - 10 min	$7.9 \ge 10^{-6}$	$7 \ge 10^{-7}$
Pd ₃ In ₇ /W/Au (10/50/140 nm)		
As deposited	Not Ohmic	
350 °C - 10 min	$7.9 \ge 10^{-6}$	$9 \ge 10^{-7}$
Pd ₃ In ₇ /W/Au (20/50/130 nm)		
As deposited	Not Ohmic	
275 °C - 10 min	$6.4 \ge 10^{-6}$	$5 \ge 10^{-7}$

Contacts containing Pt and 10 nm of Pd₃In₇ provided a minimum specific contact resistance of 6.7 x $10^{-6} \Omega$ -cm² when annealed at 325 °C for 10 min; however, this was accompanied by severe degradation of the contact surface. Similar results were obtained for contacts utilizing W as the diffusion barrier. Optimum annealing conditions for W contacts yield a specific contact resistance of 6.4 x $10^{-6} \Omega$ -cm², but agglomerations and surface roughening were observed for contacts utilizing a thicker Pd₃In₇ layer (20 nm) when annealed at temperatures greater than 275 °C for 10 min with W as the diffusion barrier. Samples containing W as the diffusion barrier also exhibited In outdiffusion (identified via EDX) and lateral diffusion of the Au capping layer into the contact gap spacings. Figure **6.6** is a SEM micrographs of samples containing W following an anneal at 325 °C for 10 min, it is clear that the stability of this contact is very limited. Degradation also occurs in samples utilizing Pt as the diffusion barrier when annealed at temperature greater than 300 °C. Figure **6.7** is an SEM micrograph of the severe surface degradation which occurs following heat treatment at 325 °C for 10 min. The semiconductor surface, which appears smooth, is identified in the micrograph. On the left and right side of the micrograph is the Pd₃In₇/Pt/Au metallization. Energy dispersive x-ray spectroscopy indicates that the surface agglomerations contain large amounts of In and Au, along with smaller amount of the remaining elements. The surface degradation of the contacts after such short annealing times precludes the use of contacts utilizing W or Pt as the diffusion barrier when shallow contacts and morphological stability at these processing temperatures is required.



Figure 6.6: SEM micrograph of $Pd_3In_7/W/Au$ (20/50/130) contacts annealed at 325 °C for 10 min.



Figure 6.7: SEM micrograph of $Pd_3In_7/Pt/Au$ (20/50/100) contacts annealed at 325 °C for 10 min

Exploration of more stable diffusion barriers was undertaken. Possible barriers, based on thermal stability, resistivity, and availability included TiN, WSi₂, and WSiN. Samples containing TiN as the diffusion barrier were next explored. Two separate metallizations containing TiN as the diffusion barrier were compared: Pd₃In₇/TiN/Au (20/100/50 nm) and Pd₃In₇/TiN/Au (20/100/100 nm). The TiN was reactively sputtered using 15 % N₂ flow during the sputtering process. All contacts were rectifying as deposited, regardless of Au thickness. A ρ_{c} value of 5.6 x $10^{^{-6}}\,\Omega\text{-}cm^{2}$ was achieved following a 30 s anneal at 325 °C. This is three times that of the Pd/In/Pd/Pt/Au contacts. The specific contact resistance does not appear to be a function of Au thickness, as the values are all within experimental error of each other, irrespective of the Au thickness. It should be noted, however, that in every case the lowest ρ_c value was achieved following the shortest anneal times. Subsequent anneals or longer annealing times resulted in an increase of the specific contact resistance. The ρ_c of contacts annealed at 325 °C for 30 s increased from 5.6 x $10^{-6} \Omega$ -cm² to approximately 1 x $10^{-5} \Omega$ -cm² when annealed an additional 30 s; and to 6 x $10^{-5} \Omega$ -cm² when annealed for a total of 120 s. The optimum specific contact resistances, as a function of temperature and time, are listed in Table 6-3 for both metallizations.

Pd ₃ In ₇ /TiN/Au (20/100/50 nm)		
Annealing condition	ρ _c (Ω−cm²)	Error
300°C – 1 min	$7.1 \ge 10^{-6}$	4.4 x 10^{-7}
325°C - 30 sec	5.6 x 10^{-6}	$4.0 ext{ x } 10^{-7}$
125°C - 60min & 300°C - 1 min	$1.1 \ \mathrm{x} \ 10^{-5}$	8.2×10^{-7}
125°C - 60min & 325°C - 30 sec	$1.3 ext{ x } 10^{-5}$	8.8×10^{-7}
Pd3In7/TiN/Au (20/100/100nm)		
Annealing condition	$ ho_{\rm c} \left(\Omega - {\rm cm}^2 \right)$	Error
275°C - 1 min	$1.0 \ \mathrm{x} \ 10^{-5}$	6.6×10^{-7}
300°C - 1 min	6.1 x 10^{-6}	$3.4 ext{ x } 10^{-7}$
325°C - 30 sec	5.7 x 10^{-6}	5.6 x 10^{-7}
$2 \Box 0 0 \Box 0$	_	2

Table 6-3: Specific contact resistance of Pd₃In₇/TiN/Au contacts

It was hypothesized that possible mechanisms for specific contact resistance degradation included In out diffusion into the barrier, or oxygen contamination of the barrier. The possibility of indium out diffusion as a result of excess liquid indium was addressed by including a 2-stage annealing scheme similar to the evaporated contacts. As seen in Table **6-3**, by including an anneal at 125 °C the ρ_c achieved was not as low as that for single stage anneals. Thus attention was turned to O₂ contamination. To identify whether O₂ contamination or barrier oxidation during the annealing process was responsible for the degradation, samples were analyzed using AES. Samples were analyzed in the as-deposited state, and following a 325 °C for 2 min and 30 min. According to AES, samples utilizing TiN as the diffusion barrier contained equal amounts of Ti and O within the barrier prior to annealing, and an increase in oxygen content of approximately 20 % following annealing. As a result, the increase in ρ_c is likely correlated with increased oxygen content in the TiN barrier. Supplemental materials characterization of contacts that included TiN as the diffusion barrier is presented Appendix B.

Attempts were made to reduce the amount of oxygen in the TiN film and included varying the sputtering pressure and N_2 %, as well as increasing the sputtering rate and negatively biasing the samples. Reduction of the O_2 was met with minimal success and degradation of the contacts persisted throughout the entire experiment. As a result, contacts containing TiN as the diffusion barrier do not meet the desired characteristics of low resistance and thermal stability. New diffusion barriers less susceptible to oxidation were next explored.

Contacts containing WSi₂ as the diffusion barrier were next explored. Silicides have been used extensively as diffusion barriers for Cu and Al in Si microelectronics and exhibit low resistivities as well as good thermal stability. [46] [48] [114] As a result, it was thought that these types of barriers would also work well for contacts to GaSb. Initial experiments focused on simply replacing the diffusion barrier with WSi_2 with the same layer thicknesses as previously mentioned. Contact layers consisted of Pd₃In₇/WSi₂/Au (20/100/50 nm). Temperatures within the range of 300 - 350 °C were used for annealing for comparison. The Pd₃In₇/WSi₂/Au contacts provided a specific contact resistance of 3.6 (± 0.3) x $10^{^{-6}}\,\Omega\text{-}cm^2$ when annealed at 350°C for 15 s. This value of ρ_c is lower than all previous resistances reported here, indicating the WSi₂ is a barrier that helps provide a lower resistance compared to Pt and W; however, similar to the TiN contacts, degradation of the specific contact resistance occurred immediately following the initial anneal. Specific contact resistance degradation was accompanied by agglomeration of the metallization surface, with severe surface degradation occurred after 3

min at 325°C or after 90 s at 350°C. Figure **6.8** is an SEM micrograph of the surface of a contact annealed for 3 min at 325°C. According to EDX in the SEM, the surface agglomerations consist mainly of In and Au, indicating the failure of the WSi₂ barrier in the same manner as the W and Pt barrier. The inability of the barrier to suppress elemental outdiffusion limits the use of such a contact when device processing at these temperatures is required. Is may also signal poor long term stability during operation at more modest temperatures.



Figure **6.8**: SEM micrograph of Pd₃In₇/WSi₂/Au (20/100/50 nm) contact annealed at 325°C for 3 min. Severe surface degradation has occurred as a result of the WSi₂ barrier failure.

A WSiN diffusion barrier was next investigated. The WSiN barrier was reactively sputtered using a WSi₂ target and a 15% N₂/Ar mixture. By incorporating nitrogen into the barrier, it may be possible to form an amorphous barrier and "stuff" any fast diffusion paths, thus reducing the diffusion of elements across the barrier. [115][116][117][118] Adding nitrogen to the barrier, however, results in an increase in the metal

resistivity occurs.[117] Two metallizations were studied: $Pd_3In_7/WSiN/Au$ (20/100/50 nm) and $Pd_3In_7/WSiN/Au$ (20/100/200 nm). The increase in the Au thickness was to compare the effect of the metal sheet resistance on contact measurements. During the calculation of ρ_c it is assumed that the resistance due to the metal film is negligible. If this condition is not met, the measured specific contact resistance will be artificially high.[77]

Contacts utilizing WSiN and 50 nm of Au achieved a ρ_c of 3.1 (± 0.3) x 10⁻⁶ Ω -cm² when annealed at 350 °C for 30 s, comparable to the WSi₂ contacts. However, these contacts exhibit no change in surface morphology throughout all annealing times and temperatures tested, indicating that the addition of nitrogen successfully retards elemental outdiffusion. Figure 6.9 is a graphical representation of the ρ_c as a function of time and temperature for several different temperatures. Degradation of contact annealed at 375 °C was immediate; however, those annealed at 325 and 350 °C stabilized within 2 min at 3.6 x 10⁻⁶ Ω -cm² and 4.4 x 10⁻⁶ Ω -cm² respectively. As noted before, surface morphology remained smooth throughout the annealing process. Figure 6.10 is an SEM micrograph of a sample annealed for 5 min at 350 °C. Samples annealed at 325 °C also exhibited no degradation in surface morphology.



Figure 6.9: Specific contact resistance of the $Pd_3In_7/WSiN/Au$ (20/100/50 nm) contact as a function of time and temperature.



Figure 6.10: Scanning electron micrograph of a Pd₃In₇/WSiN/Au contact annealed for 5 min at 350 °C. The metallization surface remains smooth with no indication of degradation.

To test the effect of metal sheet resistance on ρ_c , the Pd₃In₇/WSiN/Au contacts were next examined with a thick Au overlayer. Figure 6.11 illustrates the optimum ρ_c as a function of temperature for temperatures between 260 °C and 375 °C. Ohmic behavior of the contacts was achieved at temperatures as low as 260 °C for 1 min and as high as 375 °C for 30 s. The specific contact resistance of samples annealed at 260 °C and 375 °C are 5.4 (± 0.2) x $10^{-6} \Omega$ -cm² and 3.7 (± 0.2) x $10^{-6} \Omega$ cm², respectively. Contacts achieved an optimum specific contact resistance of 1.8 (± 0.2) x $10^{-6} \Omega$ -cm² when annealed at 325 °C for 1 min (average of 4 samples) and 1.8 (\pm 0.1) x 10⁻⁶ Ω -cm² when annealed at 350 °C for 30 s (average of 3 samples). The contacts maintained their initial values to within 5 x $10^{-7} \Omega$ -cm² for a minimum of 10 min at temperature, indicating that they are quite stable for short annealing times at elevated temperatures. The metallization surface exhibited a smooth, lustrous gold color throughout the annealing process, suggesting that the WSiN diffusion barrier prevented outdiffusion of In.



Figure 6.11: Optimum specific contact resistance as a function of annealing temperature for the $Pd_3In_7/WSiN/Au$ (20/100/200 nm) contacts. The minimum ρ_c was achieved when contacts were annealed at 325°C for 1 min or 350°C for 30 s.

Contacts utilizing WSiN as the diffusion barrier and 200 nm of Au achieved ρ_c values as low as evaporated Pd/In/Pd/Pt/Au contacts, which is half the resistance of the Pd₃In₇/WSiN/Au contacts using only 50 nm of Au. A decrease in ρ_c as a result of the increased Au thickness indicates that the metal sheet resistance plays an important role in the ρ_c measurements in this study, and a thick Au overlayer is required to minimize the contact resistance and measure the actual ρ_c .

