DEVELOPMENT OF CHEMICAL PASSIVATION ON III-V DEVICES AND
OF A NOVEL HIGH-SPEED DUAL-WAVELENGTH InAlAs/InGaAs
SCHOTTKY BARRIER PHOTODETECTOR

By

KIUCHUL HWANG

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1990
ACKNOWLEDGEMENTS

I wish to express my sincere appreciation to my thesis adviser, Dr. Sheng S. Li, for his guidance, encouragement, and support throughout the course of this research. I would also like to thank Drs. Peter Zory, Dorothy Burk, Gijs Bosman, and Murali Rao for their participation on my supervisory committee.

I am grateful to Dr. Y. C. Kao of Central Research Laboratories at Texas Instrument, Dr. T. J. Anderson at the department of chemical engineering, Dr. R. Park at the department of material science, Dr. Song-Jae Lee of Sam-Sung, professor Y. W. Lin, and Mr. C. Park for the growth of the epitaxial layers.

Thanks are extended to my friends and fellow students, Dr. C. M. Kim, Dr. Y. S. Kim, Mr. H.S. Chen, Mr. Andrew Tseng, Mr. Fred Brady, Mr. Y. H. Wang, Ms. Y. Wang and Mr. S. K. Lee for their helpful discussion and encouragements.

I wish to thank to James Chamblee and Jim Hales of the Microelectronics Laboratory for all the technical assistance they provided over the years.

I am greatly indebted to my parents, brothers, sisters, wife, wife’s family, and son for their endless love and support during my education.
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Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

DEVELOPMENT OF CHEMICAL PASSIVATION ON III-V DEVICES AND OF A NOVEL HIGH-SPEED DUAL-WAVELENGTH InAlAs/InGaAs SCHOTTKY BARRIER PHOTODETECTOR

By

KIUCHUL HWANG

December 1990

Chairman: Sheng S. Li
Major Department: Electrical Engineering

This dissertation presents studies of new surface passivation using P$_2$S$_5$/(NH$_4$)$_2$S on GaAs and InGaAs Schottky diodes, GaAs metal-semiconductor-metal (MSM) photodiodes, X-ray photoelectron spectroscopy (XPS) studies of the passivated GaAs and InGaAs surfaces, and the development of a novel high-speed dual-wavelength InAlAs/graded superlattice/InGaAs Schottky barrier photodetector for 0.8 and 1.3 μm detection. The electrical characteristic of the P$_2$S$_5$/(NH$_4$)$_2$S treated GaAs Schottky barrier diodes is investigated and compared with those of (NH$_4$)$_2$S$_x$ and NH$_4$OH/HF treated devices. Using new surface treatment, the effective barrier heights for both the Al- and Au-GaAs Schottky diodes are found to vary with the work function of metals, which is a clear evidence of the lower surface state density in these diodes. Angle-resolved XPS spectra of the P$_2$S$_5$/(NH$_4$)$_2$S passivated GaAs surface exhibit the existence of As-S and Ga-S species on the surface whereas there are no arsenic oxides. Formation of an As-S compound contributes to the reduction of surface states caused
by mostly $As_Ga$. The enhancement of Schottky barrier height and the reduction of the surface state density on n-type $In_{0.53}Ga_{0.47}As$ surfaces have been observed using $P_2S_5/(NH_4)_2S$ and $(NH_4)_2S_x$ passivation. The electrical characteristics show that the $P_2S_5/(NH_4)_2S$ passivated diodes have lower reverse leakage current and higher effective barrier height than the $(NH_4)_2S_x$ treated and the unpassivated diodes. Angle-resolved XPS spectra of the $P_2S_5/(NH_4)_2S$ treated n-type $In_{0.53}Ga_{0.47}As$ surfaces also shows the existence of $As-S$ and $Ga-S$ species on the surface. The chemical structure of $GaPO_4$ and $InPO_4$ is known to be a highly ordered nonconductive species which implies the chemical stability of $GaPO_4$ and $InPO_4$, and that these oxides are responsible for the barrier height enhancement on $GaAs$ and $InGaAs$ surfaces, respectively.

A novel high-speed dual-wavelength $InAlAs/InGaAs$ graded superlattice Schottky barrier photodiode for 0.8 and 1.3 $\mu m$ detection is demonstrated. The detector consists of a Au-Schottky contact on n-$In_{0.52}Al_{0.48}As$/graded superlattice (10 periods of GSL, 600 $\AA$)/n-$In_{0.53}Ga_{0.47}As$ epilayers grown on a semi-insulating $InP$ substrate by molecular beam epitaxy (MBE). In this planar detector structure, the top wide band gap n-$In_{0.52}Al_{0.48}As$ epilayer absorbs photons in the visible to near infrared spectrum (i.e., 0.4 to 0.9 $\mu m$) with peak response occurred around 0.8 $\mu m$, whereas the bottom n-$In_{0.53}Ga_{0.47}As$ epilayer absorbs photons in the 1.0 to 1.6 $\mu m$ wavelength regime with peak response occurred at 1.3 $\mu m$. The photodiode has a responsivity of 0.34 A/W at 0.8 $\mu m$ and 0.42 A/W at 1.3 $\mu m$. Excellent dark I-V characteristics with low reverse leakage current and low junction capacitance have been achieved in this new photodetector. The response speed measured by the impulse response method was estimated to be around 3 GHz.
CHAPTER ONE
INTRODUCTION

In spite of the great potential for III-V compounds such as GaAs and InP to be used for high-speed electronic and optoelectronic device applications, the practical use of these compound semiconductors has been hindered by the lack of adequate surface passivation techniques available for these materials. In recent years, there has been intensive research involving in the search for new dielectric films and surface passivation techniques for III-V semiconductor devices and a better understanding of surface/interface properties between the overlayers and the compound semiconductor surfaces. Various insulator deposition techniques, dielectric materials, and chemicals have been investigated for use in the surface passivation, encapsulation, and antireflection coatings of different electronic and photonic devices such as photodetectors, laser diodes, light-emitting diode (LED), solar cells, and metal-insulator-semiconductor field-effect transistors (MISFETs). Even though some promising results have been reported, no reliable technology has been developed so far, which could lead to long term stability in these devices.

The motivation of this research is to develop better passivation techniques for both the GaAs- and InP-based devices. Various sulfur compounds for surface passivation of GaAs have been reported, which showed promising results in reducing surface leakage of the devices. However, the sulfur compounds are unstable and degrading in the air with time. Recently, Lee et al.[1] used phosphorus compounds, P$_2$S$_5$ dissolved in NH$_4$OH, to treat the GaAs surface, which showed improvement in surface leakage of Schottky diode. However, the formation of arsenic sulfide during the passivation will result in the following reactions:
\[ \text{As}_2\text{S}_3 + 9\text{OH}^- \rightarrow 2\text{AsO}_3^- + 3\text{HS}^- + 3\text{H}_2\text{O} \] (1.1)

As a result, arsenic oxide, which is gradually segregated to elemental arsenic—the main source of surface states—will be formed again on the GaAs surface followed the treatment.

A new passivation material presented in this dissertation avoids the formation of arsenic oxide, which exploits an excellent passivation effect of both phosphorus and sulfur on GaAs surface.

Another goal of this thesis is aimed at developing a novel high-speed broad-wavelength Schottky photodetector for 0.4 \(\sim\) 1.6 \(\mu\)m using InAlAs/InGaAs material system. The 1.3 \(\mu\)m wavelength is generally used in long-haul large capacity optical communication systems due to the extremely low transmission loss and near zero dispersion of optical fibers at this wavelength. For middle-haul, middle- and lower-speed optical communication systems, the 0.6 \(\sim\) 0.7 \(\mu\)m wavelength region has received attention due to low-cost GaAs lasers developed for compact disk players or other uses.

This dissertation covers three major research topics:

(1) Electrical and optical characterization of the passivation layers, (2) material characterization of the passivated surfaces using X-ray photoelectron spectroscopy (XPS), and (3) development of a novel high-speed broad-wavelength InAlAs/InGaAs Schottky photodetector.

Chapter 2 presents an overview of the physical model explaining the origins of surface and interface states, reliabilities of the dielectric passivations used on metal-semiconductor field-effect transistor (MESFET) and photodetectors, process parameters affecting the properties of the dielectric films, and the chemical passivation techniques.
In Chapter 3, a new surface passivation technique using \( \text{P}_2\text{S}_5/(\text{NH}_4)_2\text{S} \) on GaAs Schottky barrier diodes is investigated, and the results are compared with those of \((\text{NH}_4)_2\text{S}_x\) and \(\text{NH}_4\text{OH/HF}\) treated devices. Using new surface treatment, the effective barrier heights for both the Al- and Au-GaAs Schottky diodes are found to vary with the work function of metals, which is a clear evidence of lowering surface state density in these diodes. Results of the I-V and C-V measurements show that \( \text{P}_2\text{S}_5/(\text{NH}_4)_2\text{S} \) passivated diodes have lower reverse leakage current and higher effective barrier height than that of the \((\text{NH}_4)_2\text{S}_x\) treated diodes.

Chapter 4 presents the XPS and Auger Electron Spectroscopy (AES) studies of \( \text{P}_2\text{S}_5/(\text{NH}_4)_2\text{S} \) passivation layers formed on GaAs (100) surface. Knowledge of the sulfur- and phosphorus- induced overlayers and the way they terminate at the GaAs surface is important for understanding the underlying physics and chemistry of the results obtained from the electrical characterization described in Chapter 3.

In Chapter 5, a novel method for enhancing the Schottky barrier height, while reducing the surface state density on n-type \( \text{In}_{0.53}\text{Ga}_{0.47}\text{As} \) surfaces using \( \text{P}_2\text{S}_5/(\text{NH}_4)_2\text{S} \) and \((\text{NH}_4)_2\text{S}_x\) passivations is described. The current-voltage (I-V) and capacitance-voltage (C-V) characteristics show that passivated InGaAs Schottky diodes have lower reverse leakage current and higher effective barrier height than that of the unpassivated diodes.

In Chapter 6, we used the XPS technique to analyze the InGaAs surfaces treated with chemical etching and \( \text{P}_2\text{S}_5/(\text{NH}_4)_2\text{S} \). In order to determine the effect of \( \text{P}_2\text{S}_5/(\text{NH}_4)_2\text{S} \) treatment on the electrical property of the surface, we employed the XPS to examine InGaAs surfaces following the acid etch and \( \text{P}_2\text{S}_5/(\text{NH}_4)_2\text{S} \) treatment.

In Chapter 7, we demonstrate a novel high-speed dual-wavelength InAlAs/InGaAs graded superlattice Schottky barrier photodiode which covers the wavelengths from 0.4 to 1.6 \( \mu \text{m} \). The detector structure consists of a Au- Schottky contact on the n-
In$_{0.52}$Al$_{0.48}$As/undoped n-In$_{0.52}$Al$_{0.48}$As/In$_{0.53}$Ga$_{0.47}$As graded superlattice (GSL)/n-In$_{0.53}$Ga$_{0.47}$As epilayers grown on a semi-insulating InP substrate by molecular beam epitaxy (MBE). In this planar detector structure, the top wide bandgap n-In$_{0.52}$Al$_{0.48}$As epilayer absorbs photons in the visible to near infrared spectrum (i.e., 0.4 to 0.9 $\mu$m) with peak response occurred around 0.8 $\mu$m, whereas the bottom n-In$_{0.53}$Ga$_{0.47}$As epilayer absorbs photons in the 1.0 to 1.6 $\mu$m wavelength regime with peak response occurred at 1.3 $\mu$m. The effect of charge trapping due to the conduction- and valence-band discontinuity ($\Delta E_c = 550$ meV, $\Delta E_v = 200$ meV) at the heterointerface of InAlAs/InGaAs, which may limit the speed of heterostructure photodiode, is significantly reduced by introducing a graded-superlattice of undoped n-In$_{0.52}$Al$_{0.48}$As/In$_{0.53}$Ga$_{0.47}$As (10 periods, 600 Å) between the n-In$_{0.52}$Al$_{0.48}$As ($E_g = 1.45$ eV) and In$_{0.53}$Ga$_{0.47}$As ($E_g = 0.74$ eV) absorbing layers.