The effect of pre-metallization surface treatment was also tested on the $Pd_3In_7/WSiN/Au$ (20/100/200 nm) contacts. Similar to the indepth study described in Ch. 7 for the evaporated Pd/In/Pd/Pt/Au contacts, contacts that utilized the conventional surface treatment of 18.5 % HCl for 30 s followed by a DI rinse exhibited contact resistance values higher than those prepared with a dilute sulfide rinse following the HCl. Three samples were tested, and it was found that the conventional surface treatment yields ρ_c values of 4.0 (± 0.5) x 10⁻⁶ Ω -cm² and 3.1 (± 0.4) x 10⁻⁶ Ω -cm² when contacts are annealed at 325 °C for 60 s and 350 °C for 30 s, respectively. This is compared to 1.8 x 10⁻⁶ Ω -cm² for samples annealed under the same conditions, but utilizing the dilute sulfide rinse. The decrease in ρ_c is attributed to the reduction of any interfacial dielectric layer at the M/S interface, as described in detail later in Ch.7.

Next, materials characterization was conducted on the Pd₃In₇/WSiN/Au (20/100/50 nm) metallization. The 200 nm of Au was unnecessary since the excess Au was simply to reduce the metal sheet resistance and should have no effect on the M/S interfacial reactions. Analysis was performed on samples prior to annealing as well as samples annealed for 1 min at 325 °C. As-deposited contacts exhibit no detectable reaction at the M/S interface, as indicated in Fig. **6.12 (a)**. Analysis via EDX (Fig. **6.12(b)**), along with TEM micrographs, indicates no intermixing between the GaSb substrate and Pd₃In₇ layer. When analyzing EDX data, it should be noted that in Fig. **6.12(b)** the "zero" line for Ga and Sb falls higher than the other elements. This is due to peak overlap of Ga with W and Au, and Sb with In. As a result, the increased signal for Ga and Sb within the WSiN layer in Fig. **6.12(b)** is considered to be noise. It should also be noted that Si is not presented in any EDX analysis as it falls exactly on the W–M energy line and can not be deconvoluted.



Figure 6.12: TEM micrograph (a) of an as-deposited Pd₃In₇/WSiN/Au (20/100/50nm) metallization on GaSb. EDX analysis (b) of the M/S interface indicates no interdiffusion of the Pd₃In₇ and GaSb.

Annealing contacts at 325°C for 1 min results in the lowest achievable ρ_c for the WSiN sputtered contacts. As a result, samples that were annealed at 325°C for 1 min were subsequently analyzed. According to TEM, the reaction that takes place is not completely uniform, however it is much more shallow than any other reported contacts to GaSb with comparably low ρ_c values. [93] [94] [103] There are two types of regions that form during annealing, both of which produce a quaternary Pd-In-Ga-Sb phase containing approximately the same composition regardless of reaction morphology. The first type of region is where the reaction is ultra-shallow (< 5 nm). In the second region, hemi-spherical grains ranging in depth up to approximately 25 nm are found. Figure 6.13(a) and (b) illustrate the two types of regions. The majority of the reacted region consists of ultra-shallow elemental interdiffusion, with the deeper reacted regions occurring every few hundred nanometers. Figure 6.14 is an EDX line scan across the metallization stack from Au to GaSb, the scan includes a large hemi-spherical reacted region grain at the M/S interface, and it can be seen that the Pd and In taper off much slower than in the asdeposited case presented in Fig. 6.12(b). The In and Pd have reacted with the GaSb substrate to form a layer with approximately the same In:Pd ratio as they are found in the metallization layer (7:3). Again, it should be noted that the increase in Ga signal within the Au layer in Fig. 6.14 is a result of peak overlap between the Ga-K and Au-L lines. Additional EDX line scans of samples annealed at 325 °C for 1 min can be found in Appendix B



Figure 6.13: Pd₃In₇/WSiN/Au (20/100/50nm) contacts annealed at 325°C for 1 min. The majority of the RR consists of ultra shallow reactions (a) with other regions exhibiting "hemi-spherical" grains (b), all reacted regions contain Pd, In, Ga, and Sb.



Figure 6.14: Energy dispersive x-ray line scan of the Pd₃In₇/WSiN/Au (20/100/50nm) metallization annealed at 325°C for 1 min.

To verify the thermal stability of contacts utilizing WSiN as the diffusion barrier, contacts were next annealed for 1 min at 325 °C in flowing N₂ to produce the low resistance, and subsequently aged in an evacuated quartz tube at 250 °C for up to 400 h. Two samples were annealed and aged at 250 °C to verify reproducibility. Figure **6.16** illustrates ρ_c as a function of aging time for both samples tested. Fifteen hours of aging at 250°C results in an increase in specific contact resistance of approximately 1.5 times from an average of $\cong 1.5 \times 10^{-6} \Omega$ -cm² to 2 x 10⁻⁶ Ω -cm². As seen in Fig. **6.15**, TEM analysis indicates that the reaction region is essentially identical to samples annealed at 325 °C
for 1 min. There appears to be an increase in density of the semihemispherical reacted regions; however, the depth of reaction remains less than 30 nm, with the majority of the interface only reacting a few nanometers. The M/S interface is not as distinct compared to previous samples, indicating that the reaction has proceeded somewhat further. EDX indicates that the Pd-In layer is uniform with respect to Pd, In, Ga, and Sb content, with no major changes in elements ratios occurring across a one micron scan that included regions with and without the RR grains. Additional EDX line scans of samples aged for 15 h can be found in Appendix B. Each scan verifies the stability of WSiN as a diffusion barrier as well as the formation of Pd-In-Ga-Sb at the M/S interface.





The slight increase in resistance may be due to degradation of the electrical properties of the WSiN barrier via the incorporation of small amount of oxygen. The barrier remains impregnable at 15 h, indicating that this contact meets all expectations for a thermally stable contact. The extent of reaction after 15 h at the M/S interface is also minimal, indicating that even after accelerated aging the contact remains shallow.

Contacts utilizing WSiN as the diffusion barrier exhibit low resistances and excellent thermal stability. This is evident in Fig. 6.16, with an increase in ρ_c of only 2.5 times after 100 h to an average $\cong 3.6 \text{ x}$ $10^{-6} \ \Omega - \text{cm}^2$. After 300 h aging, the specific contact resistance increased by a factor of 4 to an average of 5.9 x $10^{-6} \ \Omega - \text{cm}^2$. Contacts were subsequently aged an additional 100 h, which resulted in an increase in ρ_c to an average $\cong 7.2 \times 10^{-6} \ \Omega - \text{cm}^2$. This increase was also accompanied by a degradation of the surface morphology with part of the surface changing from gold to silver in one sample. This indicated a failure of the diffusion barrier and subsequent outdiffusion of elements to the surface.



Figure 6.16: Specific contact resistance as a function of annealing time for Pd₃In₇/WSiN/Au (20/100/200 nm) contacts aged at 250 °C. Contacts exhibit excellent thermal stability.

Materials characterization was performed on contacts aged for 300 and 400 h to identify the failure mechanism. Initially AES was performed on the contacts. According to AES, the contact that exhibited a degradation of surface morphology contained Ga and Sb at the contact surface where the surface color changed. In the remaining part of he sample; however, the barrier exhibited excellent thermal stability and oxidation resistance. Figure **6.17(a)** and **(b)** are the AES depth profiles of these regions of the contacts annealed at 250 °C for 300 and 400 h, respectively. Similar to contacts annealed at 325 °C for 1 min and contacts aged for 15 h, AES indicates that the reaction region includes Ga and Sb, and In and Pd in approximately the same ratio of that found within the metal layer itself. There are minor differences between the depth profiles, and negligible oxygen was detected within the barrier. Samples aged for 400 h exhibit increased interdiffusion of the Pd₃In₇ and GaSb compared to samples annealed for 300 h; however, the layered structure remained intact.



Figure 6.17: Auger depth profiles of $Pd_3In_7/WSiN/Au$ (20/100/50 nm) contacts aged at (a) 300 h and (b) 400 h.

To study the interface morphology of the aged samples TEM was next employed to study samples that were aged for 300 h. Figure **6.18** is a TEM micrograph of the contact following aging. The majority of the interface remains ultra-shallow even after aging at 250°C for 300 h. However, in some locations void formation has occurred within the Pd₃In₇ layer, which is accompanied by rounded protrusions of the metal into the semiconductor substrate, confirming diffusion of elements across the M/S interface. According to nanobeam diffraction, the Pd₃In₇ layer is polycrystalline, and combining with AES data, incorporates Pd, Ga, Sb, and In. This is similar to the reacted regions previously encountered for the pre-alloyed contacts. The resultant void formation and elemental outdiffusion in parts of the contacts may cause the observed increase in ρ_c .



Figure **6.18**: TEM micrograph of a Pd₃In₇/WSiN/Au (20/100/200) contact annealed at 325°C for 1 min and subsequently aged for 300 h in an evacuated quartz ampoule at 250°C.

Contacts that utilize WSiN as the diffusion barrier exhibit ρ_c values comparable to the lowest achievable values reported in the literature for contacts to n-GaSb.[93][94] However, there are three noteworthy

achievements in this study compared to other contacts that report comparable resistance values. First thermal stability of the Pd₃In₇/WSiN/Au (20/100/200) contact has been verified for longer times than any other reported contact. Only one other report takes into account the long term thermal stability of a contact to n-GaSb. Yang *et al.*[93] report a Pd/Te/Pd/In/Au contact that reaches a specific contact resistance less than $10^{-6} \Omega$ -cm², and remains low even after aging contacts at 200 °C for 37 h. Since less severe aging conditions were reported by Yang *et al.*[93] it is difficult to make a more direct comparison of the contacts.

Second, most contacts that achieve ρ_c values $\cong 5 \ge 10^{-6} \ \Omega - cm^2$ or lower have a narrow temperature range over which the minimal ρ_c can be accomplished. Outside this temperature range, an increase in ρ_c of an order of magnitude is reported.[94][99] Vogt *et al.*[99] report a Pd/Ge/Au/Pt/Au metallization with a specific contact resistance of 4.9 x $10^{-6} \ \Omega - cm^2$. However, a deviation of 50 °C above 300 °C leads to an order of magnitude increase in specific contact resistance, while lower annealing temperatures do not yield linear current-voltage curves. Ikossi *et al.* [94] report a specific contact resistance of 1.4 $\ge 10^{-6} \ \Omega - cm^2$ after annealing at 350 °C, but deviations in annealing temperature of 25 °C lead to an increase in specific contact provides ρ_c values < 6 $\ge 10^{-6} \ \Omega - cm^2$ over the very wide temperature range of 260 °C - 375 °C without degradation for up to 10 min annealing.

The third improvement over previously reported contacts to n-GaSb is a decreased reaction depth, resulting in less semiconductor consumption. Previously reported contacts were able to accomplish reaction depths as shallow as approximately 150 nm, [102][103] comparable to the evaporated Pd/In/Pd/Pt/Au contacts. The Pd/Te/Pd/In/Au contact reported by Yang *et al.* [93] is a very lowresistance contact with good thermal stability. However, this contact exhibits indium agglomerations one micron in size or larger on the metallization surface prior to annealing, and after annealing the contact at 250 °C for 45 min, the reaction depth of the contact is approximately 150 - 200 nm. It also appears, from the reported SEM micrographs, that the film has partially delaminated from the GaSb substrate.[93] Our Pd₃In₇/WSiN/Au contact exhibits reaction regions that penetrate no further than 30 nm into the semiconductor even after 300 h of aging at 250 °C, with the majority of the reaction being confined to approximately 5 nm. There also appears to be no delaminating of the metal overlayer. This is a reduction in reaction depth of at least 5 times.

The improved reaction morphology and thermal stability of this contact may be a result of pre-alloying the initial Pd₃In₇ layer. Pd is known to be reactive when in contact with GaSb,[42] even at room temperature;[99] Therefore, it is reasonable to hypothesize that contacts utilizing Pd as the initial layer of a multilayered contact could exhibit reaction upon deposition of the metal layers. This initial reaction, prior to annealing, may lead to reduced stability of the M/S interface, increasing the possibility for a more severe reaction to occur during annealing. We have shown that pre-alloying the Pd and In, results in no reaction at the M/S interface prior to annealing and only shallow reactions with annealing. The two layers are now more thermodynamically stable when in contact with each other. When considering the reaction: $Pd_3In_7 + GaSb \rightarrow Pd_3Ga_7$ + InSb, the free energy of reaction is approximately -15 kJ/mol.[43] This is in comparison to much more negative values for Pd-Ga and Pd-Sb compounds that range from approximately -40 kJ/mol to -80 kJ/mol.[**43**] As a result, it is likely that when in contact, the Pd₃In₇ metal will be less likely to react with the underlying GaSb substrate than a layered contact utilizing Pd as the initial layer.

6.3.2 Sputtered Pd₃In₇ Contacts Conclusions

Sputtered In-based contacts that utilize a pre-alloyed Pd₃In₇ layer as the ohmic metallization have been reported. Contacts utilizing W, Pt, and WSi₂ as the diffusion barrier exhibit a specific contact resistance 3 – $8 \times 10^{-6} \Omega$ -cm², but with limited thermal stability. As a result, a reactively sputtered WSiN barrier was tested. Contacts utilizing WSiN achieved average specific contact resistance values of $1.8 \times 10^{-6} \Omega$ -cm² when annealed for 1 min at 325 °C or 30 s at 350 °C. This value is comparable to the lowest achievable specific contact resistance values reported to date; however, the currently reported contacts exhibit improved thermal stability and reaction depth compared to all previously reported contacts.

6.4 Current Transport Mechanisms of Contacts to n-GaSb

Understanding current transport at a M/S interface is useful for identifying why low resistance contacts are achieved and how the resistance will vary when temperature or carrier concentration is varied. Understanding electron transport at the M/S interface of In-bearing contacts to n-GaSb may also help determine the role indium may play when attempting to achieve low resistance contacts. The following pages focus on identifying the current transport mechanism of contacts to n-GaSb as a function of temperature.

6.4.1 Temperature Dependence of the Specific Contact Resistance: A Theoretical Treatment

The concepts of current transport and specific contact resistance (ρ_c) were introduced in Ch. 2, where four mechanisms for current transport were discussed. Thermionic and field emission were subsequently used in the discussion of specific contact resistance as a function of doping density (Section 2.3). It is useful to present the equations for specific contact resistance again here. Specific contact resistance resistance as a result of thermionic emission (low carrier concentration or high temperatures) is expressed as: [67]

$$\rho_c = \frac{k}{qA^*T} e^{\frac{q\phi_b}{kT}}.$$
(6.3)

Specific contact resistance as a result of field emission (high carrier concentration or low temperatures) is given by: [67]

$$\rho_{c} = \left[\frac{A^{*}T\pi q}{kSin(\pi C_{1}kT)}\exp\left(\frac{-\phi_{B}}{E_{oo}}\right) - \frac{A^{*}q}{C_{1}k^{2}}\exp\left(-\left(\frac{\phi_{B}}{E_{oo}}\right) + (C_{1}\xi)\right)\right]^{-1}.$$
(6.4)

Finally, the specific contact resistance as a result of thermionic-field emission is written: [67]

$$\rho_{c} = \frac{k^{2} Cosh\left(\frac{E_{oo}}{kT}\right)}{qA^{*} \left[\pi q\left(\phi_{B} + \xi\right) E_{oo}\right]^{1/2}} \left[Coth\left(\frac{E_{oo}}{kT}\right) \right]^{1/2} \exp\left[\left(\frac{\left(\phi_{B} - \xi\right)}{E_{o}}\right) + \frac{\xi}{kT}\right].$$
(6.5)

The specific contact resistance due to thermionic emission of electrons over the barrier depends strongly on barrier height and temperature (Eq. 6.3). As the doping level is increased, a dependence on both temperature and doping concentration is developed (Eq. 6.5), but when the doping level is high enough, temperature plays only a minor role in determining the specific contact resistance (Eq. 6.4).

To identify which ρ_c equation is best suited to describe the specific contact resistance as a function of temperature and doping, researchers have identified various limits for which the field emission and thermionicfield emission equations apply.[121] Equation 6.4 describes ρ_c due to field emission and is valid if:[121]

$$1 - \frac{kT}{2E_{oo}} \ln\left(\frac{-4\phi_B}{\xi}\right) > kT\left(\sqrt{\frac{-1}{2E_{oo}\xi}}\right), \tag{6.6}$$

where ξ has been defined previously (Section 2.3) as $E_c - E_F$. Immediately one can see that the Fermi energy (E_F) must be greater than the conduction band (E_c) for field emission to be operative, otherwise the values inside the natural log and square root are no longer defined. Thermionic-field emission theory is valid under the following condition: [121]

$$\frac{\cosh^2\left(\frac{E_{oo}}{kT}\right)}{\sinh^3\left(\frac{E_{oo}}{kT}\right)} < \frac{2(\phi_B - \xi)}{3E_{oo}}$$
(6.7)

This equation yields a lower limit of carrier concentration where thermionic-field emission is the dominant transport mechanism. To identify carrier concentration levels necessary for a given transport mechanism, it is useful to identify the relationship between carrier concentration, impurity dopant concentration and the Fermi level in a semiconductor.

The carrier concentration (n) found in a semiconductor may not be the same as the impurity dopant concentration (N_D) of the semiconductor. The relationship between carrier concentration and impurity doping of the semiconductor is written as:[13]

$$N_{D} = \frac{n}{\left[1 - \frac{1}{1 + \frac{1}{2} \exp\left(\frac{E_{C} - E_{d} - E_{F}}{kT}\right)}\right]},$$
(6.8)

where E_d is the ionization energy of the impurity atom, which is dependent on the impurity atom and semiconductor in which the atom is placed (6 meV for Te in GaSb). The carrier concentration of an epitaxial layer can be experimentally determined using a Hall measurement.[79] From this measurement the impurity doping concentration can be calculated using Eq. 6.8. The value N_D is constant; it is not a function of temperature. The carrier concentration and Fermi level position are related according to the Fermi-Dirac integral:[122]

$$n = N_c \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\eta^{1/2}}{1 + \exp(\eta - \eta_c)} d\eta , \qquad (6.9)$$

where

$$N_c = 2 \left[\frac{m_e^* kT}{2\pi (h/2\pi)^2} \right]^{3/2},$$
 (6.10)

and is known as the effective density of states;

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$$\eta = \frac{E - E_c}{kT},\tag{6.11}$$

and

$$\eta_c = \frac{E_F - E_c}{kT}.$$
(6.12)

Even with simplifications, the integral contained in Eq. 6.9 can not be evaluated in closed form containing simple functions.[122] There have been, however, analytical approximations developed to describe the relationship between the Fermi energy and carrier concentration based on Eq. 6.9. A well accepted approximation is the Joyce-Dixon (JD) approximation:[123]

$$\eta_c = \frac{E_F - E_c}{kT} = \ln(n/N_c) + \frac{1}{\sqrt{8}} \frac{n}{N_c} - 4.9509 \times 10^{-3} \left(\frac{n}{N_c}\right)^2 + 1.48368 \times 10^{-4} \left(\frac{n}{N_c}\right)^3 - 4.42563 \times 10^{-6} \left(\frac{n}{N_c}\right)^4 \quad (6.13)$$

Equation 6.13 is valid for all negative values of η_c , but is only valid for positive values of η_c below about 5.[123] Figure 6.19 is a graphical illustration of the Fermi-Dirac integral and JD approximation as a function of carrier concentration for n-GaSb. The JD approximation underestimates $kT\eta_c$ (or $E_F - E_c$) in Eq. 6.13 above $n \cong 3 \ge 10^{18} \text{ cm}^{-3}$.



Figure 6.19: Comparison of the Fermi-Dirac integral and the Joyce-Dixon approximation of the Fermi-Dirac integral as a function of carrier concentration for n-GaSb.

Using the Joyce-Dixon approximation (Eq. 6.13), along with Eqs. 2.8, 6.6, 6.7, and 6.8, we are able to identify the carrier concentrations where field emission or thermionic-field emission may dominate. Figure 6.20 is a plot of E_F versus carrier concentration for GaSb at 300 K. Indicated on the plot are the regions where thermionic, thermionic-field, and field emission are valid according to Eqs. 6.6 and 6.7. According to Eq. 6.7, carrier concentrations above $\cong 4.5 \times 10^{17}$ cm⁻³ result in field emission being the dominant carrier transport mechanism for contacts to n-GaSb. The conduction band (E_c in Fig. 6.20) is fixed at 0.725 eV (E_g (GaSb) at 300 K = 0.725 eV) and the intrinsic Fermi energy is calculated according to:[122]

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$$E_{Fi} = \frac{E_g}{2} + \frac{3}{4} kT \ln\left(\frac{m_h^*}{m_e^*}\right).$$
 (6.14)



Figure **6.20**: Fermi level position as a function of carrier concentration for GaSb at 300 K according to the Joyce-Dixon approximation.

One way to experimentally identify which transport mechanism is responsible for low resistance values of ohmic contacts is to measure the specific contact resistance as a function of temperature. However, to model the temperature dependence of the specific contact resistance, one must have knowledge of how n, N_c, and η_c are affected by temperature. The temperature dependence of carrier concentration (n(T)) is directly related to η_c (= - ξ /kT). It is difficult to calculate the position of the Fermi level and carrier concentration simultaneously as a function of temperature because both are directly related to each other. However, researchers have experimentally measured n(T) for n(300) values $\cong 10^{18}$ cm⁻³. [**31**][**125**] Cederberg and Biefeld [**125**] have recently shown that the carrier concentration for Te-doped n-GaSb may be expressed as:[**125**]

$$n(T) = 3 \times 10^{17} * Ln(T) + C, \qquad (6.15)$$

where C is a constant, chosen such that the carrier concentration calculated at 300 K matches the experimentally determined value. Figure **6.21** is a graphical representation of n(T) from Eq. **6.15**.



Figure 6.21: Carrier concentration of GaSb as a function of temperature, values are based on Eq. 6.15 (with extrapolation from 50 - 15 K).

All the temperature-dependent values (n, N_c, and η_c) have now been discussed, and it is possible to use the Joyce-Dixon approximation (Eq. 6.13) to identify the location of the Fermi level with respect to the conduction band edge as a function of temperature. Figure 6.22 is a graphical illustration of the Fermi level position with respect to the conduction band (kT η_c) for n-GaSb as a function of temperature. The

values along the y-axis, as taken from Eq. 6.12, correspond to $E_F - E_c$. The carrier concentration was chosen to be 1 x 10¹⁸ cm⁻³, similar to Refs. [31] and [125].



Figure **6.22**: Fermi level position with respect to the conduction band edge for n-GaSb as a function of temperature.

Understanding the effect of temperature on the Fermi level position allows for the calculation of the specific contact resistance as a function of doping and temperature. Most low resistance ohmic contacts to n-GaSb are on epitaxial layers with carrier concentrations of 9×10^{17} cm⁻³ or greater.[93][94][99] As a result, the low specific contact resistance for such contacts is expected to be the result of field emission of electrons through the barrier (Fig. 6.20). Using Eq. 6.4 and each of the temperature dependent variables associated with this equation, we are able to simulate how the specific contact resistance will behave as a function of temperature for a given carrier concentration or barrier height. Figure 6.23(a) illustrates the temperature dependence of the specific contact resistance ($\rho_c(T)$) from 300 K to 75 K for a fixed barrier height (0.7 eV). Figure **6.23(b)** illustrates how the barrier height affects the contact resistance for a given carrier concentration. It is clear that both the carrier concentration and barrier height at 300 K affect the value of ρ_c at 300 K, but not its temperature dependence for heavily doped semiconductors. Lower barrier heights and higher carrier concentrations lead to lower $\rho_c(300)$ values. The temperature dependence of ρ_c is related to n(T). When n(T) falls off faster as temperature is decreased, ρ_c increases at a greater rate over the same temperature range. According to Eq. **6.4**, and based on the ability to correctly model carrier concentration as a function of temperature, the specific contact resistance should increase approximately 1.5 – 2 times for 8 x $10^{17} \le n(300) \le 2 \times 10^{18} \text{ cm}^{-3}$ as the temperature is decreased from 300 K to 77 K.



Figure 6.23: Specific contact resistance as a function of temperature for (a) various carrier concentrations at a fixed Φ_B (0.7eV) and (b) for various Φ_B values at a fixed carrier concentration (1 x 10¹⁸ cm⁻³). (Simulation)

6.4.2 Modeling Experimental Results of Temperature Dependence

All contacts presented in this thesis until now have been prepared on n-GaSb with n \cong 2 x 10¹⁸ cm⁻³. As a result, based on Fig. **6.20**, field emission is expected to be the dominant mechanism for current transport at the M/S interface. To test this expectation, several samples were fabricated and the specific contact resistance was measured at 300 K and 77 K. Three sets of samples were prepared and included Pd/In/Pd/Pt/Au (4/40.3/5.7/50/100), Pd/WSiN/Au (50/100/200) and Pd₃In₇/WSiN/Au (20/100/200).

The purpose of fabricating contacts that included only Pd was two fold. First, to identify whether In plays role in the lowering ρ_c values by reducing the barrier at the M/S interface, and second, to find out if $\rho_c(T)$ is contact independent. Samples containing WSiN were also tested on n-GaSb epitaxial layers with $n \cong 1 \ge 10^{18}$ cm⁻³ to investigate how n(300) influences $\rho_c(T)$ experimentally. All contacts were prepared using the previously described procedure (Section **3.3.1**), and measurement of contacts at 77 K was accomplished by submersing samples in liquid nitrogen during each measurement. The Pd/In/Pd/Pt/Au samples were annealed at 125 °C for 60 min followed by 350 °C for 10 min. Sputtered contacts containing Pd₃In₇ were annealed for 30 s at 350 °C, and contacts containing Pd without In were annealed for 10 min at 350 °C. The specific contact resistance values at 300 K and 77 K for all metallizations and epitaxial layers are listed in Table **6–4**.