In Chapter 8, summary and conclusions are given, and followed by recommendation for future research.
CHAPTER TWO
OVERVIEW OF PASSIVATION

2.1. Introduction

It is well known that the atomically clean III-V compound semiconductor surfaces when exposed to air at room temperature become contaminated with a mixture of native oxides, adsorbed water, and carbon molecules, which can lead to the formation of a metastable complex [2]. As a result, the surface of these materials is always covered by at least one or two monolayers of native oxides. Overlayers of dielectrics or metals on III-V compound semiconductor surfaces can create complex interfaces which are difficult to control, and can result in unfavorable electrical and structural properties. The effects of the thin oxide layer on device characteristics have been studied recently. By understanding the chemistry of surface oxide formation, one can gain physical insight into the nature of the oxidized surface. For example, it has been generally observed that the deposition of metals on the air-exposed GaAs surface always shows the pinning of the surface Fermi level within a certain narrow range in the energy gap. Thus, the Schottky barrier \( \Phi_B \) was determined by the pinning position, a fact which was emphasized by Bardeen [3], not by the work function difference between the metal and the semiconductor proposed by Schottky [4]. As a result, the shift of the Fermi level as well as the corresponding change in the charge of the states due to the metal effect are small. The pinning was often ascribed to defect states in the band gap induced by the surface reactions. As such, GaAs Schottky barriers can not be controlled by using different kind of or metals. Similar problems also exist in other III-V compounds such as InGaAs and InP.
2.2. Physical Defect Model

Although several physical models [5,6,7,8,9,10] have been proposed to interpret the observed surface phenomena occurring at the metal-semiconductor interface, none of these models appears to be able to elucidate the mechanisms which are responsible for the observed surface and interface states in the III-V compounds. At present, the following three models are generally being used to explain the phenomena related to the surface or interface states of these materials.

2.2.1 Unified Defect Model (UDM)

On the cleaved (110) faces of GaAs, there were no intrinsic surface states in the band gap. Many groups, however, had seen the Fermi level pinning on clean-cleaved (110) n-type GaAs [11]. The explanation based on the experimental results was that the pinning observed on clean-cleaved n-GaAs (110) was due to extrinsic states produced by defects formed in the cleaving process, not intrinsic surface states. Spicer and his co-workers [9] tried to determine the mechanism for the Fermi level pinning by metal or oxygen deposition. The pinning positions for a number of metals and oxygen on GaAs in Fig. 2.1 showed little difference of the Fermi level pinning position between metal and oxygen, and even among the metals. They thought that if the pinning states were produced indirectly, for example, by the formation of vacancies or other defects, then the energy levels of these defects would not have necessarily depended on the details of the adatoms. Thus, they suggested that the pinning produced by the adatoms was due to defects produced at or near the surface of the semiconductor from the deposition of the adatoms and the interaction of the adatoms with the semiconductor surface. These defects could have been a mixture of different defects such as vacancies, antisite defects, and various combinations of vacancies, etc.
Figure 2.1 Energy level diagram showing the pinning positions obtained on n- and p-GaAs with very low coverages (1 monolayer or less) of the indicated element measured at room temperature ($E_g = 1.42$ eV).
From the experimental results, it has been shown that the pinning level of the as-cleaved n-type GaAs at 0.75 eV is the dominant acceptor level whereas the second level at 0.5 eV is the donor level. From both the synchrotron radiation and sputter Auger techniques, they have consistently found sizable amounts of semiconductor material in the metal of the Schottky barriers. They thought that the heat of bonding of the metal to the free GaAs surface was the driving force for disruption of the GaAs and its movement into the metal, since the heat of condensation is much larger than the kinetic energy associated with the metal atom after evaporation. Thus, at the moment of adsorption on the GaAs surface, the metal gives up energy comparable to or considerably larger than the heat of formation of the semiconductor. The elemental atoms on the semiconductor then gain the energy from the adsorbed metals, and are momentarily excited into the metal. If only a few atoms of the semiconductor are moved into the metal for each hundred metal atoms bound to the surface, then this movement can account for the local departure from stoichiometry and resulting defect states which produce the Fermi level pinning.

2.2.2 Advanced Unified Defect Model (AUDM)

Since UDM was first proposed, several groups [12,13] have ascribed the As$_{Ga}$ antisite (an As atom on a Ga site in the GaAs lattice) as the main source of defects on the GaAs surface. Weber et al.[13] have attributed the As$_{Ga}$ antisite as a double donor. However, in order for the Fermi level to pin at 0.75 eV for n-GaAs as confirmed by many experimental results, Spicer et al.[14] proposed that a double acceptor level which is most likely due to a Ga$_{As}$ antisite (a Ga on an As site in GaAs) positioned between the lower donor level and the valence band maximum (VBM). From these arguments, Spicer et al.[14] suggested the defect model for the interface shown in Fig. 2.2. The As$_{Ga}$ antisite provides the pinning levels at 0.75 and 0.5 eV. From computer
Figure 2.2 Energy band diagrams showing double donor states compensated by double acceptors at the surface.
modeling of the Fermi level position at the surface, Spicer et al.[14] concluded that the number of As\textsubscript{Ga} antisites must be close to twice the number of Ga\textsubscript{As} antisites and other acceptors in order to explain the n- and p-type pinning phenomena shown in Fig. 2.1. In fact, there is ample evidence for the presence of a larger number of As\textsubscript{Ga} provided by such diverse experiments as the ubiquitous presence of the EL-2 center in the as-grown bulk materials. There is much data related to the presence of excess As or Ga at the interface and changes in the Fermi level with change of the As to Ga ratio. Based on AUDM, an As/Ga increase enhances the ratio of As\textsubscript{Ga}/Ga\textsubscript{As} antisites in the GaAs near the interface, which is expected to move the Fermi level toward the conduction band minimum (CBM), whereas a decrease in the ratio should move it toward the VBM. Changes in the Fermi level in the MBE grown clean surface due to an increase in the As excess were shown to be in agreement with this AUDM. AUDM may be used to relate the interfacial chemistry to changes in the Fermi level and enhance the Schottky barrier height.

2.2.3 Effective Work Function Model

This model [10,15] suggests that the Fermi level at the surface or interface is not fixed by surface states but rather is related to the work function of microclusters of the one or more interface phases formed by native oxides, hydrocarbon containing molecules, moisture in the air, and the reactions between the metal and the contaminants during metallization. Microscopically, each phase has its own work function which is different from that of the depositing overlayer. Therefore, the work function of the mixture of microclusters of different phases is an average of the work functions of the different interface phases. Thus, the ideal Schottky barrier height is modified to include this averaged work function ($\Phi_{\text{eff}}$). The Schottky barrier height on n-type semiconductor is the difference between $\Phi_{\text{eff}}$ (not $\Phi_M$) and the electron affinity of the
semiconductor ($\chi$). The work function $\Phi_{\text{eff}}$ is mostly due to $\Phi_{\text{anion}}$; the work function of the anion occurring as a result of the following reactions during metallization or oxidation.

Anion Oxide + Compound $\rightarrow$ Anion + Cation Oxide \hspace{1cm} (2.1)

Metal + Compound $\rightarrow$ (Anion or Metal Anion complex) + (Metal - Cation) \hspace{1cm} (2.2)

For most of the III-V compounds including GaAs, conventional metallization under non-ultra high vacuum (UHM) conditions results in a condition in which $\Phi_{\text{eff}}$ is mostly due to $\Phi_v$, the work function of the group V element. Schottky barrier height on GaAs, for instance, is determined by the arsenic clusters, which are excess anions at the interface. From the phase diagram, an arsenic phase is expected at equilibrium for Au-GaAs contact. Thus a knowledge of both the oxide and reactive metal chemistry should allow accurate prediction of the Schottky barrier height of the metal-semiconductor contact, including transport properties.

Although efforts to account for the surface Fermi level pinning have produced a number of physical models, at present no universal model exists which can explain the mechanism occurring on the surface and interface between the overlayers and GaAs. Since overlayers such as metal and insulator interfaces are basic constituent elements of all electronic devices or planar integrated circuits, elimination or reduction of the surface Fermi level pinning effect is a key scientific and technological issue for further advance of GaAs technology.

2.3. Dielectric Passivation

In spite of the inherent interface problem of the deposited insulator/III-V interface due to the possibility of a non-abrupt interfacial mismatch and its associated trap states, efforts have been made to obtain a good device quality insulator on top
of III-V semiconductor surface for the following applications: gate insulator for MIS-FET, passivation layer, etching, annealing, or diffusion mask, and insulating layer for interconnections. For example, the GaAs MESFET is widely used for microwave device applications. Unfortunately, the trapping of surface charges causes the formation of an unstable depletion region on the channel surface. As a result, microwave amplifiers assembled with MESFET's exhibit a time dependent drift in RF gain and other parameters. Tenedorio et al. [16] found that silicon nitride films deposited using a plasma enhanced chemical vapor deposition (PECVD) technique eliminate the time dependent drift of amplifier performance without a significant degradation to the microwave gain. Donzelli et al. [17] reported that a Si$_3$N$_4$ passivated MESFET showed a stability under an accelerated life test (300 °C in N$_2$ for 500 h). Recently, the effects of passivation on the performance of photodiodes based on the InGaAs/InP material system have been studied due to the practical applications of this material system for long-wavelength (1.1 μm ~ 1.6μm) optical communication systems. Saul et al. [18] found that projected median lives exceed $10^7$ h at 30 °C on their planar type p-i-n photodiodes passivated with SiNx film on an InGaAs layer when the devices were screened through burn-in for 10 h at 200 °C and -20 V. Chin et al. [19] analyzed the failure modes of these devices. They found that microplasma resulting from pinholes in the diffusion mask were the major sources of nonrecoverable device degradation. Tashiro et al. [20] performed accelerated life tests on the planar type p-i-n photodiodes with an InGaAsP cap layer passivated with SiNx film to study the mechanism of the degradation. They found that the recoverable surface degradation below 180 °C was due to hole trapping at the interface or hole injection into the SiNx passivation film and that the nonrecoverable degradation at higher than 180 °C was due to deterioration in the alloy contact. Ishihara et al. [21] used two passivation films, SiNx and CVD-SiO$_2$, on InP cap layer of planar type p-i-n photodiodes to eliminate
pinholes. They found that there was no significant degradation after aging for 5500 h at 250 °C and -10 V and that the activation energy of degradation was higher than 0.9 eV. Kuhara et al.[22] used polyimide thin film on planar type InGaAs/InP p-i-n photodiodes and performed reliability tests at different temperatures. They observed no degradation in the dark current after it aged for 7000 h in a room temperature life test. They explained the degradation of the devices under accelerated life test by the model of accumulation and diffusion of mobile ions at the junction perimeter. Table 2.1 summarizes the recently reported results of dielectric passivations on MESFETs and photodiodes.

Although there are many important parameters affecting the properties of the dielectric films, the associated particle energies and the temperatures appear to be very important process parameters from many experimental results.

2.3.1 Deposition Technique

Various types of techniques including thermal evaporation, electron-beam evaporation, chemical vapor deposition (CVD), and sputtering have been employed for depositing dielectric films on III-V semiconductors. The ion-based deposition processes are associated with energetic ions striking on the surface and the influence of ion bombardment on the film structure, adhesion, and chemical composition. To reduce the defect generated on a semiconductor surface during deposition- and hence interface states, it is important to use a deposition technique which imparts only a small amount of energy into the surface. Otherwise, the bombardment with energetic particles during deposition could damage the surface of the semiconductor layer and the growing film. For example, the plasma-enhanced chemical vapor deposition (PECVD) technique commonly used for depositing dielectric film on III-V semiconductor devices may create plasma related surface damage. The recently developed
Table 2.1 Summary of dielectric passivations on MESFETs and photodiodes.

<table>
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<tr>
<th>Material</th>
<th>Deposition Technique</th>
<th>Device</th>
<th>Feature of Passivation</th>
<th>Ref.</th>
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</thead>
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<tr>
<td>Si$_3$N$_4$</td>
<td>RF Plasma Sputtering</td>
<td>n-InP/P$^+$-InP</td>
<td>Reduction of leakage current.</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>InGaAsP/p$^+$-InP APD</td>
<td>Degradation due to atmospheric moisture</td>
<td></td>
</tr>
<tr>
<td>Polyimide</td>
<td>Spin Coating</td>
<td>n-InP/P$^+$-InP</td>
<td>Reduction of leakage current.</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>InGaAsP/p$^+$-InP APD</td>
<td>Degradation at high baking temp. due to dopant diffusion.</td>
<td></td>
</tr>
<tr>
<td>Photoresist</td>
<td>Spray</td>
<td>InGaAsP/p$^+$-InP APD</td>
<td>High electron affinity of SF$_6$ reduce excess surface charge. High dielectric const. Help lower fringing field at exposed junction.</td>
<td></td>
</tr>
<tr>
<td>Si$_3$N$_4$</td>
<td>CVD</td>
<td>InGaAs pin-PD</td>
<td>Degradation due to microplasma resulting from pinhole.</td>
<td>19</td>
</tr>
<tr>
<td>Si$_3$N$_4$</td>
<td>CVD</td>
<td>InGaAs pin-PD</td>
<td>Hole trapping at interface</td>
<td>20</td>
</tr>
<tr>
<td>Si$_3$N$_4$</td>
<td>PECVD</td>
<td>GaAs MESFET</td>
<td>No time dependent drift of gain.</td>
<td></td>
</tr>
<tr>
<td>SiO</td>
<td>Thermal Evaporation</td>
<td>GaAs MESFET</td>
<td>Not effective.</td>
<td>16</td>
</tr>
<tr>
<td>Polyimide</td>
<td>Spin Coating</td>
<td></td>
<td>3500 Å No improvement of drift.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>6500 Å Improved but low gain.</td>
<td></td>
</tr>
</tbody>
</table>
photo-assisted CVD technique appears to be an approach which can avoid plasma related damage. Figure 2.3 shows the typical energy ranges associated with deposition processes. The heat of formation of surface or interface defects is usually smaller than the energies associated with the insulator deposition processes. Therefore, it is expected that virtually any deposition techniques may form the surface and interface defects. As reported by Spicer [9], even the heat of condensation of a metal on a semiconductor surface is sufficient for defect formation on III-V semiconductor surface.

2.3.2. Deposition Temperature

The most important factor to be considered for dielectric film deposition is the substrate temperature. High-quality dielectric films are usually obtained at relatively elevated temperatures because the insulating and mechanical properties of the deposited film degrade with decreasing temperature. However, the substrate temperature should always be maintained below the evaporation temperature (e.g., GaAs ~657°C) since preferential loss of the column V (e.g., As) element from the surface will create vacancy defects which are thought to be the source of Fermi-level pinning for a variety of III-V semiconductors. In addition to that, higher temperatures also increase the rate of oxidation, surface reaction, and diffusion. Therefore, a compromise temperature is usually selected.

The postdeposition treatments after the dielectric film deposition consist of annealing at relatively high temperatures in a variety of forming gas ambient. The purposes of this treatment are (1) to reduce the interface state and fixed charge densities, (2) to make the deposited insulator more dense without pinholes, and (3) to remove moisture from the deposited insulator. Pinholes in the deposited film can effectively shunt dc current through the film. Grain boundaries in polycrystalline
Figure 2.3  Energy ranges associated with various deposition techniques.
dielectrics may also provide shunt paths for dc leakage current. Direct current conduction in dielectric film may occur by electronic conduction via hopping transport from one trap site to another or via some other types of tunneling processes involving insulator traps. Traps in the dielectric film may be caused by impurities or nonstoichiometry defects. A reasonable criterion for a good quality dielectric film requires that its dielectric resistivity be greater than $10^{15}\Omega \cdot \text{cm}$. This requires that the insulator has wide band gap, free of impurities, stoichiometric, and is amorphous rather than polycrystalline.

Although these parameters appear to affect the quality of dielectric film, it is not apparent that thin native oxides on III-V compounds are desirable for the formation of dielectric film on them. In III-V compounds, dielectric films deposited on an unavoidable pre-existing native oxide appear to result in a two heteroepitaxial dielectric layers on the surface. Some of the researchers have claimed that a thin (less than 20 $\sim$ 30 Å) interfacial oxide could conceivably alleviate the interfacial mismatch between the deposited dielectric film and the semiconductor, thereby minimizing the amount of interfacial strain and defect formation. However, a more reasonable consensus supported by many experimental evidences is that the initial oxidation of III-V compounds after cleavage in UHV has been shown to cause surface Fermi level pinning due to the creation of defects.

2.4. Chemical Passivation

Recently, considerable interest has been generated towards the development of novel surface passivation techniques using photochemical and chemical treatments. Some promising results have been reported. Table 2.2 summarizes the recent reported results of chemical passivation techniques. In this section, several well known popular methods will be discussed.
Table 2.2  Summary of chemical passivations.

<table>
<thead>
<tr>
<th>Material</th>
<th>Deposition Technique</th>
<th>Device</th>
<th>Feature of Passivation</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anodic Oxide</td>
<td>3% Tartaric Acid Propylene Glycol (1:3)</td>
<td>InP MOSFET</td>
<td>Annealing &gt; 300 °C, Interface State Density (Nss) increase. At 200 °C, Nss decrease.</td>
<td>24</td>
</tr>
<tr>
<td>Langmuir Blodgett</td>
<td>22-tricosanoic Acid Dip down-up in L-B trough</td>
<td>GaAs MIS</td>
<td>Interface trap density lower than Anodic Oxide.</td>
<td>25</td>
</tr>
<tr>
<td>Langmuir Blodgett</td>
<td>Cadmium stearate or Arachidate in L-B trough</td>
<td>InGaAs PD</td>
<td>Increase Schottky-barrier height.</td>
<td>26</td>
</tr>
<tr>
<td>(Na$_2$S)$_9$H$_2$O</td>
<td>Spin Coating</td>
<td>GaAs HBT</td>
<td>Increase Current gain 60, PL intensity 250.</td>
<td>27</td>
</tr>
<tr>
<td>(Na$_2$S)$_9$H$_2$O</td>
<td>Dip, Spin Dry</td>
<td>GaAs pn</td>
<td>Reduce recombination current. Shunt laekage at low forward. Aging due to atmospheric humidity.</td>
<td>28</td>
</tr>
<tr>
<td>(NH$_4$)$_2$S</td>
<td>Dip, N$_2$-dry</td>
<td>GaAs pn</td>
<td>Reduce recombination current. No shunt leakage.</td>
<td></td>
</tr>
<tr>
<td>P$_2$S$_5$/(NH$_4$)$_2$S</td>
<td>Dip, N$_2$-dry</td>
<td>GaAs MSM-PD</td>
<td>Reduce reverse leakage current. Barrier height enhancement. Increase responsivity.</td>
<td>29</td>
</tr>
</tbody>
</table>
2.4.1. Anodic Oxide

Although the growth of an anodic oxide on III-V compounds is a quick and easy technique, the mechanism of anodization is complex and many details of process are not well understood [30]. The procedure of anodization is to connect a semiconductor in which the anodic oxide grows to the positive terminal of a battery and then dip the structure into an appropriate electrolyte solution along with an inert electrode connected to the negative terminal of the battery. As the oxide is growing on the semiconductor surface, the resistance due to the oxide increases. This oxide resistance is often highly nonlinear and decreases with the applied voltage. The growth of a thick oxide at room temperature requires a very high electric field across the oxide, and under this condition the oxide resistance is relatively low compared to that of a good insulator. For the anodization of GaAs, a few percent of tartaric or citric acid is added to the water. Thus both the mass and charge are transported in the electrolyte. The following four parameters have to be considered to use an electrolyte: the viscosity of the electrolyte, the current density during growth, the anion species, and the PH of the electrolyte. In order to accelerate the reaction, a strong light with energies greater than the bang gap of the semiconductor is sometimes used. The anodic oxide technique has been used to fabricate MIS structure on GaAs by various researchers [31].

2.4.2. Langmuir-Blodgett Film

When a material composed of molecules which are polar at one end and also contain a sufficiently large hydrophobic region (usually a long (CH₂)n chain) is introduced (usually from solution) onto a water surface, it may form a monomolecular layer rather than merely dissolving or forming an insoluble precipitate or lens. Such a layer can be compressed until it forms a quasi-solid which is one molecule thick, and
within which the long chains are generally being lined up touching and nearly normal
to the surface [32]. If a suitable substrate is then repeatedly dipped through the wa-
ter surface (the surface pressure being maintained with a suitable device), then with
appropriate monolayer materials one monolayer may be transferred to the substrate
on each excursion through the water surface. A film of great perfection can thus be
built up monolayer by monolayer. Such films, which classically have employed fatty
acids or other long chain aliphatic materials, are usually referred to as Langmuir-
Blodgett (LB) or Langmuir films; other names include monolayer (or monomolecule)
films, multilayers and built-up films.

There has been much interest in the incorporation of LB films into semicon-
ductor devices because it has been shown to exhibit good insulating properties with
high breakdown strengths, and to deposit readily onto semiconductor surfaces. III-V
compounds, which do not possess a natural oxide of the required quality, have had
great difficulty in the past in obtaining a satisfactory insulator layer by conventional
techniques, whereas silicon already has a good insulating oxide. Several groups [26]
employed LB films to passivate GaAs and InP, and demonstrated the capability of
forming excellent insulating LB films with low surface state densities on GaAs and
InP surfaces. This is of great significance with regard to the prospect for using LB
films in a number of practical devices, although the films have many problems which
must be solved before serious commercial applications can be implemented.

2.4.3. Sulfur Compounds

The sulfide chemical treatment as a surface passivation for GaAs has received
considerable attention in the technical literature recently [1,27,28,33]. Various prop-
erties of this passivation have been demonstrated, including the dramatic reduction
of the surface recombination and the possible reduction of elemental arsenic which is
presumably the source of the surface states [10]. Additionally, a tremendous increase in the heterojunction bipolar transistor (HBT) current gain is observed after the treatment due to a reduction in the perimeter recombination current of the emitter-base junction [27]. Several groups claimed that this treatment unpinned the GaAs surface. However, after several electrical and spectroscopic methods have been used to characterize the effects of treatments, contradictory results have been observed. In fact, the large reduction in surface recombination velocity is accompanied by a Fermi level movement toward the valence band edge instead of moving toward the flatband condition. Furthermore, also the Fermi level is still pinned. Spindt et al. [34] explained this contradiction using AUDM. In this model, the Fermi level position will be determined by the number of donors, \(N_d\), and compensating acceptors, \(N_a\). Svensson et al. [35] found there was some dependence of the barrier height on the surface As/Ga ratio. The trend was a higher barrier height on n-GaAs by creation of a lower As/Ga ratio and a lower barrier height for a higher surface As/Ga ratio. This result was also confirmed by the work of Wang [36]. Before the sulfide treatment, the Fermi level was pinned somewhere between the two donor levels formed by As\(_{Ga}\) antisite defects depending upon the compensation of GaAs acceptor levels. By supposing that the sulfur reduces some of the excess As, then one can see that it will allow the GaAs compensators to move the Fermi level down toward the lower donor level. Therefore, the band bending of a sulfur treated surface is increased. Thus far, this explanation is the most reasonable.