		$\rho_{\rm c}(\ {\rm x}\ 10^{-6}\ \Omega-{\rm cm}^2)$		
Sample	n (cm ⁻³)	300 K	77 K	$\rho_{\rm c}(77)/\rho_{\rm c}(300)$
Pd/In/Pd/Pt/Au	$2 \ge 10^{18}$	$2.2 (\pm 0.3)$	$2.7 (\pm 0.3)$	$1.2 (\pm 0.3)$
(4/40.3/5.7/50/100 nm)				
Pd ₃ In ₇ /WSiN/Au	$2 \ge 10^{18}$	$1.7 (\pm 0.3)$	$2.3 (\pm 0.4)$	$1.4 (\pm 0.5)$
(20/100/200 nm)	$1 \ge 10^{18}$	$7.5 (\pm 0.4)$	13 (± 1.2)	$1.7 (\pm 0.3)$
Pd/WSiN/Au	2×10^{18}	36(+03)	57(+05)	$1.6(\pm 0.3)$
	2×10^{18}	$0.0(\pm 0.0)$	$0.7 (\pm 0.0)$	$1.0(\pm 0.0)$
(50/100/200 nm)	$1 \ge 10^{10}$	$14(\pm 1.1)$	21 (± 1.4)	$1.5(\pm 0.3)$

Table 6-4: Specific contact resistance values of Pd/WSiN/Au and Pd₃In₇/WSiN/Au contacts as a function of temperature.

Evident from Table **6-4** is that the resistance values measured for the Pd₃In₇ contacts (sputtered and evaporated) are approximately 2 times lower than contacts containing Pd without In, regardless of the carrier concentration tested, indicating that In does reduce the barrier at the M/S interface. All contacts, however, exhibit approximately the same ρ_c temperature dependence regardless of metallization. Since all tested contacts exhibit the same $\rho_c(T)$ on both n-GaSb epitaxial layers, the remainder of the discussion will focus on the ρ_c results measured for the Pd₃In₇/WSiN/Au contacts with n = 2 x 10¹⁸ cm⁻³.

Initial ρ_c modeling was based on $n(300) = 2 \times 10^{18} \text{ cm}^{-3} (N_D(300) = 8.8 \times 10^{20} \text{ cm}^{-3}$ from Eq. **6.8**), with the best fit resulting when a barrier height of 3.3 eV was used. This value is much larger than the band gap of GaSb (0.725 eV) and is unrealistic when compared to practical Schottky contacts to n-GaSb. Researchers report Schottky contacts to n-GaSb exhibit barrier heights of $\cong 0.5 - 0.7 \text{ eV}, [10][11][12][126][127]$ with the reported values being relatively independent of the deposited metal. The true barrier height for each sample tested is not known, and reported

values for n(300) on the tested epitaxial layers may not be as high as initially expected. Based on theoretical calculations presented in the previous section, for a given carrier concentration, the barrier height may be adjusted to yield $\rho_c(300)$ within experimental error of measured values. This results in a range of Φ_B and n(300) values that would yield $\rho_c(300)$ values similar to those experimentally measured. Figure 6.24 is a graphical representation of various barrier height and carrier concentration combinations that yield $\rho_c(300)$ values within experimental error of the measured $\rho_c(300)$ values reported in Table 6-4 (w/ n = 2 x 10^{18} cm⁻³). Also included in Fig. 6.24 are the calculated values for N_D from Eq. 6.8. Arrows in Fig. 6.24 indicate which y-axis each plot is associated. The barrier height for a given n(300) value for the Pd/In/Pd/Pt/Au contact falls between the values presented in Fig. 6.24 for the Pd/WSiN/Au and Pd₃In₇/WSiN/Au contacts.



Figure 6.24: Combinations of carrier concentration and barrier heights that yield $\rho_c(300)$ values approximately equal to the experimentally determined values for contacts to n-GaSb with the reported n(300) = 2 x 10^{18} cm⁻³. N_D is also included.

Given the unrealistic carrier concentration-barrier height combination when $n(300) = 2 \ge 10^{18} \text{ cm}^{-3}$, the carrier concentration was subsequently fixed for the purpose of simulation at $9 \ge 10^{17} \text{ cm}^{-3}$ (N_D = 3.9 $\ge 10^{19} \text{ cm}^{-3}$), and the barrier height was varied from 0.55 eV to 0.725 eV for illustrative purposes (E_g for GaSb = 0.725 eV). Figure **6.25** is a graphical illustration of the modeled $\rho_c(T)$ compared to the experimentally determined values for contacts to n-GaSb presented in Table **6-4**. Figure **6.25** contains all three measured contacts enclosed in a shaded region. The shaded region encompases all possible barrier heights at $n(300) = 9 \ge 10^{17} \text{ cm}^{-3}$ that yield $\rho_c(T)$ values comparable to the experimentally measured values. The limits of the shaded region are 0.55 eV and 0.725 eV. Both sputtered contacts exhibit very similar $\rho_c(T)$ values to the modeled data. The Pd/In/Pd/Pt/Au contact appears less dependent on temperature; however, when taking into account experimental error the temperature dependence variation is similar to the sputtered contacts.



Figure 6.25: Comparison of experimentally determined and calculated $\rho_c(T)$ values for ohmic contacts to n-GaSb at 300 K and 77 K. The shaded region illustrates the range of Φ_B possible for $n(300) = 9 \times 10^{17} \text{ cm}^{-3}$ that would yield $\rho_c(T)$ values similar to the experimentally determined values.

There are several features of importance that can be deduced from Fig. 6.25. First, it is clear that the reported n(T) yields a good fit to the experimentally determined $\rho_c(T)$. Second, while the value of $\rho_c(300)$ is lower for the In-bearing contacts, the temperature dependence of ρ_c

appears to be independent of the contact metallization for heavily doped n-GaSb in this thesis work. The same is true for contacts to less heavily doped epitaxial layers such as those reported in Table 6-4 (n = 1 x 10¹⁸ cm⁻³). Lastly, it is clear from Table 6-4 and Fig. 6.25, that the presence of indium does reduce the barrier to electron transport at the M/S interface. This reduction is \cong 100 meV and results in a lower $\rho_c(300)$ value. The Pd/In/Pd/Pt/Au contact was shown to form $In_xGa_{1-x}Sb$ at the M/S interface. The formation of $In_xGa_{1-x}Sb$, however, is not responsible for the reduced barrier height of the sputtered contacts, since $In_xGa_{1-x}Sb$ does not form. It is not known if the phase formed after annealing the sputtered contacts is metallic or semiconducting. The concentration of Pd in this phase is low; however, and the similar ρ_c values compared to contacts that form $In_xGa_{1-x}Sb$ suggest that this phase might have a similar band gap.

While it is generally not good practice to limit a fit to only a few data points, in this case useful conclusions can be drawn. Several fits were attempted using both the thermionic and thermionic-field emission equations. The attempted fits using the thermionic-field emission equation resulted in an increase in ρ_c by at least three orders of magnitude (more for thermionic emission), while the field emission equations are quite close to the observed values. A comparison of $\rho_c(T)$ based on thermionic, thermionic-field, and field emission is illustrated in Fig. **6.26**. The carrier concentration and barrier heights were adjusted for each fit such that $\rho_c(300)$ matched the experimentally determined value for the Pd₃In₇/WSiN/Au contacts. From Fig. **6.26**, it is clear that thermionic and thermionic-field emission exhibit temperature dependencies well outside the observed values, allowing a 2-point fit with the field emission equation to still be of value.



Figure 6.26: Comparison of the specific contact resistance as a function of temperature for thermionic (TE), thermionic-field (TFE), and field emission (FE). Both TE and TFE exhibit strong temperature dependencies.

6.4.3 Current Transport Conclusions

It has been shown here that field emission is the dominant current transport mechanism for contacts to heavily doped (n > 7 x10¹⁷cm⁻³) n– GaSb. The temperature dependence of three contacts on two different epitaxial n–GaSb layers has been compared to calculated values of $\rho_c(T)$. The barrier height and n(300) affect only the absolute value of ρ_c for heavily doped n–GaSb epitaxial layers, and do not appear to affect how ρ_c will behave as a function of temperature when field emission is the dominant current transport mechanism. Indium has also been shown to reduce the barrier at the M/S interface by approximately 100 meV, allowing for $\rho_c(300)$ values 2 times lower than when In is not present.

6.5 Contact Formation Mechanisms and the Influence of Indium on Contacts to n-GaSb

Two mechanisms for ohmic contact formation were set forth in **2.4** as possible explanations for the ohmic behavior of the In-based contacts previously discussed. These mechanisms included the solid phase regrowth mechanism and the exchange mechanism. In the following pages the relationship of each mechanism with In-based ohmic contacts to n-GaSb in this study will be discussed.

The regrowth mechanism may be responsible for ohmic contact formation if Pd forms a ternary phase with GaSb at lower temperatures, followed by a regrowth of the GaSb substrate with incorporated In at elevated temperatures. Based on work presented in Ch. 4, this mechanism is a viable explanation for Pd-bearing contacts with Pd as the first layer. The Pd/GaSb thin film work confirmed that Pd reacts with GaSb at room temperature, which is the first requirement for regrowth. To check if indeed the regrowth mechanism was responsible, sputtered contacts were next prepared using a pre-alloyed Pd₃In₇ target. Pre-alloying the Pd and In precludes the formation of a Pd_xGaSb ternary phase necessary for the regrowth mechanism. Thus if a pre-alloyed Pd-In ohmic contact with similar specific contact resistances and phase formation were achieved, the regrowth mechanism might be excluded as a possibility. A Pd₃In₇/WSiN/Au (20/100/200 nm) contact provided a specific contact resistance $\cong 1.8 \times 10^{-6} \Omega$ -cm² (n $\cong 2 \times 10^{18}$ cm⁻³). This value is comparable to the best achievable resistances for evaporated Pd/In/Pd/Pt/Au contacts to the same n-GaSb epitaxial layer. Based on ρ_c values alone, the regrowth mechanism would not appear to be nessasary for low resistance contacts. However, the regrowth mechanism can not be excluded in the Pd/In/Pd/Pt/Au contacts because the formation of In_xGa_{1-x}Sb did not occur in the pre-alloyed Pd₃In₇, contacts and thus they can not be directly compared to the layered Pd/In/Pd/Pt/Au contacts. While it is impossible for the sputtered contact to participate in regrowth, the layered contacts may still exhibit regrowth based on phase formation at the M/S interface (Pd_yGa_{1-y} and In_xGa_{1-x}Sb) presented earlier in this thesis work (Fig. **6.5**).

The exchange mechanism is another possible mechanism for indium incorporation into the GaSb.[73] As discussed earlier, the exchange mechanism is simply an exchange of In and Ga at the M/S interface without the formation of any new phases off of the $In_xGa_{1-x}Sb$ or $Pd_yIn_xGa_{1-x}$ solid solution lines. One must take into account phase formation at the M/S interface of pre-alloyed contacts presented in this study to identify whether the exchange mechanism is possible. It is useful to review Figs. 6.13, 6.14, and 6.17. According to AES and EDX, phase formation at the M/S interface includes the presence of quaternary Pd-In-Ga-Sb phases that consume the semiconductor. These phases are present following the ideal annealing conditions, as well as after aging the contacts at 250 °C. As a result, it appears that the exchange mechanism does not properly describe the incorporation on indium into the GaSb epitaxial layer because $In_xGa_{1-x}Sb$ is not formed in the pre-alloyed contacts following heat treatment. Comprehensively studying layered and pre-alloyed contacts suggests the formation of In-bearing ohmic contacts to n-GaSb can not be simply explained by the regrowth or exchange mechanism suggested in the literature for In-bearing contacts to GaAs. Instead, the actual mechanism for indium incorporation into GaSb appears to be dependent on the arrangement of layers in the contact before annealing. Reaction products that appear to be responsible for ohmic behavior vary between evaporated and sputtered contacts. The presence of indium as part of a pre-alloyed contact, however, does play an important role in improving contacts to n-GaSb. This role is two-fold. Indium has been shown to reduce the barrier at the M/S interface, thus reducing ρ_c . The reduction in ρ_c may not be dramatic (> 10x), but combining this with the increased morphological stability of the contact yields an optimized In-bearing contact that provides the best combination of low resistance and thermal stability reported to date.

Chapter 7

Sulfur Passivation of n-GaSb

GaSb has a very reactive surface, and the native oxide on GaSb grows faster and thicker than on GaAs and GaP. [127] As a result, treatments must be employed to minimize the surface oxides prior to metallization or other processing steps, such as the deposition of a dielectric or growth of an epitaxial layer on a GaSb substrate. [128] Either acid treatments to minimize the oxide thickness [9] or surface passivation techniques may be used. To reduce device leakage currents and improve surface stability, passivation of the GaSb surface using sulfur has generated much interest in the last decade.[1] Studies have shown that sulfur passivation significantly decreases surface state density, [129][130] increases photoluminescence, [129][130][131] and improves the thermal stability of Schottky contacts. [132] When passivating GaSb-based structures with shallow active regions, one must also be aware that sulfur passivation etches GaSb. [128] [133] [134] Na₂S-based passivation treatments result in non-uniform etch rates, while $(NH_4)_2S$ -based solutions etch n- and p-GaSb at a steady rate. [133]

It has been reported that a dielectric layer forms at the GaSb surface;[128][130][133] however, the composition, structure, and thickness of this layer have not been conclusively determined. Dutta *et al.*[130] attribute a reduction of the surface state density following passivation, evident from an increase in photoluminescence intensity, to the formation of a thin sulfur-based dielectric layer at the GaSb surface. Papis *et al.*[128][133] detect and characterize a superficial film after passivation, fitting ellipsometric data to various models that include one or two of the following: an oxide layer, a Cauchy material [128] [133] (presumably a sulfide), a mixed layer of oxide and Cauchy material, surface roughness, and interfacial roughness. (A Cauchy material typically consists of a compound containing sulfur) They conclude that layer thickness is dependent on concentration of the solution and duration of treatment, with higher concentration solutions leading to faster growth rates and thicker superficial layers. Liu et al.[9] used photoluminescence and x-ray photoelectron spectroscopy (XPS) to examine the effect of treating GaSb with a saturated aqueous Na₂S solution (0.186 g/ml). By deconvoluting the Ga 2p3 from XPS, they observed a dramatic reduction in Ga-O bonding along with the formation of Ga-S bonds at the surface. The Sb 4d spectra were also deconvoluted into Ga-Sb, Sb-O, Sb-Sb, and Sb-S bonds, with the aqueous sulfide treatment leaving the GaSb surface richer in Sb than Ga. In contrast, Lin *et al.*[135] examined the GaSb surface using XPS after an HCl etch and passivation of the GaSb surface using $(NH_4)_2S:H_2O$ (1:45) and (1:4), and they report that Sb_2S_5 and Ga_2O_3 are the major components of the surface layer. In the following discussion, the structure, thickness, and composition of surface layers formed during passivation with (NH₄)₂S is reported. The results are obtained using TEM, which provides information not available in previous reports. The influence of sulfur passivation on the resistance of an ohmic contact is also discussed.

7.1 Results and Discussion

Gallium antimonide wafer substrates were utilized for materials characterization studies of sulfur passivated samples. Samples for electrical measurements were prepared from the same epilayer described in Table 3–3. Samples were prepared using one of the surface treatments listed in listed in Table 3–3, and again in Table 7–1. Treatments 1 – 6 included a 21% (NH₄)₂S passivation for various times. Treatments 2, 4, and 6 also included a 30 s etch in 18.5 % HCl and DI water rinse. Treatment 7 excluded the rinse in DI water following the HCl etch and utilized a 2.1% (NH₄)₂S rinse instead. The samples were then promptly loaded into a vacuum chamber and pumped to a base pressure of 10^{-7} Torr, after which blanket layers of TaN (50 nm) or Pd/In/Pd (4/40.3/5.7 nm) films were deposited by sputtering or electron beam evaporation, respectively.

Treatment	Solution	Time (s)
1	21% (NH ₄) ₂ S	300
2	18.5% HCl	30
	DI H ₂ O	3 - 5
	21% (NH ₄) ₂ S	60
0		60
3	21% (NH ₄) ₂ S	60
4	18.5% HCl	30
	DI H ₂ O	3 - 5
5	21% (NH.) S	10
0	2170 (10114)25	10
6	18.5% HCl	30
	DI H ₂ O	3 - 5
	$21\% (NH_4)_2 S$	10
7	18.5% HCl	30
	$2.1\% (NH_4)_2S$	5

Table 7-1: GaSb surface treatments

Samples that included TaN as the metallization were studied both in the as-deposited state and following a 20 min anneal at 500 °C. TaN is expected to be stable when in contact with the passivated semiconductor and therefore is not expected to react with or consume any superficial layer that may form on the semiconductor surface during passivation. For this reason, a TaN layer was used to assist in the measurement of the superficial layer thickness via TEM. Samples that included Pd/In/Pd as the metallization were utilized to identify the effect of an interfacial layer on the reaction at the M/S interface. To test the effect of surface passivation on the resistance of the ohmic contacts, Pd/In/Pd/Pt/Au contacts were fabricated in the same fashion as described in Section **3.3.1**.

Initially the GaSb surface passivation consisted of Treatment 1 (5 min passivation) prior to the deposition of TaN. As seen in Fig. 7.1(a), a layer is evident between the TaN and GaSb. The layer is 13.6 (\pm 1.4) nm thick and is identified as an amorphous Ga-S compound via NBD and EDX. A typical EDX line scan, illustrated in Fig. 7.1(b), of the TaN/GaSb as-deposited sample indicates the presence of only Ga and S. The sulfide layer contains very little oxygen. This conclusion is based on EDX scans in the GaSb substrate region and sulfide region with no change in the integrated peak intensity for oxygen. The metal/sulfide and sulfide/GaSb interfaces are uniform to within 2 nm, indicating uniform etching and sulfide growth during passivation.



Figure 7.1: TEM micrograph of (a) GaSb passivated for 5 min in 21% (NH₄)₂S (Treatment 1) followed by deposition of TaN. The intervening layer is identified to be amorphous via NBD, and (b) EDX indicates the layer consists of Ga and S.

Additional samples with the TaN metallization were annealed for 20 min at 500 °C in an attempt to crystallize the sulfide layer for phase identification via NBD. Following the anneal, the sulfide layer remained intact; however, as shown in Fig. **7.2**, the TaN/sulfide and sulfide/GaSb interface roughened. The sulfide layer is now nano-crystalline, as determined by NBD, with three distinct rings corresponding to d-spacings of $3.5 (\pm 0.2)$ Å, $2.2 (\pm 0.1)$ Å, and $1.4 (\pm 0.1)$ Å. Unfortunately, it was not possible to identify the sulfur-based phase. Antimony precipitates were identified via EDX at the sulfide/GaSb interface as a result of reaction between the sulfide and GaSb, and voids (not shown) ranging from 7 - 18 nm wide and 3 - 8 nm thick were also observed at the sulfide/GaSb interface. As a result of this reaction, the sulfide has become enriched in Ga.



Figure 7.2: TEM micrograph of a TaN/sulfide/GaSb sample after a 20 min anneal at 500 °C. Precipitates of Sb are identified via EDX.
Initial experiments that included the Pd/In/Pd metallization involved passivating the semiconductor surface using Treatment 1. Figure 7.3 is a TEM micrograph of the passivated metal/semiconductor reaction as a result of annealing. Treatment 1 results in a thick Ga-S layer measuring 9 - 14 nm with an average thickness of 10 (\pm 1) nm following heat treatment at 350 °C for 10 min. Nano-beam diffraction indicates the layer is amorphous, similar to those samples involving TaN. From Fig. 7.3 it is apparent that the sulfide layer is stable when in contact with this reactive metal overlayer up to 350 °C for 10 min, and the presence of the thick sulfide layer completely prohibits reaction between the metal and GaSb.



Figure 7.3: TEM micrograph of Pd/In/Pd/sulfide/GaSb sample after anneal at 125 °C for 60 min followed by 350 °C for 10 min.

The presence of a thick dielectric layer, such as a native oxide or sulfide layer following passivation, is not desirable when fabricating ohmic contacts. The presence of such a layer could result in non-uniform reactions between the metallization and semiconductor and/or an increased contact resistance. To reduce the thickness of the sulfide layer and possibly promote uniform reaction between Pd/In/Pd and GaSb,

several different surface preparations were next tested. These treatments include shortened exposure times to 21% (NH₄)₂S. A conventional treatment with 18.5% HCl for 30 s and DI rinse (Treatment 4) was also performed as a control sample. The first preparation consisted of 30 s in 18.5% HCl and a DI water rinse, followed by 60 s in 21% $(NH_4)_2S$ (Treatment 2). As shown in Fig. 7.4(a) and Fig. 7.4(b), a 3 - 7 nm layer with occasional discontinuities or thin spots is observed between the annealed contact metallization and GaSb. According to NBD the layer is amorphous, and EDX indicates the presence of In, Ga, and S, along with some Sb. However, it should be noted that the primary Sb and secondary In peaks overlap. For this reason, the detection of Sb within the sulfide layer may be an artifact. As demonstrated in Fig. 7.4(B), reaction between the metal and semiconductor is greatly influenced by the presence of the sulfide layer, with reaction occurring primarily where the intervening layer thickness is at a minimum (≤ 1 nm) or missing. Samples prepared with Treatment 3 prior to the deposition of the Pd/In/Pd contact exhibit very similar characteristics to those described for Treatment 2. Thus, excluding the HCl etch prior to passivation with $(NH_4)_2S$ does not appear to influence the final sulfide layer characteristics when passivating for 60 s (Treatment 3).



Figure 7.4: Annealed Pd/In/Pd/GaSb contact prepared using surface Treatment 2 showing non-uniform reaction at (a) lower and (b) higher magnification.

The GaSb surface was also prepared simply using a conventional 18.5% HCl etch for 30 s followed by DI water rinse prior to deposition (Treatment 4) for comparison. As seen in Fig. **7.5**, Treatment 4 results in a thin, discontinuous oxide layer at the metal/semiconductor interface,

even after annealing at 125 °C for 60 min and 350 °C for 10 min. The oxide layer is non-uniform, with a thickness of 1 - 3 nm where it is present. Metal/semiconductor regions where the oxide is thicker react less severely than those with little to no oxide, indicating that the presence of even very thin (1 - 3 nm) oxide layers can retard or prohibit the reaction between the metal and semiconductor.



Figure **7.5**: Annealed Pd/In/Pd/GaSb contact prepared using a conventional HCl treatment (Treatment 4).

The presence of a sulfide or oxide layer proved to be an important factor influencing reactions between Pd/In/Pd and GaSb. Thus, efforts to reduce the thickness of the sulfide even further, while preventing the growth of an oxide, prompted the testing of three additional surface treatments. Passivating the GaSb surface with 21% (NH₄)₂S for 10 s without a prior HCl etch (Treatment 5) results in an inhomogeneous dielectric layer and reaction morphology. Figure **7.6(a)** is a typical example of the reaction morphology following heat treatment. The majority of the metal/GaSb interface includes a sulfide layer 2.0 (± 0.3)

nm thick, illustrated in Fig. 7.6(b), and EDX indicates that the intervening layer is again contains sulfur. Because we shortened the passivation time, the resultant sulfide is thinner following heat treatment compared to the layer formed during Treatment 2 and 3; however, the extent of reaction is still greatly influenced by the presence of the sulfide layer. Reaction between the metal and semiconductor takes place mainly where the sulfide is very thin (≤ 1 nm) or missing. As seen in Fig. 7.6(b), regions where the sulfide is ~ 2 nm thick exhibit little to no reaction between the metal and GaSb.





Figure 7.6: Annealed Pd/In/Pd/GaSb contact prepared using surface Treatment 5 at (a) lower and (b) higher magnification illustrating the influence of the sulfide layer on reaction between the contact and GaSb.

An HCl etch prior to the 10 s 21% (NH₄)₂S passivation treatment was next examined (Treatment 6) in an attempt to lightly passivate a cleaner GaSb surface (< 1 nm oxide). Treating the GaSb surface with HCl prior to the 10 s passivation actually results in more intimate contact between the Pd/In/Pd film and GaSb substrate. As seen in Fig. 7.7, it is difficult to detect a sulfide or oxide layer at the interface, although it is still possible to detect the original metal/semiconductor interface. The reaction between the metal and GaSb is not perfectly planar; however, it is much more uniform than observed for any of the other samples in this study. The reaction is less inhibited by the presence of a dielectric layer. It is possible that the difference between Treatment 5 and 6 lies in the rate S replaces O or Sb when forming a gallium sulfide. If O is replaced more readily than Sb, a thicker sulfide will form during the 10 s passivation step if the oxide is present than if it is not. Including an etch in HCl prior to passivation (Treatment 6), a reduced oxide layer is expected. This results in a sulfide layer that is thin enough (≤ 1 nm) to be dispersed by the contact metallization.



Figure 7.7: Annealed Pd/In/Pd/GaSb contact prepared using surface Treatment 6, showing extensive reaction between the metal and semiconductor with no detectable sulfide layer.