Recently, Olego et al. [37] used amorphous phosphorus for passivating the GaAs surface. It has been observed that 300 Å of amorphous phosphorus deposited in a molecular beam epitaxy apparatus at room temperature provides physical and chemical continuity to the GaAs surface because of its polymeric nature. When deposited at temperatures below 200°C, its microscopic network is layer-like with a small num-
ber of dangling bonds. The arrangement of the phosphorus atoms in the layers closely mimics the atomic patterns of III-V surfaces. The amorphous phosphorus is a high resistivity semiconductor that has also shown excellent interfacial properties with InP surface, producing a low density of states near the conduction band. From Raman and Photoluminescence (PL) spectroscopy, it has been found that the amorphous phosphorus lowered the barrier height from 0.7 to 0.18 eV and reduced the surface recombination velocity by one order of magnitude on a GaAs surface.
CHAPTER THREE
A STUDY OF NEW SURFACE PASSIVATION USING P$_2$S$_5$/(NH$_4$)$_2$S ON GaAs

3.1. Introduction

Recently, there has been considerable interest in developing new passivation techniques for reducing the surface state density on GaAs surface. Due to the pinning of the surface Fermi level near the middle of the forbidden gap, the barrier height of a GaAs Schottky diode is almost independent of the metal work function. The GaAs metal-insulator-semiconductor field-effect transistor (MISFET) could not be realized due to this large surface state density. To reduce the surface state density, different approaches, such as the sputtering etch on the surface with nitrogen [38], light induced photochemical wash of GaAs surface [39] and surface treatment by chemisorbed ruthenium [40], have been investigated. Although some promising results on passivation of the GaAs surface by sulfide solution treatment have been reported, these studies revealed only temporary improvement. For example, Sandroff et al. [27] have reported that (Na$_2$S).9H$_2$O passivation on GaAs not only enhanced the photoluminescence (PL) intensity, but also improved the current gain of a GaAs heterojunction bipolar transistor (HBT). However, the improvement in the current gain of their GaAs HBT would persist only for a few days. Other groups [28,41] have also reported that (NH$_4$)$_2$S or (NH$_4$)$_2$S$_2$ passivation on GaAs surface produces a similar reduction in surface state density as that of the (Na$_2$S).9H$_2$O treatment, with better stability. More recently, Lee et al. [1] reported that P$_2$S$_5$ passivation also increased the PL intensity by a factor of 5, and its intensity persisted for ten days after exposure to the air.
3.2. Approach

In this chapter, a new surface passivation study using \( \text{P}_2\text{S}_5/(\text{NH}_4)_2\text{S} \) (0.02g/ml) on GaAs is reported, and the results are compared with other types of surface treatments (e.g., \((\text{NH}_4)_2\text{S}_x\)). An n-type GaAs Schottky diode was used as a test structure to evaluate the effects of these two different surface passivations on the reverse leakage current of GaAs Schottky diodes. These passivation schemes were then applied to the metal-semiconductor-metal (MSM) GaAs Schottky-barrier photodiodes. To improve the responsivity of a photodiode, the reverse leakage current should be minimized. Even though the MSM photodiodes have a very small capacitance due to the planar structure, the performance of these photodiodes is highly dependent on the surface condition. This is due to the fact that one Schottky-barrier contact of the MSM photodiodes is always reverse-biased. As a result, the noise in an MSM photodiode is always limited by the reverse leakage current and the surface state density.

The Schottky diodes used in this study were fabricated on a 2 \( \mu \text{m} \) thick n-GaAs epilayer \((N_d = 6 \times 10^{15} \text{ cm}^{-3})\) grown on n\(^+\)-GaAs substrate by molecular-beam epitaxy (MBE). The samples were first degreased in trichloroethane(TCE), acetone, methanol, and de-ionized water, and were then blown dry with nitrogen gas. The ohmic contact was formed on n\(^+\)-GaAs substrate by evaporating Au-Ge/Ni/Au (1000/200/2000 Å) and by alloying at 450 °C for 1 min. The finished diodes were then etched in \( \text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O} \) (20:7:100) for 15 sec., followed by a brief dip in buffered HF (BOE) to remove the native oxide on the GaAs surface prior to surface passivation. These diodes were then immersed directly into the \( \text{P}_2\text{S}_5/(\text{NH}_4)_2\text{S} \) (0.02g/ml) or \((\text{NH}_4)_2\text{S}_x\) containing 6 % excess sulfur passivation solution for 30 sec. After the diodes were taken out, the surface was blown dry with nitrogen, and quickly loaded into an electron-beam evaporator. The unpassivated reference diodes were also loaded in the electron-beam chamber to be used later for comparison with the passivated diodes.
The gold and aluminum (2000 Å) Schottky contacts with a diameter of 400 μm were evaporated separately on the passivated or chemically etched GaAs surface. MSM photodiodes were fabricated on an n-GaAs epilayer \( (N_d = 1 \times 10^{16} \text{ cm}^{-3}) \) grown on a S.I.-GaAs substrate by liquid phase epitaxy (LPE). Gold contacts (2000 Å) were made by electron-beam evaporation and conventional lift-off process. Gold fingers are 8 μm wide by 200 μm long with an interelectrode spacing of 12 μm (Fig. 3.1). These diodes have gone through the same chemical etching and passivation procedures before metal deposition. Each sample thus prepared was then immersed directly into each passivation solution again and blown dry.

### 3.3. Result and Discussion

The current-voltage (I-V) characteristics were measured using an HP4140B pA meter. Figures 3.2 and 3.3 show the forward and reverse I-V curves for both the Au- and Al-GaAs Schottky diodes, respectively. The forward log \( J_F \) vs. \( V \) data for all the diodes studied are on a straight line except in the high current density regime where series resistance effect becomes dominant. It is noted that both the Au- and Al-Schottky contacts formed on the different passivated GaAs surfaces showed a large variation of the current densities, which can be observed only when the density of surface states is low. The new \( P_2S_5/(NH_4)_2S \) passivated Au/GaAs diodes have a lower forward and reverse current densities than that of the \( (NH_4)_2S_x \) passivated GaAs diodes. The lowest reverse leakage current density of 4.6 nA at -5 V was observed in the \( P_2S_5/(NH_4)_2S \) treated Au/GaAs Schottky diode, which has a reverse leakage current density more than one order of magnitude lower than the unpassivated diodes.

The barrier height \( \Phi_{bn} \) and the ideality factor were determined from a least-square fit of the linear portion of the forward I-V curve using the expressions [42]:

\[
\Phi_{bn} = \left( \frac{kT}{q} \right) \ln \left( \frac{A \cdot T^2}{J_s} \right) \tag{3.1}
\]
Figure 3.1  Top view of the MSM Schottky barrier photodiode.
Figure 3.2  Forward-bias current-voltage (I-V) characteristics for the passivated and unpassivated Au- and Al-GaAs Schottky diodes.
Figure 3.3 Reverse-bias current-voltage (I-V) characteristics for the same diodes shown in Fig. 3.2.
\[ n = \frac{q}{k_B T \partial (\ln J)} \] 

(3.2)

where \( A^* = 4 \pi q m^* k_B^2 / h^3 \) is the effective Richardson constant (8.16 A/cm\(^2\)K\(^2\) for GaAs) for the thermionic emission, and \( J_\text{s} \) is the reverse saturation current density. The capacitance-voltage (C-V) characteristics were measured at 1 MHz using an HP4280A capacitance meter. The built-in voltage of the Schottky diode was determined from the \( 1/C^2 \) vs. reverse bias voltage plot, as shown in Fig. 3.4, and the effective barrier height is then calculated from the expression [42]:

\[ \Phi_{\text{Bn}} = V_1 + V_n + \frac{k_B T}{q} \] 

(3.3)

where \( V_1 \) is the built-in voltage, and \( V_n \) is the potential difference between the Fermi level and the conduction band edge. The C-V characteristics for these GaAs Schottky diodes were also shown that \( P_2 S_5/(NH_4)_2 S \) passivated surface had a higher barrier height than that of the \( (NH_4)_2 S_x \) passivated surface. The effective barrier height, the saturation current density, and the ideality factor for the diodes studied are summarized in Table 3.1. From the Table 3.1, it was found that the Schottky barrier height determined from C-V measurements was different from the one obtained from I-V measurements. This difference was observed on the commonly used materials such as Si, GaAs, and InP. Crowell and Rideout [43] claimed that this difference is due to the influence of thermionic field emission on the charge transport through the interface. Srivastava and Arora [44] attributed the barrier height difference to an interfacial and/or interface states. Song et al. [45] explained the difference by introducing a Gaussian distribution of barrier height over the contact area and a temperature dependence of the real barrier height. It has also been suggested that the surface contamination, deep level impurity, and edge leakage current cause the difference of the measurements. In this passivation study, however, the most plausible explanation
Figure 3.4  $1/C^2$ vs voltage plot for the same diodes shown in Fig. 3.2.
Table 3.1  Values of saturation current densities \((J_s)\), ideality factors \((n)\), and effective barrier heights \((\Phi_{Bn})\) for the Au- and Al-GaAs Schottky diodes determined from the I-V and C-V measurements.

<table>
<thead>
<tr>
<th>Surface treatment</th>
<th>Metal</th>
<th>(J_s) ((A/cm^2))</th>
<th>(n)</th>
<th>(\Phi_{Bn}) (I-V) ((V))</th>
<th>(\Phi_{Bn}) (C-V) ((V))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P_2S_5/(NH_4)_2S)</td>
<td>Al</td>
<td>(5.12 \times 10^{-7})</td>
<td>1.04</td>
<td>0.72</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>(2.18 \times 10^{-11})</td>
<td>1.03</td>
<td>0.99</td>
<td>1.09</td>
</tr>
<tr>
<td>((NH_4)_2S_x)</td>
<td>Al</td>
<td>(2.53 \times 10^{-6})</td>
<td>1.08</td>
<td>0.68</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>(1.85 \times 10^{-10})</td>
<td>1.03</td>
<td>0.93</td>
<td>0.97</td>
</tr>
<tr>
<td>(NH_4OH/HF)</td>
<td>Al</td>
<td>(2.09 \times 10^{-8})</td>
<td>1.05</td>
<td>0.81</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>(3.12 \times 10^{-10})</td>
<td>1.02</td>
<td>0.92</td>
<td>0.93</td>
</tr>
</tbody>
</table>
for the difference is the effect of the surface nonuniformities of the passivation layers. The densities of the interface states \(D_s\) for these diodes were calculated by using the data given in Table 3.1 and the following equations [46]:

\[
\Phi_{Bn} = C_2 \Phi_m + C_3 \quad (3.4)
\]
\[
D_s = 1.1 \times 10^{13} \frac{(1 - C_2)}{C_2} \quad (3.5)
\]

where \(\Phi_m\) is the work function of metal. Our calculated values are \(D_s = 9.46 \times 10^{12}/\text{cm}^2\text{eV}\) for the \(P_2S_5/(NH_4)_2S\) treated GaAs surface, and \(D_s = 4.76 \times 10^{13}/\text{cm}^2\text{eV}\) for the etched surface. The reduction of the surface state density \(D_s\) is by a factor of 5 for the former case.