The final surface treatment (Treatment 7) was designed to reduce even further the extent of the dielectric layer at the metal/semiconductor interface. This treatment included an HCl etch (30 s) followed by a rinse in 2.1% (NH₄)₂S for approximately 5 s. As shown in Fig. **7.8**, Treatment 7 results in no detectable dielectric layer at the metal/semiconductor interface following a mild anneal at 125 °C for 60 min (Fig. **7.7(a)**) and intimate mixing of all elements following a subsequent anneal at 350 °C for 10 min (Fig. **7.7(b)**).



(b)

Figure 7.8: A Pd/In/Pd/GaSb contact annealed at 125°C for 60 min (a) showing no detectable dielectric layer at the metal/semiconductor interface and (b) intimate mixing of all elements following a subsequent anneal at 350°C for 10 min.

Surface preparation is important when intimate contact is required between a metal and semiconductor. To date, the focus has been to reduce the oxide at the metal/GaSb interface.[9] By replacing the DI water rinse with an alcohol rinse, Liu *et al.* [9] were able to reduce the native oxides on the GaSb surface to 1 - 2 nm. Our data suggests, however, that the dielectric layer must be reduced to less than 1 nm for intimate contact to truly be achieved. Dielectric layers as thin as 1 nm are still capable of affecting the reaction between the metal and semiconductor.

The previous description of the sulfide layer formed during passivation is in good agreement with that of Liu *et al.*, [**9**] as no oxide was detected. However, our results differ from those presented by Lin *et al.*,[**135**] who claim that with an increase in concentration of $(NH_4)_2S:H_2O$ to 1:4 comes an increase in the thickness of a Ga₂O₃ layer. Sulfide layer thicknesses presented here for samples treated for 60 s in 21 % $(NH_4)_2S$ (Treatment 2 and 3) are in good agreement with work by Papis *et al.*,[**133**] who estimate a layer thickness of 8.2 nm after treatment for 60 s in 21% $(NH_4)_2S$, assuming a mixed oxide-sulfide layer. By replacing the DI water rinse with a brief dilute $(NH_4)_2S$ rinse following the HCl etch, we are able to further reduce any dielectric layer thickness, allowing for intimate contact between the metal and semiconductor.

To investigate the effect that the surface preparation has on the resistance of ohmic contacts, we also tested the specific contact resistance of contacts prepared using some of the surface treatments investigated using TEM. The conventional Pd/In/Pd/Pt/Au contact was prepared with a 30 s etch in 18.5% HCl followed by a DI rinse. This contact provides a specific contact resistance of 6.6 (± 0.4) x $10^{-6} \Omega$ -cm²

when annealed at 125 °C for 60 min followed by 325 °C for 10 min, and 2.4 (±0.1) x $10^{-6} \Omega$ -cm² when annealed at 125 °C for 60 min and 350 °C for 10 min.

Contacts that utilized Treatment 2 or 3 (60 s in 21% (NH₄)₂S) did not exhibit ohmic behavior, instead displaying non-linear current-voltage curves. These treatments resulted in a dielectric layer $\sim 2 - 3$ nm in thickness, enough to limit reaction at the M/S interface. Figure 7.9 is a graphical summary of several treatments that yielded ohmic contacts. Treatment 6 (HCl; DI rinse; 10s in 21% (NH₄)₂S) yielded a specific contact resistance of 2.1 (± 0.7) x $10^{-5} \Omega$ -cm² when contacts were annealed at 125 °C for 60 min and 325 °C for 10 min. The increase in specific contact resistance following passivation compared to the previously reported contact indicates that a further reduction of the interfacial dielectric layer thickness was needed. The final surface treatment tested included an 18.5% HCl etch (30 s) and 2.1% (NH₄)₂S rinse (5 s) (Treatment 7). Excluding the DI rinse, decreasing the $(NH_4)_2S$ solution concentration, and reducing passivation time resulted in little to no dielectric layer on the GaSb and ultimately yielded an improved contact over that of the conventionally treated one. We were able to decrease the specific contact resistance from 6.6 (±0.4) x $10^{-6} \Omega$ -cm² (Treatment 4) to 3.2 (± 0.3) x $10^{-6} \ \Omega$ -cm² (Treatment 7) for contacts annealed at 125 °C for 60 min and then 325 °C for 10 min. Similarly, the specific contact resistance was reduced from 2.4 (±0.1) x $10^{-6} \Omega$ -cm² to 1.8 (± 0.3) x $10^{-6} \Omega$ -cm² for contacts annealed at 125 °C for 60 min and then 350 °C for 10 min. The reduction in specific contact resistance verifies that surface preparation is a critical part of fabricating high quality ohmic contacts to n-GaSb.



Figure 7.9: Specific contact resistance measurements as a function of temperature for various GaSb surface treatments.

7.2 Conclusions

The result of passivating GaSb using 21% and 2.1% $(NH_4)_2S$ at room temperature is studied using TEM. During sulfur passivation using 21% $(NH_4)_2S$ a dielectric layer is formed and consists of S and Ga with negligible O. This sulfide layer is amorphous and approximately 14 nm thick when formed during a 5 min soak in 21% $(NH_4)_2S$. The resultant sulfide layer prohibits reaction between the metal and semiconductor, and even a thin sulfide layer (~ 2 nm) interferes with reaction between a Pd/In/Pd contact metallization and n-GaSb after annealing at 125 °C for 60 min followed by 350 °C for 10 min. With sufficient reduction of the $(NH_4)_2S$ solution concentration and passivation time, a reduction in the specific contact resistance of an ohmic contact to n-GaSb was achieved, as compared to the conventionally treated samples

Chapter 8

Thesis Summary and Future Work

8.1 Thesis Summary

At the onset of this thesis, there was a move in the compound semiconductor community toward Pd-bearing contacts to n-GaSb because Pd was believed to lead to solid phase reactions at the metal/semiconductor interface as well as disperse native oxides on the GaSb surface. As a result, understanding the reaction morphology and phase formation between Pd thin films and GaSb substrates became the first priority in this thesis research for developing high quality ohmic contacts to n-GaSb. This work gave insight into temperature ranges required for solid phase regrowth of Pd-bearing contacts to n-GaSb as well as phase formation responsible for low resistance ohmic contacts to n-GaSb. The Pd/GaSb thin film research also lead to the identification of previously unknown Pd_xGaSb phases. These phases, according to EDX, range from Pd₄GaSb to Pd₇GaSb at 100 °C and up to approximately Pd₁₀GaSb at 200 °C. At 200 °C the ternary Pd_xGaSb phases begin to decompose into Pd-rich Pd-Ga and Pd-Sb binary phases that lead to ohmic behavior of a Pd (50 nm)/n-GaSb contact.

Examination of the Pd-rich portion of the Pd-Ga-Sb phase diagram was next undertaken as a means to learn more about the structure of the Pd_xGaSb phases identified in the thin film reactions. Samples were initially annealed at 500 °C and 600 °C, but these samples did not equilibrate. As a result, samples were annealed at 700 °C and then examined by x-ray

diffraction (for structure) and electron probe microanalysis (for composition). Structure analysis was met with little success, but EPMA revealed the presence of up to eight Pd-rich ternary phases, with four of these phases closely matching those identified in the Pd/GaSb thin film experiments, verifying the presence of phases that range in concentration from Pd₄GaSb to Pd₁₀GaSb.

Next, ohmic contacts to n-GaSb were explored. These contacts were Pd-bearing and contained indium in an attempt to reduce the band gap of the GaSb through reaction with the contact. Indium alone, however, forms large agglomerations when deposited on III-V compound semiconductors. Including Pd as part of the metallization facilitated smoother surface morphologies as well as improved reaction morphologies following annealing. Based on the Pd/GaSb thin film study, it was also suspected that the use of Pd would lead to the regrowth of the GaSb (after annealing) to include In, similar to that for In-bearing contacts to n-GaAs in which n-In_xGa_{1-x}As forms. Experiments initially focused on evaporated contacts. The optimized Pd/In/Pd/Pt/Au evaporated contacts was used to verify, for the first time, the formation of In_xGa_{1-x}Sb at the metal/semiconductor interface, which was initially considered responsible for the low resistance of the contact. Along with In_xGa_{1-x}Sb was the formation of Pd-Ga phases at the metal/semiconductor interface. While the phases did not form in a layered structure, phase formation following annealing is consistent with the solid phase regrowth mechanism. However, these contacts exhibited poor interfacial reaction morphologies and limited thermal stability, which had to be addressed.

To address the shortcomings of the evaporated contacts, and to examine if solid phase regrowth or the exchange mechanism was responsible for the ohmic behavior, sputtered contacts were next examined. An optimized Pd₃In₇/WSiN/Au contact provided resistance values as low as those achievable using the layered Pd/In/Pd/Pt/Au contact. The sputtered Pd₃In₇/WSiN/Au contact was also an improvement over previously reported contacts to n-GaSb. This contact exhibited resistances comparable to other reported contacts, but with unmatched thermal stability and shallow reaction depths. The formation of quaternary Pd-In-Ga-Sb phases at the metal/semiconductor interface and consumption of GaSb in the sputtered contacts indicated that the exchange mechanism was not responsible for the low resistance contacts.

Materials characterization indicated that the use of indium as part of an ohmic contact to n-GaSb is at least partly responsible for low resistance. The current transport mechanism, however, needed to be addressed to more closely identify how low resistance ohmic contacts are achieved on n-GaSb (n $\ge 10^{18}$ cm⁻³). If the semiconductor is heavily doped, a decrease in the barrier height (via the incorporation of In) may not affect the resistance as dramatically as expected. As a result, the specific contact resistance as a function of temperature was examined to identify if thermionic (TE), thermionic-field (TFE), or field emission (FE) dominated the current transport at the metal/semiconductor interface. If the specific contact resistance is heavily dependent on the temperature, then TE or TFE would be the likely transport mechanism, and a decrease in the barrier height would result in a considerable decrease in the specific contact resistance. If the specific contact resistance is relatively independent of the temperature, then FE would be the likely current transport mechanism and a change in the barrier height would not lead to dramatic reductions in the specific contact resistance. Three sets of

samples were made, one that included only Pd at the metal/semiconductor interface (Pd/WSiN/Au) and two others that included Pd and In (Pd₃In₇/WSiN/Au and Pd/In/Pd/Pt/Au). Comparing measured specific contact resistance values at 300 K and 77 K revealed that the specific contact resistance is relatively independent of temperature, indicating that FE dominates electron transport at the metal/semiconductor interface. Comparison of the contacts also indicated that In does reduce the barrier at the metal/semiconductor interface by ~ 100 meV (regardless of phase formation), enough to lower the specific contact resistance by 2 times.

Gallium antimonide is well known for fast growing oxides on its surface. However, there had been little correlation between surface treatments and contact resistance for contacts to n-GaSb. As a result, a study was undertaken to identify how the presence of an interfacial dielectric layer (oxide or sulfide) may affect the reaction morphology and contact resistance of ohmic contacts to n-GaSb. Gallium antimonide epitaxial layers and wafer substrates were subjected to various surface treatments that included an etch with HCl followed by a rinse in deionized water, or passivation with 21% or 2.1% (NH₄)₂S solutions. Comparison of different passivation treatments helped correlate interfacial dielectric layer thickness with reaction morphology and specific contact resistance. This work also showed that the lowest specific contact resistance values and most uniform interfacial reaction morphologies resulted when the dielectric layer at the metal/semiconductor interface was minimized or eliminated. It also lead to a new, modified surface treatment that retarded the regrowth of an oxide layer following treatment. The modified surface treatment was subsequently used for all remaining contact studies and is

useful as a processing step to improve the overall performance of Sbbased devices.

The work presented in this thesis was a comprehensive effort to understand and use Pd and In in ohmic contacts to n-GaSb. The early stages of reaction between Pd and GaSb were examined, which lead to an improved understanding of how Pd may affect the reaction morphology of Pd-bearing contacts. This knowledge was then used to engineer two low resistance contacts to n-GaSb, one of which is an improvement over all other reported contacts to n-GaSb.

8.2 Future Work

Although work presented in this thesis has addressed many aspects of ohmic contacts to n-GaSb, it has also lead to several ideas that may be addressed in the future to further our understanding of ohmic contacts to n-GaSb. Low resistance contacts to n-GaSb ($\rho_c \le 5 \ge 10^{-6} \ \Omega \ cm^2$) presented here and in the literature have only been reported for carrier concentrations greater than 9 $\ge 10^{17} \ cm^{-3}$. Work presented in this thesis indicates that field emission of electrons at the metal/semiconductor interface is the dominant transport mechanism at these doping levels. To truly understand how indium may affect the contact resistance by reducing the barrier to electron transport, it would be instructive to test contacts developed in this thesis work on less heavily doped epitaxial layers (n < 8 $\ge 10^{17} \ cm^{-3}$). However, acquiring high quality n-type GaSb epitaxial layers doped < 8 $\ge 10^{17} \ cm^{-3}$ was quite difficult. As discussed in Ch.1, this is due to a background hole concentration approximately equal to $10^{17} \ cm^{-3}$.[1] Attempts during this thesis work to obtain a high quality, lightly doped, n-GaSb epitaxial layer from several institutions was met with little success and work was limited to n-GaSb with carrier concentrations $\geq 1 \ge 1 \ge 10^{18}$ cm⁻³. As epitaxial growth technology improves, further studies should be possible to identify how indium influences contact resistance by reducing the barrier height at the metal/semiconductor interface of ohmic contacts to n-GaSb.