The spectral response of the passivated MSM photodiodes was measured by using a Digikrom 240 monochromator and tungsten light source. The optical power of the incident radiation divided by a beam splitter (50:50) was focused on a reference detector and on an MSM photodiode. The source was chopped at a 35-Hz rate to eliminate the effects of background signals and ambient variations. The detected signals were recorded as a function of wavelength with a phase-sensitive “lock-in” amplifier. Figure 3.5 shows the spectral response for each different surface treatment. From this curve, it is noted that the \(P_2S_5/(NH_4)_2S\) treated photodiode shows the highest responsivity.

The passivation mechanisms for these sulfur compounds on GaAs surface can be explained in two different ways. One theory is that sulfur compounds actively react with residual native oxide and arsenic segregated from \(As_2O_3\) molecules by gallium atoms which thereby form \(Ga_2O_3\). This molecule (\(Ga_2O_3\)) is very easy to form because it has a higher heat of formation than \(As_2O_3\). The sulfur compounds are then able to etch out the oxide and arsenic, and form a monolayer of stable sulfur complexes with elemental arsenic and gallium atoms on the oxide-free GaAs surface.
Figure 3.5  Spectral response of passivated and unpassivated GaAs metal-semiconductor-metal photodiodes.
Thus, the arsenic and gallium vacancies which are the cause of interface states on GaAs surface, according to unified defect model (UDM)[9], are no longer present on the surface. As a result, the Fermi level is unpinned. Another interpretation is based on the advanced unified defect model (AUDM)[14]. In this model, the main source of interface states is due to $\text{As}_{\text{Ga}}$ (As atom on Ga site) antisite defect which has two donor levels. The Fermi level lies between the two donor levels, and its position depends on the compensation of $\text{As}_{\text{Ga}}$ by $\text{Ga}_{\text{As}}$ (Ga atom on As site) antisite defect which has two acceptor levels. As the sulfur compounds reduce the arsenic atoms, the Fermi level moves down towards the lower donor level, and band bending therefore increases on n-type GaAs. As for increasing the rate of compensation, or to enhance the passivation effect, $\text{P}_2\text{S}_5/(\text{NH}_4)_2\text{S}$ is superior to $(\text{NH}_4)_2\text{S}_x$ because the phosphorus oxide has a higher heat of oxide formation than that of gallium oxide. Therefore, the phosphorus helps in the segregation of gallium from $\text{Ga}_2\text{O}_3$ in addition to the segregation of arsenic from $\text{As}_2\text{O}_3$ on the surface. While the gallium atoms compensate the $\text{As}_{\text{Ga}}$ antisite defect, sulfur reduces some of the excess arsenic and is thereby able to form stable sulfur complexes. From the I-V and C-V characteristics of the passivated Al- and Au-GaAs Schottky diodes, it is shown that the $\text{P}_2\text{S}_5/(\text{NH}_4)_2\text{S}$ surface passivation is better than that of $(\text{NH}_4)_2\text{S}_x$. Also, from the spectral response curve, it is shown that the $\text{P}_2\text{S}_5/(\text{NH}_4)_2\text{S}$ passivated GaAs MSM photodiode has the highest relative spectral responsivity. Thus, the result of I-V data is consistent with that of the spectral response measurement. The barrier heights of the passivated Schottky diodes are dependent on the metal work function as shown in Fig. 3.6.

The Schottky barrier height of Al-GaAs is lower than that of the unpassivated diode. Massies et al.[47] have formed Al - GaAs Schottky by depositing aluminum in situ in a MBE system on a MBE - grown (100) GaAs epilayer exposed to $\text{H}_2\text{S}$. These Schottky barriers are much lower than the barriers formed by depositing aluminum
Figure 3.6 Barrier heights vs metal work functions on the passivated and the unpassivated surfaces.
directly on an as-grown epilayer. This study showed that a ratio of 0.02 g of P$_2$S$_5$ to 1 ml of (NH$_4$)$_2$S yielded the best result. It is important to point out that the observed change of barrier height in both the Au- and Al-GaAs Schottky diodes clearly indicates that the density of surface states was reduced significantly in the passivated devices. To study the long term stability, the P$_2$S$_5$/(NH$_4$)$_2$S-treated diodes were exposed to the air, and measured again over a period of few weeks. There was no observable change in diode characteristics, implying that this passivation was very stable.

3.4. Summary and Conclusion

In summary, the effects of P$_2$S$_5$/(NH$_4$)$_2$S surface treatment on the diode characteristics of Al- and Au-Schottky contacts formed on n-type GaAs have been investigated and compared with that of (NH$_4$)$_2$S$_x$ and NH$_4$OH/HF treatment. The Schottky contact formed on the P$_2$S$_5$/(NH$_4$)$_2$S-treated surface showed a higher barrier height than that of (NH$_4$)$_2$S$_x$-treated surface. The increase of the effective barrier height is attributed to phosphorus which enhances the compensation of As$_{Ga}$ antisite defect at the GaAs surface. Also, the effects of a P$_2$S$_5$/(NH$_4$)$_2$S and (NH$_4$)$_2$S$_x$ treatment on the dark current of MSM GaAs Schottky photodiodes have been investigated. The dark current on the passivated surface has been reduced, and as a result, the passivated MSM photodiodes show an improved spectral responsivity. Therefore, the passivation techniques presented here are very useful for improving the performance of photonic devices. These results clearly show that the surface of GaAs was effectively passivated and stabilized by the new P$_2$S$_5$/(NH$_4$)$_2$S treatment.
CHAPTER FOUR
XPS STUDY OF PASSIVATION LAYER ON GaAs SURFACE

4.1. Introduction

From the electrical and optical characterizations discussed in Chapter three, it is seen that the $P_2S_5/(NH_4)_2S$ treated surface shows more improved passivation than that of $(NH_4)_2S_2$. To understand this, it is important to analyze the passivated surface with other analytical tools to see the chemical constitution of the treated surface.

X-ray photoelectron spectroscopy (XPS) is considered as one of the most important techniques for studying the chemical bonding within the passivation layer formed on GaAs. This is due to the fact that XPS studies of passivation layers formed on GaAs point out that the core shifts measured in these studies serve to distinguish between the various states of the Ga and As atoms [48,49,50]. This chapter presents the XPS and Auger Electron Spectroscopy (AES) studies of $P_2S_5/(NH_4)_2S$ passivation layers formed on GaAs (100) surface. The knowledge of the sulfur- and phosphorus- induced overlayers and the way they terminate the GaAs is important to better understand the physics and chemistry behind the decrease in surface states.

4.2. Basic Principles of X-ray Photoelectron Spectroscopy (XPS)

When electromagnetic radiation of sufficient optical energy is incident on a material, electrons in the material absorb energy from the light and emission of electrons is observed. This phenomena is called the "photoelectric effect". Emission of photoelectrons is a very direct way of obtaining information which is characteristic of atoms.
Provided that the exciting energy is high enough, the core level spectra can be obtained for all elements of the periodic table except for hydrogen and helium (since these have no core levels), and the determined binding energies of these core levels are sufficiently unique for their unambiguous assignment. The ionization energy (or binding energy) of core electrons are essentially constant, within narrow limits, and characteristic of the atom concerned. They are sufficiently characteristic that there is usually no uncertainty in the assignment of the various signals in a complex XPS spectrum. XPS therefore finds application as a surface analysis technique. While it is true that the core ionization energies of a particular atom are sufficiently invariant to provide a characteristic of the atom, there are nonetheless small but measurable changes within the chemical environment of the atom. In other words, core electron ionization energies show a chemical shift effect when data from a range of compounds containing the atom in question are compared. When atoms of a given element are present in a sample as more than one type (i.e. differing oxidation state, chemical environment, etc.) they may have differing binding energies and give rise to multiple peaks. These peaks are often not separated sufficiently to appear well resolved. In order to obtain accurate peak positions and areas it is necessary to resolve the multiplet envelope into its component single peaks. This operation is referred to as curve resolution or deconvolution. One drawback inherent in the use of chemical shift data is the general lack of reproducibility from laboratory to laboratory of charging effects and their corrections. This charging effect is an equilibrium phenomenon determined by: (i) the rate at which electrons are ejected from the sample surface and (ii) the rate at which stray electrons in the vacuum, and electrons conducted from earth through the bulk interior of the sample, arrive at the sample surface to neutralize the positive holes. The steady-state current conditions are normally such that there is an equilibrium positive charge on the surface of a sample during the experiment. The trouble
with sample charging is that it influences apparent ionization energies. The sample charging effect tends to bedevil the accurate measurement by photoelectron spectrum of electron binding energies in solids. A further and more serious problem arises if there is inhomogeneous charging of the sample surface. This can lead to extensive broadening or even a multiplication of individual photoelectron signals. The resolution problem in XPS is however much less severe when core electrons are studied, since core photoelectron signals are rather broad and one is normally dealing with substantially lower photoelectron kinetic energies than in the case of valence electron ionization. Nonetheless, it is usually found that binding energies from elements in a range compounds fall into ‘bands’ which can be associated with formal oxidation states. The nondestructive determination of oxidation states in the solid state from a single parameter represents a major analytical advance, especially when this relates to the surface of materials. Mg Kα (1253.6 eV) X-rays satisfy this requirement and are commonly used excitation sources. The photoelectrons can escape from only a very short distance beneath the surface (e.g. 20 Å or so). As applied to solids, photoelectron spectroscopy is thus a surface sensitive technique. When one is interested in the surface of a material rather than its bulk, photoelectron spectroscopy can provide information about the surface states of the solids. It has indeed already been proved as a powerful technique to study the surface science. A large number of core levels available for study coupled with the range of information levels from a single experiment are the main advantage of the XPS technique [51].

4.3. Experiment

The samples used in this study are 2 μm thick n-GaAs epilayer ($N_d = 6 \times 10^{15}$ cm$^{-3}$) grown on $n^+$-GaAs substrate by molecular-beam epitaxy (MBE), which are the same samples used in the electrical characterization. The samples were first
degreased in trichloroethane (TCE), acetone, methanol, and de-ionized water, and were then blown dry with nitrogen gas. The cleaned samples were then etched in NH$_4$OH:H$_2$O$_2$:H$_2$O (20:7:100) for 15 sec., followed by a brief dip in buffered HF (BOE) to remove the native oxide on the GaAs surface prior to surface passivation. These samples were then immersed directly into the P$_2$S$_5$/(NH$_4$)$_2$S (0.02g/ml) passivation solution for 30 sec. After the samples were taken out, the surface was again blown dry with nitrogen. The samples were then introduced to the spectrometer. X-ray photoelectron spectra were recorded on a Perkin-Elmer PHI-5100 spectrometer. The X-rays employed in XPS were the Mg K\(\alpha\) (\(h\nu = 1253.6\) eV) lines emitted by magnesium when the metal is bombarded with high-energy electrons (The designation K\(\alpha\) indicates the emission process 2p\(\rightarrow\)1s subsequent to creation of a 1s or K hole by electron impact). These K\(\alpha\) X-rays are relatively soft – that is, of low photon energy. The Mg X-ray was operated at 15 KV and 300 W. Background pressure in the analysis chamber was always less than 1 \(\times\)10\(^{-9}\) Torr. To improve the surface sensitivity of the measurements, the ejection angle of the detected photoelectrons measured from the surface normal of the sample, \(\theta\), was taken at two angles, 15° and 45°. Since electron mean free paths and hence sampling depths are so short, changing to a higher take-off angle (i.e., 15°) specifically enhances surface features. A comparison of spectra recorded at two different take-off angles provides a means of interpreting the vertical homogeneity of the sample. In order to see the changes of the chemical composition with time for the P$_2$S$_5$/(NH$_4$)$_2$S treated surface, the spectra of the angle-resolved XPS have been collected from three samples. The first sample (sample 1) is unpassivated, the second one (sample 2) is exposed in the ambient environment for one day after the surface treatment, and the third one (sample 3) is exposed in air for five months after the surface passivation. Auger depth profiles were taken on the passivated samples which had been exposed in air for three months.
4.4. Results and Discussion

XPS spectra were collected from different energy regions of the sample, in the vicinity of the Ga 3d (14 ~ 24 eV), As 3d (30 ~ 50 eV), and P 2p (127 ~ 147 eV) core states. High resolution data were expanded and fitted with Gaussian/Lorentzian curves so as to aid the assignment of components in the spectra of passivated surface on the basis of the chemical shifts. The Ga and As 3d photoelectron lines are useful for the quantitative chemical analysis of the overlay formed by the either oxidation or passivation of GaAs because they are strong signals and overlapped by no others. All the binding energies coded are referenced to the binding energy C 1s peak at 284.6 eV. Therefore, other spectra have been shifted by the offset value. Figure 4.1 shows the overall survey of the passivated surface to select and study a specific range of binding energy. The spectrum of C 1s of sample 2 shows the overlap of several different carbons at both take-off angles (Fig. 4.2). This is probably from the sample mounting stage or contamination which was not unexpected given the methods of preparation, transportation, storage and handling of the sample. Note that all spectra shown here were corrected by subtracting the appropriate linear background from the experimental curves which were taken using pulse counting and signal averaging.

As shown in Fig. 4.3, the Ga 3d level of sample 1 appears to have two components, one due to electrons originating from bulk (Ga atoms in GaAs epilayer), and another at higher binding energy due to Ga bonded to oxygen. For the bare surface (sample 1 in Fig. 4.3), the spectra are the same at both angles, which indicates the native oxide on the air-exposed side has the same chemical composition as the oxide close to the semiconductor surface whereas the spectra of sample 2 exhibit the dependence on the angle.

The Ga 3d spectrum of the sample 2 at 45° (Fig. 4.3 (b)) shows almost no oxide peak. On the other hand, there exists a small oxide peak at 15° (Fig. 4.3
Figure 4.1 GaAs XPS survey spectra for bare surface (sample 1), 1 day after passivation (sample 2), and 5 months after passivation (sample 3).
Figure 4.2  C 1s high resolution spectra for 2 samples.
Figure 4.3 (a) Ga 3d expanded and curve fitted spectra at 15° take-off angle.
Figure 4.3 (b) Ga 3d expanded and curve fitted spectra at 45° take-off angle.
(a)). The reason is that the heats of formation for Ga$_2$O$_3$ and P$_2$O$_5$ are high enough that these species are easily formed on the air-exposed surface. Therefore, the air-exposed passivated surface is easily oxidized, and less oxide exists toward the interface between the passivation layer and the GaAs epilayer. As a result, the Ga-O peak is found at high take-off angle. It is noted that the oxygen on the outside surface penetrates toward the semiconductor surface gradually and the passivation layers become oxidized with time as shown in the spectra of sample 3 (Fig. 4.3). When comparing the spectra of sample 2 with that of sample 1 in Fig. 4.3, the spectra at 45° exhibit a strong passivation effect of the P$_2$S$_5$/$(NH_4)_2$S on the surface. Even though the width of FWHM and the peak shape of the Ga 3d state (substrate) in sample 2 seem to be one peak from the underlying GaAs surface, the peak should be overlapped with the Ga 3d line of Ga-S. This is due to the fact that the heats of formation of the likely compounds of gallium and arsenic with sulfur, phosphorus, and oxygen (Table 4.1) show that the bulk Ga-S reaction is energetically favored over the As-S reaction. Also, published result [70] showed that the Ga-S bonding is stronger than the As-S bonding. However, smaller spin orbit splitting and binding energy shift of Ga cannot resolve the Ga 3d$_{5/2}$ and 3d$_{3/2}$ levels on a clear sulfide peak. As shown in Fig. 4.4, the spectra of As 3d of sample 2 exhibit a clear peak of As-S bonding, which indirectly supports the existence of the Ga-S bonding. The peaks due to oxidized Ga were reported to be shifted by about 0.9 eV from the bulk GaAs component, compared to the 0.55 eV shift seen on Ga-S components. The peaks shifted by ~ 2 eV at 15° and 1.73 eV at 45° from the substrate in the spectra of the sample 3, which are probably due to contribution from Ga-oxygen bonding, seem to be at higher binding energy than the peaks from Ga-O in the spectra of the sample 1 and 2. This is due to the fact that the chemical constitution of the passivation layer changes with time owing to the oxidation. But Grunthaner et al.[52] have investigated the spectrum of the Ga
3d state in the thin oxides and have concluded that it has at least two components, one at 1.3 eV and the second at 1.9 eV. Nishitani et al.[71] observed that the chemical shift of Ga 3d of GaP-oxide is 2 eV from the substrate, and also identified that the spectrum of the Ga 3d photoelectron from the GaP surface exhibited similar features to that from the GaAs surface. Comparing with published data and referring to the spectra of P 2p, the peak at higher binding energy is due to the contribution of Ga 3d electrons from GaPO₄ or GaPOₓ.

The photoemission spectra for the As 3d are shown in Fig. 4.4, along with its decomposition into substrate and reacted component. In sample 1, the As 3d core level of substrate has a peak centered at 40.33 eV, and another at 43.44 eV, which is at ~ 3 eV higher binding energy from the substrate peak. This peak is due to As-O compound (probably As₂O₃), and is believed to be the main source of the surface or the interface states. The reported XPS data [50,53] suggest two oxidation states for As atoms, one characterized by a chemical shift of 2.9 ~ 3.1 eV (As₂O₃), and the second by a large shift of 4.6 eV (As₂O₅). Formation of As₂O₅ is more favorable than that of As₂O₃ due to the higher heat of formation of As₂O₅. However, there was no peak appearing on the high binding energy side (i.e., either 2.9 ~ 3.1 or 4.6 eV) of the As 3d unshifted peak from the spectra of sample 2 as shown in Fig. 4.4. It is clearly shown that there is no arsenic oxide on the passivated surface. The absence of the As oxide peak from the spectrum of the P₂S₅/(NH₄)₂S -treated sample clearly indicates that the phosphorus atoms in the vicinity of the arsenic oxide gradually extract oxygen from the arsenic oxide to form phosphorus oxide. On the other hand, elemental arsenic atoms, which, as previously mentioned, are the major cause of surface states, are bonded to sulfur. As a result, it is expected that the density of surface states is considerably reduced on the surface after passivation. As speculated before, a clear peak of As-S compound species (probably As₂S₃) has been shown from the spectra of
Table 4.1  The heats of formation (Kcal/mole) of various compounds.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Heats of Formation (Kcal/mole)</th>
<th>Compounds</th>
<th>Heats of Formation (Kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga$_2$O$_3$</td>
<td>-258</td>
<td>As$_2$O$_3$</td>
<td>-156</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>-356</td>
<td>As$_2$O$_5$</td>
<td>-186</td>
</tr>
<tr>
<td>P$_2$O$_3$</td>
<td>-196</td>
<td>In$_2$O$_3$</td>
<td>-221</td>
</tr>
<tr>
<td>InPO$_4$</td>
<td>-300</td>
<td>Ga$_2$S$_3$</td>
<td>-120</td>
</tr>
<tr>
<td>As$_2$S$_3$</td>
<td>-40</td>
<td>In$_2$S$_3$</td>
<td>-101</td>
</tr>
<tr>
<td>In$_5$S$_6$</td>
<td>-227</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.4 (a)  As 3d expanded and curve fitted spectra at 15° take-off angle.
Figure 4.4 (b) As 3d expanded and curve fitted spectra at 45° take-off angle.
sample 2 (Fig. 4.4). This chemical shift, which is 1.8 ~ 1.9 eV shift referenced to the peak of the substrate, is characteristic of an As-S compound. Spindt et al.[70] used surface sensitive synchrotron radiation photoemission spectroscopy and observed a chemically shifted component due to sulfur bonding at 1.7 eV toward higher binding energy. From the spectra of sample 3, it was observed that the passivated surface became oxidized when the sample was exposed to the air. A more important and encouraging observation from this spectra is that there still exists As-S species close to the substrate, not the air-exposed top surface.

The spectrum of the P 2p level shown in Fig. 4.5 has one broad peak. Although there are many possible species during the passivation via the following chemical reactions, it seems unlikely that phosphorus oxides (P₄O₆, P₄O₁₀) would exist for any length of time on samples because P₄O₁₀ readily sublimes at ambient temperature under the conditions of XPS experiment.

\[
\begin{align*}
\text{Ga}_2\text{O}_3 + \text{P}_2\text{O}_5 & \rightarrow 2\text{GaPO}_4 \quad (4.1) \\
\text{P}_2\text{S}_5 + 2\text{As}_2\text{O}_5 & \rightarrow \text{P}_2\text{O}_5 + \text{As}_2\text{S}_5 \quad (4.2) \\
2\text{P}_2\text{S}_5 + 2\text{Ga}_2\text{O}_3 & \rightarrow \text{P}_4\text{O}_6 + 2\text{Ga}_2\text{S}_3 + 4\text{S} \quad (4.3) \\
2\text{P}_2\text{S}_5 + 2\text{As}_2\text{O}_3 & \rightarrow \text{P}_4\text{O}_6 + 2\text{As}_2\text{S}_3 + 4\text{S} \quad (4.4) \\
\text{P}_4\text{O}_6 + 4\text{S} & \rightarrow \text{P}_4\text{O}_6\text{S}_4 \quad (4.5)
\end{align*}
\]

As shown in Fig. 4.5, the spectra of P 2p of sample 2 are not symmetric, but they appear to be an overlap of two peaks. One at the higher binding energy is definitely from the phosphorus oxide compound and the other at lower energy probably from the elemental phosphorus. The peaks at ~ 134 eV for all samples probably consist of GaPO₄ due to the high heats of formation of Ga₂O₃ (-258 Kcal) and P₂O₅ (-345 Kcal). Lucovsky [53] suggested two possible bonding models for P₂O₅ + Ga₂O₃. In
Figure 4.5 (a) P 2p expanded and curve fitted spectra at 15° take-off angle.
Figure 4.5 (b) P 2p expanded and curve fitted spectra at 45° take-off angle.
fact, he exhibited from experimental results that the relaxed structure of Fig. 4.6 (b) is more favorable than the structure of Fig. 4.6 (a). He stated that this type of network requires a very high degree of chemical ordering. However, it should be kept in mind that the phenomena involved in the oxidation are more complicated than these equations may suggest. Furthermore, the surface chemistry of oxides of phosphorus is somewhat complicated by the possibility of the presence of surface nitrogen-bonded species etc, because phosphorus pentoxide reacts with ammonia to give a white powdery solid of unknown structure containing both P-N-P as well as PONH\textsubscript{4} during treatment.

In order to observe the presence of sulfur after the passivated samples were exposed in air, sulfur Auger spectra were collected because the XPS spectra of S 2p and S 2s are overlapping with other spectra. As shown in Fig. 4.7, almost no sulfur Auger peak is observed from sample 2 which has been exposed in air for five months.

AES depth profiles were taken from the passivated samples which had been exposed to the ambient for three months. The spectrum of GaAs surface after P\textsubscript{2}S\textsubscript{5}/(NH\textsubscript{4})\textsubscript{2}S treatment is shown in Fig. 4.8. Several observations are immediately apparent from these profiles and correlate to the nature of the treatment. The profile shows that the passivated surface still contains a very low concentration of arsenic with a gradual increase of arsenic towards the substrate, which is a promising result in terms of long term stability. It also shows an increase of oxygen which is reasonable in view of the fact that the sample has been exposed for a long period of time.