A second item that may be addressed in the future, based on the advances of n-GaSb epitaxial growth, is the engineering of a contact that uses field emission of electrons to its advantage for lightly doped n-GaSb epitaxial layers. Less heavily doped epitaxial layers exhibit less impurity scattering and higher mobilities, which could ultimately lead to faster devices without sacrificing resistance in the ohmic contact. One particular contact that could prove very useful for less heavily doped epitaxial layers is a Pd-Te pre-alloyed contact to n-GaSb. Tellurium is the most widely used dopant for n-GaSb, but is also known to be very volatile and can poison vacuum systems. Pre-alloying Te and Pd as a Te-rich metallization (such as PdTe₂) could serve two purposes. First, the Te should remain with the Pd as a compound, thus reducing the change of poisoning a vacuum system. Second, the use of a pre-alloyed PdTe₂ contact may lead to the desired thermal stability while creating an n⁺ region at the PdTe₂/GaSb interface that exploits field emission as the current transport mechanism. Tellurium has already been used as part of an ohmic contact to n-GaSb and has helped yield the lowest specific contact resistances reported. [93] A PdTe₂ contact may yield ρ_c values lower than any other reported contact while maintaining the shallow

reaction depth and morphological stability required for many Sb-based devices.

Lastly, contacts presented in this thesis form low resistance, thermally table contacts to n-GaSb. This leads to the possibility that they may form Schottky contacts on p-GaSb with an enhanced barrier height. Acquisition of p-type GaSb epitaxial layers and study of contacts on these layers would provide greater insight into the metal contacts to GaSb studied in this thesis.

Bibliography

- 1. P.S. Dutta, H.L. Bhat, and V. Kumar, J. Appl. Phys. 81 (9), 5821 (1997)
- L.M. Fraas, J.E. Avery, H.X. Huang, and R.U. Matinelli, Semicond. Sci. Technol. 18, S165 (2003)
- A.G Milnes and A.Y. Polyakov, Solid-State Electron. 36 (6),803 (1993)
- 4. J. Lince and R. Williams, J. Vac. Sci. Technol. B, 3 (4), 1217 (1985)
- 5. W.S. Tse et al., Appl. Phys. A 54, 556 (1992)
- 6. S. Basu, N. Basu, and P. Barman, Mater. Sci. Eng. B 9, 47 (1991)
- 7. S. Basu and P. Barman, J. Kor. Phys. Soc. 35, S379 (1999)
- 8. Y. Mizokawa, O. Komoda, and S. Miyase, Thin Solid Films 156, 127 (1988)
- 9. Z.Y. Lui, B. Hawkins, and T.F. Kuech, J. Vac. Sci. Technol. B 21, 71 (2003)
- 10. W.E. Spicer, I. Lindau, P. Skeath, C.Y. Su, and P. Chye, Phys. Rev. Lett. 44, 420 (1980)
- Z.M. Lü, D. Mao, L. Soonckindt, and A. Kahn, J. Vac. Sci. Technol. A 8 (3), 1988 (1990)
- K.M. Schrim, P. Soukiassian, P.S. Mangat, and L. Soonckindt, Phys. Rev. B 49 (8), 5490 (1994)
- S.M. Sze, *Physics of Semiconductor Devices*. New York, New York: Wiley-Intersciences (1981)
- 14. M.S. Daw and D.L. Smith, Phys. Rev. B 20, 5150 (1979)
- 15. W. ^{Monch}, Rep. Prog. Phys. 53, 221 (1990)

- 16. S. Subbanna, G. Tuttle, and H. Kroemer, J. Electron. Mater. 17, 297 (1988)
- 17. S. J. Eglash, H. K. Choi, Appl. Phys. Lett. 57, 1292 (1990)
- 18. A. Furukawa, N. Mizuta, Electron. Lett. 24, 1378 (1988)
- 19. J.F. Chen and A.Y.Cho, J. Appl. Phys. 70, 277 (1991)
- 20. G.W. Turner, S.J. Eglash, A.J. Strauss, J. Vac. Sci. Technol. B 11, 864 (1993)
- T.H. Chiu, J.A. Ditzenberger, H.S. Luftman, W.T. Tsang, and N.T. Ha, Appl. Phys. Lett. 56, 1688 (1990)
- 22. B.R. Bennett, R. Magno, N. Papanicolaou, J. Cryst. Growth 251, 532 (2003)
- 23. F. Dimroth, C. Agert, A.W. Bett, J. Cryst. Growth 248, 265 (2003)
- F. Nakamura, K. Taira, K. Funato, H. Kawai, J. Cryst. Growth 115 (1991) 474
- 25. M. Ichimura, K. Higuchi, Y. Hattori, and T. Wada, J. Appl. Phys. 68, 6153 (1990).
- 26. K.F. Longenbach and W.I. Wang, Appl. Phys. Lett. 59, 2427 (1991)
- I. Poole, M. E. Lee, K. E. Singer, J. E. F. Frost, T. M. Kerr, C. E. C. Wood, D. A. Andrews, W. 3. M. Rothwell, and G. Davis, J. Appl. Phys. 63, 395 (1988)
- 28. H Gotoh, K. Sasamoto, S. Kuroda, T. Yakanoto, K. Tamamura, M. Fukushima, and M. Kimata, Jpn. J. Appl. Phys. 20, L893 (1981)
- D. Mclean, T. M. Kerr, D. I. Westwood, C. E. C. Wood, and D. F. Howell, J. Vac. Sci. Technol. B 4, 601 (1986)
- D. M. Collins, J. N. Miller, Y. G. Chai, and R. Chow, J. Appl. Phys. 53, 3010 (1982)

- A. Baraldi, F. Colonna, C. Ghezzi, R. Magnanini, A. Parisini, L. Tarrcone, A. Bosacchi, S. Franchi, Semicond. Sci. Technol. 11, 1656 (1996)
- 32. V. Sestakova, B. Stepanek, Thermochim. Acta 209, 277 (1992)
- J. Sestak, V. Sestakova, and B. Stepanek, J. Therm. Anal. Calor. 56, 749 (1999)
- J. Sestak, B. Stepanek, and V. Sestakova, Czech. J. Phys. 48 12, 1627 (1998)
- H. Ehsani, J. Bhat, C. Hitchcock, R.J. Gutmann, G. Charche, and M. Freeman, J. Cryst. Growth 195, 385 (1998)
- 36. D.A. Porter and K.E. Easterling, *Phase transformations in metals and alloys*, 2nd ed., Nelson Thornes, UK (1992)
- 37 R. Beyers, K.B. Kim, and R. Sinclair, J. Appl. Phys. 61, 2195 (1987)
- 38 S.S. Wadhwa and R.Richter, Int. J. Electron. 68 (1), 39 (1990)
- H. Baker, Ed., ASM Handbook, Alloy Phase Diagrams, ASM International, 1992
- 40. F.N. Rhines, *Phase diagrams in metallurgy: their development and application*, McGraw Hill, New York, NY (1956)
- 41. C. Leuf, H. Flandorfer, K.W. Richter, and H. Ipser, J. Electron. Mater. 32, 43 (2003)
- 42. K.W. Richter and H. Ipser, Ber. Bunsenges. Phys. Chem. 102, 1245 (1998)
- 43. W.E. Liu and S.E. Mohney, J. Electron. Mater. 32 (10), 1090 (2003)
- 44. W. E. Liu, M.S. Thesis, The Pennsylvania State University, p. 32 (2002)
- 45. M. Ellner and M. El-Boragy, J. Less-Common Met. 161, 147 (1990)
- 46. D.L. Smith, *Thin Film Deposition*. McGraw Hill: Boston. (1995)
- 47. P.S. Ho, Thin Solid Films 96, 301 (1982)

- 48. M. Ohring, *Materials Science of Thin Films: deposition and structure*. Academic Press: San Diego. (2002)
- 49. A. Piotrowska, E. Kaminska, T. Piotrowski, and S. Kasjaniuk, Acta Phys. Pol. A 87, 419 (1995)
- 50. M. Wittmer, J. Vac. Sci. Technol. 2, 273 (1984)
- 51. T. Sands, V.G. Keramidas, R. Gronsky, and J. Washburn, Mater. Lett. 3 (9,10), 409 (1985)
- 52. U. Gösele and K.N. Tu, J. Appl. Phys. 86, 2619 (1989)
- 53. K.N. Tu, S.R. Herd, and U. Gösele, Phys. Rev. B 43, 1198 (1991)
- 54. U. Gösele and K.N. Tu, J. Appl. Phys. 53, 3252 (1982)
- 55. R.B. Schwartz and W.L. Johnson, Phys. Rev. Lett. 51, 415 (1983)
- 56. R.B. Schwartz, Mater. Sci. Eng. B 97, 71 (1988)
- 57. D. Turnbull, Metall. Trans. A 12A, 695 (1981)
- 58. W.L. Johnson, Prog. Mater. Sci. 30, 81 (1986)
- 59. R.W. Bené, J. Appl. Phys. 61, 1826 (1987)
- 60. K. Sawmer, H. Schroder, and K. Pampus, Mater. Sci. Eng 97, 63 (1988)
- 61. A.L. Greer, Phil. Mag. B 61, 525 (1990)
- 62. A.L. Greer, N. Karpe, and J. Bottinger, J. Alloys and Comp. 194, 199 (1993)
- 63. W.J. Meng, C.W. Nieh, and W.L. Johnson, Appl. Phys. Lett. 51, 1693 (1987)
- 64. M.A. Nicolet, Thin Solid Films 52, 415 (1978)
- 65. E.H Roderick and R.W. Williams, *Metal-Semiconductor Contacts*, Oxford: Clarendon Press (1988)
- 66. J. Bardeen, Phys. Rev. 7, 717 (1947)

- C.W. Wilmsen Ed., *Physics and Chemistry of III-V compound* semiconductor interfaces, New York, New York: Plenum Press (1985)
- 68 C.Y. Chang, Y.K. Fang, and S.M. Sze, Solid-State Electron. 14, 541 (1971)
- 69. Y.K. Su, F.S. Juang, and K.J. Gan, Jpn. J. Appl. Phys. 30, 914 (1991)
- 70. T. Sands, E.D. Marshall, and L.C. Wang, J. Mater. Res. 3, 914 (1988)
- L.C. Wang, X.Z. Wang, S.S. Lau, T. Sands, W.K. Chan, and T.F. Kuech, Appl. Phys. Lett. 56, 2129 (1990)
- 72. I. Vurgaftman, J.R. Meyer, and L.R. Ram-Mohan, Appl. Phys. Rev. 89, 5815 (2001) *and references there in.*
- 73. D. Swenson, C.H. Jan, and Y.A. Chang, J. Appl. Phys. 84 4332 (1998)
- 74. K.M. Yu, W. Walukiewicz, J.M. Jaklevic, E.E. Haller, and T. Sands, Appl. Phys. Lett. 51, 189 (1987)
- 75. D. Marlow and M. Das, Solid-State Electron. 25(2), 91 (1981)
- M. Ahmad and B.M. Arora, Solid-State Electron. 35(10), 1441 (1992)
- 77. S.H. Wang, S.E Mohney, B.A. Hull, and B.R. Bennett, J. Vac. Sci. Technol. B 21, 633 (2003)
- B. Tadayon, C.S. Kyono, M. Fatemi, S. Tadayon, and J.A. Mittereder, J. Vac. Sci. Technol. B 13, 1 (1995)
- 79. D.K. Schroder, *Semiconductor material and device characterization*, Wiley-Interscience, New York, NY (1998)
- 80. P. Villars and L.D. Calvert, *Pearson's Handbook of Crystallographc Data for Intermetallic Phases*; ASM International, Materials Park, OH (1991)
- 81. W. Kraus, G. Nolze, programmers; *PowderCell for Windows Ver.* 2.3, Aug., 2000: <u>http://ccp14.minerals.csiro.au/ccp/web-</u> mirrors/powdcell/a_v/v_1/powder/e_cell.html