4.5. Summary and Conclusion

In order to determine how the P\textsubscript{2}S\textsubscript{5}/(NH\textsubscript{4})\textsubscript{2}S treatment causes such improvement in the electrical quality of GaAs surface, XPS was used to examine GaAs surfaces
Figure 4.6  Local atomic order in (a) $\text{P}_2\text{O}_5 + \text{Ga}_2\text{O}_3$, and
(b) $\text{P}_2\text{O}_5 + \text{Ga}_2\text{O}_3 \rightarrow \text{GaPO}_4$. 

- Gallium
- Arsenic
- Oxygen
- Phosphorus
Figure 4.7 (a) Sulfur Auger spectra for sample 2 and 3 at 15°.
Figure 4.7 (b) Sulfur Auger spectra for sample 2 and 3 at 45°.
Figure 4.8  Auger Electron Spectroscopy (AES) depth profile for the passivated sample which was exposed in air for 3 months.
following an acid etch and \( \text{P}_2\text{S}_3/(\text{NH}_4)_2\text{S} \) treatment. Angle-resolved spectra of As 3d and Ga 3d levels exhibit the existence of As-S and Ga-S species on the surface. Formation of an As-S compound contributes to the reduction of surface states caused by mostly As\(_{Ga}\) antisite defects. From the spectra of Ga 3d and P 2p, it has been observed that there exist oxygen species such as GaPO\(_4\). According to Lucovsky, the chemical structure of GaPO\(_4\), formed by the reaction of Ga\(_2\)O\(_3\) and P\(_2\)O\(_5\), is highly ordered, which implies the chemical stability of GaPO\(_4\) whereas native oxides, Ga\(_2\)O\(_3\) and As\(_2\)O\(_3\), are very unstable, volatile, and inhomogeneous. The degradation of the passivation with time is due to the breaking of As-S and Ga-S bonds and their replacement by bonds to oxygen at the surface, which leads to the formation of arsenic. As shown in Table 4.1, the heats of formation of As and Ga sulfides are far less than the heats of formation of the As and Ga oxides. Another possible degradation mechanism is that exposure to the atmosphere will result in a change of the chemical structure of GaPO\(_4\) owing to the absorption of moisture. Once the passivation layer is disrupted by these reactions, its electrical characteristic will deteriorate. Results of AES spectra on GaAs sample exposed in air for three months show the existence of a relatively large amount of phosphorus and sulfur and the increase of oxide species. However, the amount of arsenic is low.
CHAPTER FIVE
SCHOTTKY BARRIER HEIGHT ENHANCEMENT OF n-In$_{53}$Ga$_{47}$As
BY A NOVEL CHEMICAL PASSIVATION TECHNIQUE.

5.1. Introduction

With its high electron mobility ($\sim 13800$ cm$^2$V$^{-1}$s$^{-1}$ at 300 °K) [54,55], and high saturation velocity ($\sim 2.5 \times 10^7$ cm/s) relative to other III-V compound semiconductors such as GaAs or InP, the In$_{53}$Ga$_{47}$As ($E_g = 0.74$ eV) has been widely used in the 1.3 $\mu$m lightwave communications and high-speed devices [56,57,58]. Unfortunately, the low Schottky barrier height ($\sim 0.2$ eV) on n-In$_{53}$Ga$_{47}$As has resulted in excessive leakage current [59] in this device. To overcome this problem, various approaches have been sought to enhance the effective Schottky barrier height of n-In$_{53}$Ga$_{47}$As. One method is to deposit a thin insulating layer, which is thin enough for tunneling, on the top of the n-In$_{53}$Ga$_{47}$As. If the thickness of the insulating film is less than 10 nm, the metal will be in equilibrium with the semiconductor surface, and the contact will exhibit the characteristics of a Schottky barrier with an increased effective barrier height. On the basis of Schottky theory [60], in the presence of an interfacial film (thickness d), the saturation current density is given by

\[
J_s = A^* T^2 \exp(-q\Phi'_B/kT) \\
\Phi'_B = \Phi_B + Dd
\]

where

\[
D = 2\beta kT/q \\
\beta = \left[\frac{2m^*(E_o - E)}{\hbar^2}\right]^{1/2}
\]
\( \Phi'_B \) is the effective barrier height, and \( \Phi_B \) the barrier height of the clean surface (no insulating film). \( E_o \) is the potential barrier height and \( E \) the electron energy. Thus, the reverse leakage current reduces with increasing oxide thickness. It has been reported that a large increases in the effective barrier height has been achieved by using a thin layer of \( \text{SiO}_2 \), \( \text{Al}_2\text{O}_3 \), and \( \text{MgO} \) to form MIS structure in \( \text{InGaAs} \). Recently, it has been shown that it is possible to reduce the reverse leakage current to an acceptable level by growing a clean native oxide in the 100 °C deionized water under flowing oxygen [61], or epitaxially growing a thin layer of large bandgap material between the \( n-\text{In}_{0.53}\text{Ga}_{0.47}\text{As} \) and the electrode metal with MBE [62] growth technique.

### 5.2. Approach

In this chapter, a new simple technique for enhancing the effective barrier height of \( n-\text{In}_{0.53}\text{Ga}_{0.47}\text{As} \) Schottky diode through the use of chemical passivation is presented [63]. The thermochemical calculations and measurements of the In-Ga-As-O phase diagram have demonstrated that the only stable species that can exist in thermodynamic equilibrium on an oxidized \( \text{InGaAs} \) surface are \( \text{Ga}_2\text{O}_3 \), \( \text{In}_2\text{O}_3 \), and \( \text{As}_2\text{O}_3 \). Among these oxide species, \( \text{As}_2\text{O}_3 \) reacts with \( \text{GaAs} \) and \( \text{InAs} \) of the \( \text{InGaAs} \) alloy to form \( \text{Ga}_2\text{O}_3 \) and \( \text{In}_2\text{O}_3 \) plus free arsenic [64]. As a result, the segregated arsenic is expected to be always a thermodynamically stable constituent of an oxidized \( \text{InGaAs} \) surface. Thus, the effect of the elemental arsenic on \( n-\text{In}_{0.53}\text{Ga}_{0.47}\text{As} \) is expected to be an analogous to that of free arsenic on \( \text{GaAs} \). Several groups have reported that Fermi level pinning on \( \text{GaAs} \) may be due to this arsenic layer formed on the surface. From the fact that the surface chemistry of \( \text{InGaAs} \) is similar to that of \( \text{GaAs} \), two different chemicals, \( \text{P}_2\text{S}_5/(\text{NH}_4)_2\text{S} \) and \( (\text{NH}_4)_2\text{S}_x \), which are very effective passivation schemes on \( \text{GaAs} \) surface, have been used [29]. The Schottky diodes used in this study were fabricated on a 0.8 \( \mu \text{m} \) thick \( n-\text{In}_{0.53}\text{Ga}_{0.47}\text{As} \) epilayer (\( N_d = 8 \times 10^{16} \))
cm\(^{-3}\)) grown on n\(^+-\)InP substrate by hydride vapor phase epitaxy (VPE). The samples were first degreased in trichloroethane(TCE), acetone, methanol, and de-ionized water, and were then blown dry with nitrogen gas. The ohmic contact was formed on n\(^+-\)InP substrate by evaporating Au-Ge/Ni/Au(1000/200/2000 Å) and by alloying at 450 °C for 1 min. The samples were then etched in NH\(_4\)OH:H\(_2\)O\(_2\):H\(_2\)O(20:7:100) for 5 sec., followed by a brief dip in buffered HF (BOE) to remove the native oxide on the InGaAs surface prior to surface passivation. These samples were then immersed directly into the P\(_2\)S\(_5\)/(NH\(_4\))\(_2\)S (0.03g/ml) or (NH\(_4\))\(_2\)S\(_x\) containing 6 % excess sulfur passivation solution for 30 sec. After the samples were taken out, the surface was blown dry with nitrogen, and quickly loaded into an electron-beam evaporator. The unpassivated reference samples were also loaded in the electron-beam chamber to be used later for comparison with the passivated samples. Gold (2000 Å) Schottky contacts with a diameter of 400 μm were evaporated separately on the passivated or chemically etched InGaAs surface.

5.3. Result and Discussion

The current-voltage (I-V) characteristics were measured using an HP4140B pA meter. Figures 5.1 and 5.2 show the forward and reverse I-V curves for these Schottky diodes. The departure from a straight line on the forward log I vs. V data points is due to the series resistance at high bias. It is noted that forward and reverse I-V curve for the diodes with gold contact on NH\(_4\)OH/HF etched bare surface look like ohmic due to the low barrier height and high surface state density. Passivated Schottky diodes, however, show much improved I-V characteristics. The lowest reverse leakage current density of 9.6 μA at -2 V was observed in the P\(_2\)S\(_5\)/(NH\(_4\))\(_2\)S treated Au/InGaAs Schottky diode, which has a reverse leakage current density more than two orders of magnitude lower than the unpassivated diodes.
Figure 5.1 Forward-bias current-voltage (I-V) characteristics for the passivated and unpassivated Au-InGaAs Schottky diodes.
Figure 5.2  Reverse-bias current-voltage (I-V) characteristics for the same diodes shown in Fig. 5.1.
The breakdown voltage of around -3 V was measured on the \( \text{P}_2\text{S}_5/(\text{NH}_4)_2\text{S} \) passivated diodes. This low breakdown voltage may be partially due to the relatively high doping density and low barrier height. The effective barrier height \( \Phi_{\text{Bn}} \) and the ideality factor ‘n’ were determined from a least-square fit of the linear portion of the forward I-V curve using Eqs. (3.1 and 3.2): \( A^*(= 4\pi q m^* k_B^2 / h^3) \) is the effective Richardson constant (4.92 A/cm\(^2\)K\(^2\) for n-InGaAs) for the thermionic emission, and \( J_s \) is the reverse saturation current density. The barrier height of 0.54 and 0.38 eV, and the ideality factor n of 1.53 and 1.31 were measured from \( \text{P}_2\text{S}_5/(\text{NH}_4)_2\text{S} \) and \( (\text{NH}_4)_2\text{S}_x \) passivated diodes, respectively. The capacitance-voltage (C-V) characteristics were measured at 1 MHz using an HP4280A capacitance meter (Fig. 5.3). Due to high leakage, we were unable to measure C-V curve in the unpassivated Au/InGaAs Schottky diodes. \( (\text{NH}_4)_2\text{S}_x \) passivated diode show the C-V characteristics, even though the value of the capacitance is high. The built-in voltage of \( \text{P}_2\text{S}_5/(\text{NH}_4)_2\text{S} \) passivated Schottky diode was determined from the \( 1/C^2 \) vs. reverse bias voltage plot, as shown in Fig. 5.4. Due to the relatively high doping level and low breakdown voltage, only low bias regime showed linear plot. The effective barrier height is calculated from Eq. (3.3) [42]: \( V_i \) is the built-in voltage, and \( V_n \) is the potential difference between the Fermi level and the conduction band edge. From Fig. 5.4 and Eq. (3.3), the effective Schottky barrier heights for \( \text{P}_2\text{S}_5/(\text{NH}_4)_2\text{S} \) passivated diodes were determined to be 0.51 eV. The C-V characteristics for these InGaAs Schottky diodes also showed that \( \text{P}_2\text{S}_5/(\text{NH}_4)_2\text{S} \) passivated surface had a higher barrier height than that of the \( (\text{NH}_4)_2\text{S}_x \) passivated surface.