- 82. C. Wannek and B. Harbrecht, Z. Anorg. Chem. 626, 1540 (2000)
- 83. C. Wannek and B. Harbrecht, J. Cryst. Growth 316, 99 (2001)
- 84. G. Cliff and G.W. Lorimer, *Proc. Fifth Cong. Electron Microscopy*, 140 143 (1972)
- 85. G. Cliff and G.W. Lorimer, J. Microscopy 103, 205 207 (1975)
- 86. J.R. Taylor, *Introduction to error analysis*, 2nd ed., University Science Books, Sausalito, CA (1997)
- 87. Z. Horita, T. Sano, M. Nemoto, Ultamicroscopy 21, 271 276 (1987)
- 88. J. Hubbell and S. Seltzer, National Institute of Standards and Technology: Physical Reference Data, http://physics.nist.gov/PhysRefData/XrayMassCoef/cover.html
- 89. D.B. Williams and C.B. Carter, *Transmission electron microscopy*, Plenum Press, New York (1996)
- B.D. Cullity, *Elements of X-ray Diffraction*, 2nd ed., Addison-Wesley, Reading, MA. (1978)
- A.A. Godoy Von Zuben, J.L. Herrera-Perez, M.B.Z. Morosini, and N.B. Patel, 5th Brazilian School Semiconductor Physics, 400-404 (1992)
- 92. T. Sands, Mater. Sci. Eng. B1, 289 (1989)
- 93. Z.C. Yang ., P.H. Hao, and L.C. Wang, Electron. Lett. 32, 2348 (1996)
- 94. K. Ikossi, M. Goldenberg, J. Mittereder, Solid-State Electron. 46, 1627 (2002)
- 95. C. Luef, H. Flandorfer, K.W. Richter, and H. Ipser, J. Electron. Mater. 32, 43 (2003)
- D.Y. Chen, Y.A. Chang, and D. Swenson, J. Appl. Phys. 81, 297 (1997)

- 97. J. Ding, J. Washburn, T. Sands, V.G. Keramidas, Appl. Phys. Lett. 49, 818 (1986)
- 98. A. Piotrowska, E. Kaminska, Thin Solid Films 193/194, 511 (1990)
- A. Vogt, A. Simon, J. Weber, H.L. Hartnagel, J. Schikora, V. Buschmann, and H. Fuess, Mater. Sci. Eng. B 66, 199 (1999)
- A. Vogt, H.L. Hartnagel, G. Miehe, H. Fuess, and J. Schmitz, J. Vac. Sci. Technol. B 14, 3514 (1996)
- K. Varblianska, K. Tzenev, and T. Kotsinov, Phys. Stat. Sol. 163, 387 (1997)
- 102. J. Sigmund, M. Saglam, A. Vogt, H.L .Hartnagel, V. Buschmann, T. Weider, and H. Fuess, J. Cryst. Growth 227-228, 625 (2001)
- 103. A. Vogt, A. Simon, H.L. Hartnagel, J. Schikora, V. Buschmann, M. Rodewald, H. Fuess, S. Fascko, C. Koerdt, and H. Kurz, J. Appl. Phys. 83, 7715 (1998)
- 104. Y.K. Su, N.Y. Li, F.S. Juang, and S.C. Wu, J. Appl. Phys. 68, 646 (1990)
- 105. T. Sands, V.G. Keramidas, R. Gronsky, and J. Washburn, Thin Solid Films 136, 105 (1986)
- C.L. Yaws, *Handbook of Vapor Pressure* v.4, Gulf Publishing Company, Houston 1994
- 107. C.H. Heinz, Int. J. Electronics 54, 247 (1983)
- 108. X. Li and A.G. Milnes, J. Electrochem. Soc. 143, 1014 (1996)
- A. Subetki, V.W.L. Chin, and T.L. Tansley, Solid-State Electron. 39, 329 (1996)
- M. Rolland, S. Gaillard, E. Villemain, D. Riguad, M. Valenza, J. Phys. III France 3, 1825 (1993)
- E. Villemain, S. Gaillard, M. Rolland, and A. Joullie, Mater. Sci. Eng. B 20, 162 (1993)

- 112. S. Wei and A.Zunger, Appl. Phys. Lett. 72, 2011 (1998)
- C.E.T. White, H. Okamoto, eds. *Phase diagrams of indium alloys and their engineering applications.* Materials Park: ASM International, 216 (1992)
- 114. C.E. Ramberg, E. Blanquet, M. Pons, C. Bernard, and R. Madar, Microelectronic Eng. 50, 357 (2000)
- E. Blanquet, A.M. Dutron, V. Ghetta, C. Bernard, and R. Madar, Microelectronic Eng. 37/38, 189 (1997)
- S. Bystrova, J. Holleman, and P.H. Woerlee, Microelectronic Eng. 55, 189 (2001)
- 117. J.S. Reid, E. Kolawa, C.M. Garland, M.A. Nicolet, F. Cardone, D. Gupta, and R.P. Ruiz, J. Appl. Phys. 79 (2), 1109 (1996)
- 118. M.A. Nicolet, Appl. Surf. Sci. 91. 269 (1995)
- 119. I.Y. Gorshkov and N.A. Goryunova, Rus. J. Inorg. Chem. 3 (3), 668
- 120. V.G. Deibuk, Semiconductors 37, 1151 (2003)
- 121 A.Y.C. Yu, Solid-St Electron. 13, 239 247 (1970)
- 122. R. Pierret, *Semiconductor Device Fundamentals*, Addison-Wesley, New York, NY; (1996)
- 123. W.B. Joyce and R.W. Dixon, Appl. Phys. Lett. 31, 34 (1977)
- 124. R. Passler, Phys. Stat. Sol. B 216, 975 (1999)
- J.G. Cederberg and R.M. Biefeld, Semicond. Sci. Technol. 19, 953 (2004)
- 126. P. Skeath, C.Y. Su, I. Lindau, W.E. Spicer, J. Appl. Phys. 57(11), 5089 - 5092 (1985)
- R. Mosca, E. Gombia, A. Motta, A. Bosacchi, S. Franchi, C. Beneventi, C. Ghezzi, and R. Magnanini, Mater. Sci. Eng. B 44, 24 -27 (1997)

- 128. Y. Mizokawa, O. Komoda, and S. Miyase, Thin Solid Films 156, 127 (1987)
- 129. E. Papis, A. Kudla, T. T. Piotrowski, K. Golaszewska, E. Kaminska, and A. Piotrowska, Mater. Sci. Semicond. Proc. 4, 293 (2001)
- M. Perotin, P. Coudray, L. Gouskov, H. Luquet, C. Llinares, J. J. Bonnet, L. Soonckindt, and B. Lambert, J. Electron. Mater. 23, 7 (1994)
- P. S. Dutta, K. S. Sangunni, H. L. Bhat, and V. Kumar, Appl. Phys. Lett. 65, 1695 (1994)
- Z. Y. Liu, T. F. Kuech, and D. A. Saulys, Appl. Phys. Lett. 83, 2587 (2003)
- 133. G. Eftekhari, Jpn. J. Appl. Phys. 35, 564 (1995)
- 134. E. Papis, A Piotrowska., E. Kaminska, K. Golaszewska, W. Jung, J. Katcki, A. Kudla, M. Piskorski, T. T. Piotrowski, and J. Adamczewska, Vacuum 57, 171 (2000)
- 135. I. A. Andreev, E. V. Kunitsyna, V. M. Lantratov, T. V. L'vova, M. P. Mikhailova, and Y. P. Yakovlev, Semiconductors 31, 556 (1997)
- 136. C. L. Lin, Y. K. Su, T. S. Se, and W. L. Li, Jpn. J. Appl. Phys. 37, L1543 (1998)

Appendix A

Pd-Ga-Sb diffraction patterns



Figure A.1: X-ray diffraction pattern of the equilibrated $Pd_{73.7}Ga_{9.9}Sb_{17.1}$ sample. The sample consists of 5% of either Pd_5Sb_2 or Pd_8Sb_3 , 20% $Pd_{75}(GaSb)_{25}$, and 75% $Pd_{74}Ga_9Sb_{17}$.

2θ value (Deg)	d-spacing (Å)	Relative Intensity
35.51	2.528	21
37.84	2.377	19
39.10	2.304	58
39.56	2.278	20
41.10	2.196	73
44.08	2.054	22
47.52	1.913	22
47.67	1.908	2
50.38	1.811	4
52.83	1.733	3
54.24	1.691	3
54.55	1.682	8
56.19	1.637	7
57.23	1.610	5
59.51	1.553	2
59.72	1.548	11
60.95	1.520	15
61.10	1.517	6
63.25	1.470	2
65.89	1.418	3
67.05	1.396	20
68.27	1.374	12
68.94	1.362	6
69.40	1.354	2
72.85	1.298	8
73.79	1.284	12
74.15	1.279	9
75.18	1.264	7
75.88	1.254	4
76.02	1.252	13
77.81	1.228	11
78.15	1.223	12
78.37	1.220	14
78.57	1.218	7
79.28	1.208	21
80.68	1.191	5
80.88	1.189	3
81.51	1.181	4
83.53	1.157	6
83.87	1.154	9
85.13	1.140	12
89.28	1.097	4

Table A-1: Unidentified XRD peaks assosiated with the $Pd_{67}Ga_{26.5}Sb_{6.5}$ ternary phase from the equilibrated $Pd_{60}Ga_{35}Sb_5$ sample.



Figure A.2: X-ray diffraction pattern of the equilibrated Pd₆₇Ga₁₆Sb₁₇ sample.



Figure A.3: X-ray diffraction pattern of the equilibrated $Pd_{75}(GaSb)_{25}$ sample..

Appendix B

Supplemental Materials Characterization of Pd₃In₇/X/Au samples

B.1 Materials Characterization of Pd₃In₇/TiN/Au Contacts



Figure B.1: TEM micrographs of $Pd_3In_7/TiN/Au$ contacts (a) as deposited and (b) annealed for 30 min at 325 °C.



Figure **B.2**: AES depth profile of a Pd₃In₇/TiN/Au contact annealed at 325 °C for 30 min showing large amounts of oxygen in the TiN barrier. The nitrogen signal is artificially large due to peak overlap with Ti.

B.2 Materials Characterization of Pd₃In₇/WSiN/Au Contacts



Figure **B.3**: EDX line scan of a $Pd_3In_7/WSiN/Au$ contact annealed at 325°C for 1 min. The scan is horizontally across a hemispherical reacted region that results from annealing. GaSb is on either side of the protrusion.



Figure **B.4**: EDX line scan of $Pd_3In_7/WSiN/Au$ contact aged for 15 h at 250°C showing that WSiN is a very stable diffusion barrier. The scan also includes a semispherical reacted region at the M/S interface where all four elements are present.



Figure **B.5**: EDX line scan of $Pd_3In_7/WSiN/Au$ contact aged for 15 h at 250°C. The scan includes the Pd_3In_7 layer and a hemispherical reacted region. Evident from the scan is that the Pd_3In_7 layer remains intact even after aging for 15 hrs.
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PUBLICATIONS

- 1. J.A. Robinson and S.E. Mohney; "A Low Resistance, Thermally Stable Ohmic Contact to n-GaSb;" J. Appl. Phys. (Accepted June 2005)
- 2. J.A. Robinson and S.E. Mohney; "Solid State Phase Formation between Pd Thin Films and GaSb;" J. Electon. Mater. (submitted March 2005)
- S. H. Wang, S. E. Mohney, and J. A. Robinson; "Design of thermally stable gate metallizations for AlGaAsSb/InAs HEMTs;" Semicon. Sci. Technol. 20: 755 - 760 (2005)
- S. H. Wang, J. A. Robinson, S. E. Mohney, and B. R. Bennett; "Shallow and Thermally Stable Pt/W/Au Ohmic Contact to p-Type InGaSb;" J. Vac. Sci. Technol, 23(2): 293 – 298 (2005)
- E.D. Readinger, J.A. Robinson, R. Therrien, and S.E. Mohney; "Thermal Stability of Metallizations on GaN/Al_xGa_{1-x}N/GaN Heterostructures;" Semicon. Sci. Technol. 20, 389 - 397 (2005)
- J.A. Robinson and S.E. Mohney; "An Improved In-based Ohmic Contact to n-GaSb;" Solid-State Electron. 48:1667-1672 (2004)
- J.A. Robinson and S.E. Mohney; "Characterization of Sulfur Passivated n-GaSb using Transmission Electron Microscopy and the Influence of Passivation on Ohmic Contact Resistance;" J. Appl. Phys. 96 (5):2684-2688 (2004)
- S. H. Wang, S. E. Mohney, J. A. Robinson, and B. R. Bennett; "Sulfur Passivation for Shallow Pd/W/Au Ohmic Contacts to p-InGaSb;" Appl. Phys. Lett. 85 (16): 3471 – 3473 (2004)
- 9. P. Gabriel, H. Hand, D. M. Schaefer, J. Robinson, and A. Amare; "Infrared Imaging," Adhesives Age, 20 - 30, (2001)