The passivation mechanisms for the sulfur compounds on n-In\(_{53}\)Ga\(_{47}\)As surface can be explained as follows. The \( \text{Ga}_2\text{O}_3 \) and \( \text{In}_2\text{O}_3 \) on InGaAs surface are very easy to form because the free-energy changes for the formation of these oxides are more negative than \( \text{As}_2\text{O}_3 \). Therefore, arsenic is easily segregated from the unstable \( \text{As}_2\text{O}_3 \)
Figure 5.3  Capacitance vs voltage plot for the same diodes shown in Fig. 5.1.
Figure 5.4  $1/C^2$ vs voltage plot for the same diodes shown in Fig. 5.1.
molecules by gallium and indium atoms, which thereby form Ga$_2$O$_3$ and In$_2$O$_3$, respectively. It is also known that the segregated arsenic on InGaAs surface, which has similar surface chemistry to GaAs, is the main cause of high surface recombination velocity and surface leakage. Furthermore, In$_2$O$_3$ is conductive, and thus is likely to cause surface leakage [65]. Ga$_2$O$_3$, however, does not cause surface leakage because it is a wide bandgap nonconductive species. Therefore, the first step of this sulfur treatment for InGaAs must be the removal of As$_2$O$_3$, In$_2$O$_3$, and arsenic. Sulfur compounds actively react with residual native oxide and arsenic. Sulfur etches out the oxides and arsenic, and forms a monolayer of stable sulfur complexes on the oxide-free InGaAs surface. Thus, the arsenic, gallium, and indium vacancies which are the cause of interface states, according to unified defect model (UDM)[9], are no longer present on the surface. However, from I-V and C-V characteristics, we see the enhanced passivation effect from P$_2$S$_5$/(NH$_4$)$_2$S compared to (NH$_4$)$_2$S$_x$ and NH$_4$OH/HF treatments. One possible explanation for this result can be made as follows. The phosphorus oxide compound formed on InGaAs surface by the P$_2$S$_5$/(NH$_4$)$_2$S treatment has the most negative free energy of formation comparing to Ga$_2$O$_3$, In$_2$O$_3$, and As$_2$O$_3$. Therefore, the phosphorus helps in the segregation of elemental Ga, In, and As from the oxides. These segregated elements react with sulfur, and form stable sulfur complexes. At the same time, the phosphorus oxide forms a thin insulating layer on the InGaAs surface. As a result, the barrier height and ideality factor of P$_2$S$_5$/(NH$_4$)$_2$S treated diodes are higher than the unpassivated diodes. Thus, it is believed that P$_2$S$_5$/(NH$_4$)$_2$S passivated surface forms a metal-insulator-semiconductor (MIS) like structure. This study showed that a ratio of 0.03 g of P$_2$S$_5$ to 1 ml of (NH$_4$)$_2$S yielded the best result. The observed barrier height enhancement and lower leakage current on the passivated diodes clearly indicate that the density of surface states was reduced significantly in the passivated diodes. It is important to point out that the P$_2$S$_5$/(NH$_4$)$_2$S surface
treatment can achieve both the reduction of surface state density and the formation of a thin phosphorus oxide insulating layer for enhancing the barrier height. Furthermore, this passivation provides an advantage over the epitaxial growth technique which introduces a thin barrier-enhancement layer between n-InGaAs and the metal contact [66,67]. A number of passivated diodes were probed at the chip level to check for reproducibility and device-to-device variability of I-V and C-V characteristics. Figure 5.5 shows a histogram of the dark current at room temperature and -1 V bias. About two-thirds of the devices had dark current less than 3 μA for P2S5/(NH4)2S passivation and 0.5 mA for (NH4)2Sx passivation. The thickness of P2S5/(NH4)2S passivation layer was estimated to be around 50 Å by sputtering Auger electron analysis. An ellipsometry evaluation of the same passivation layer led to the average value of 60 Å. To study the long term stability, the passivated diodes were exposed to the air, and measured again over a period of month. There was no observable change in diode characteristics, implying that this passivation is very stable.

5.4. Summary and Conclusion

In summary, it has been demonstrated that the barrier height enhancement on n-In0.53Ga0.47As can be made with a simple chemical passivation. The Schottky contact formed on the P2S5/(NH4)2S-treated surface showed a higher barrier height than that of (NH4)2Sx and NH4OH/HF-treated surfaces. The increase of the effective barrier height is attributed to the MIS like structure formed by the phosphorus oxide which has the most negative free energy compared to Ga2O3, In2O3, and As2O3. In view of the higher barrier height, lower reverse leakage current, and the simple process, the P2S5/(NH4)2S chemical passivation on n-In0.53Ga0.47As reported here is a viable and promising technique for improving stability and performance of InGaAs devices.
Figure 5.5  Histograms of the dark current for 128 passivated diodes at -1 V bias.
CHAPTER SIX
XPS STUDY OF PASSIVATION LAYER ON InGaAs SURFACE

6.1. Introduction

From the electrical characterizations discussed in Chapter five, it is seen that the InGaAs surfaces passivated using P₂S₅/(NH₄)₂S shows a higher Schottky barrier height and a lower reverse leakage current than the unpassivated surface and the (NH₄)₂S₂ treated surface. Although limited investigations of the surface chemistry of InGaAs samples have been reported recently, there is much still to be established concerning the surface chemistry of the unpassivated and passivated samples. It is, therefore, important to analyze the passivated surface with other analytical tool to see the chemical constitution of the treated surface. X-ray photoelectron spectroscopy (XPS) is considered as one of the most important techniques for studying the chemical bonding within the passivation layer formed on InGaAs. This is due to the fact that XPS studies of the passivation layer formed on InGaAs point out that the core shifts measured in these studies serve to distinguish between various states of the In, Ga, and As atoms although the native oxide and passivation layer on InGaAs is far more complex than that found on GaAs [68,69].

In this chapter, XPS and Auger Electron Spectroscopy (AES) have been used to study the surface chemistry of the P₂S₅/(NH₄)₂S passivated InGaAs surface. The knowledge of the sulfur- and phosphorus- induced overlayers and the way they terminate the InGaAs is important to understand the physics and chemistry behind the decrease in surface recombination and the increase in barrier height.
6.2. Experiment

The samples used in this study are 0.8 μm thick n-InGaAs epilayer \((N_d = 8 \times 10^{16} \text{cm}^{-3})\) grown on n⁺-InP substrate by hydride vapor phase epitaxy (VPE), which are the same samples used in the electrical characterization. The samples were first degreased in trichloroethane (TCE), acetone, methanol, and de-ionized water, and were then blown dry with nitrogen gas. The cleaned samples were then etched in \(\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}(20:7:100)\) for 5 sec., followed by a brief dip in buffered HF (BOE) to remove the native oxide on the InGaAs surface prior to surface passivation. These samples were then immersed directly into the \(\text{P}_2\text{S}_5/(\text{NH}_4)_2\text{S}\) (0.03g/ml) passivation solution for 30 sec. After the samples were taken out, the surface was blown dry with nitrogen. The samples were then introduced to the spectrometer. X-ray photoemission spectra were recorded on a Perkin-Elmer PHI-5100 spectrometer. The X-rays employed in XPS were the Mg Kα (\(h\nu = 1253.6\) eV) lines emitted by magnesium when the metal is bombarded with high-energy electrons (The designation Kα indicates the emission process \(2p\rightarrow1s\) subsequent to the creation of a 1s or K hole by electron impact). These Kα X-rays are relatively soft - that is, of low photon energy. The Mg (1253.6 eV) X-ray was operated at 15 KV and 300 W. Background pressure in the analysis chamber was always less than \(1 \times 10^{-9} \text{Torr}\). To improve the surface sensitivity of the measurements, the ejection angle of the detected photoelectrons measured from the surface normal of the sample, \(\theta\), was taken at two different angles, 15° and 45°. Since electron mean free paths and hence sampling depths are so short, changing to a higher take-off angle (i.e., 15°) specifically enhances surface features. A comparison of spectra recorded at two different take-off angles provides a means of interpreting the vertical homogeneity of the sample. In order to see the changes of the chemical composition with time for the \(\text{P}_2\text{S}_5/(\text{NH}_4)_2\text{S}\) treated surface, the spectra of the angle-resolved XPS have been collected from three samples. The first sample
(sample 1) is unpassivated, the second one (sample 2) is exposed in the ambient environment for one day after the surface treatment, and the third one (sample 3) is exposed in air for five months after the surface passivation. Auger depth profiles were taken on the passivated samples which had been exposed to the ambient environment for two days.

6.3. Results and Discussion

XPS spectra were collected from different energy regions, in the vicinity of the Ga 3d (10 ~ 30 eV), As 3d (35 ~ 45 eV), In 3d (440 ~ 460 eV), and P 2p (129 ~ 139 eV) core states. High resolution data were fitted with Gaussian/Lorentzian curves so as to aid in the assignment of components in the spectra of passivated surface on the basis of the chemical shifts. The Ga, In, and As 3d photoelectron lines are useful for the quantitative chemical analysis of the overlay formed by either the oxidation or passivation of InGaAs because they are strong signals and overlapped by no others. All the binding energies coded are referenced to the binding energy C 1s peak at 284.6 eV. Therefore, other spectra have been shifted by the offset value. Figure 6.1 shows the overall survey of the passivated surface to select and study a specific range of binding energy. The spectrum of C 1s of sample 2 shows the overlap of several different carbons at both take-off angles (Fig. 6.2). This is probably from the sample mounting stage or contamination which was not unexpected given the methods of preparation, transportation, storage and handling of the sample. The all spectra shown here were corrected by subtracting the appropriate linear background from the experimental curves which were taken using pulse counting and signal averaging.

The spectra of Ga 3d in Fig. 6.3 appear to be the overlap of four peaks, two peaks at the low energy side due to the In 4d level from the InGaAs substrate and the In-O species, and two peaks at the high energy side due to the Ga 3d level.
Figure 6.1 InGaAs XPS survey spectra for bare surface (sample 1), 1 day after passivation (sample 2), and 5 months after passivation (sample 3).
Figure 6.2  C 1s high resolution spectra for 3 samples.
Figure 6.3 (a) Ga 3d expanded and curve fitted spectra at 15° take-off angle.
Figure 6.3 (b) Ga 3d expanded and curve fitted spectra at 45° take-off angle.
The Ga 3d and In 4d peaks interfere with each other in the vicinity of 17 eV. Consequently, in fitting the In and Ga peaks, the fit was not unique. After decomposition into its component signal peak, four peak components are identified. For the bare surface (sample 1 in Fig. 6.3), the spectra are the same at both angles, which indicates the native oxide on the air-exposed side has the same chemical composition as the oxide close to the semiconductor surface. The Ga 3d spectra of sample 2 (Fig. 6.3) show relatively small GaO peaks at the both angles whereas the peak intensity of the In 4d due to the In-O is relatively high, which implies the phosphorus in the P2S5/(NH4)2S effectively absorbs the oxygen species from the Ga2O3. Considering the high heats of formation of Ga2O3 and P2O5, the peak shifted by ~1.7 eV towards higher binding energy from the Ga 3d level of the InGaAs substrate appears to be GaPO4, not just Ga-O compound. According to the reported values for InGaAs native oxide [68], the binding energy difference between the peak of Ga 3d due to oxidized Ga and that of In 4d from the InGaAs substrate was found to be about 3.2 eV. As shown in Fig. 6.3, the difference between these two peaks are 3.42 eV at 15° and 3.63 eV at 45°, which seems to be higher than the reported values. These higher values are attributed to the presence of GaPO4 because, as seen in Ga 3d level of InGaAs, the binding energy shift of Ga 3d level of oxidized Ga with respect to the substrate component are 1.44 eV at 15° and 1.73 eV at 45°, which are higher than the binding energy shift expected at the presence of Ga2O3 that are usually shifted by 0.9 ~ 1.2 eV from the substrate in the case of GaAs. As shown in Fig. 6.3, the spectra of the sample 3 exposed in air for five months shows that the peak has been shifted by more than ~2 eV towards higher binding energy due to the oxidation of the passivated surface. The In 4d level shifted by ~1 eV from the peak of In 4d substrate in sample 2 and 3 is probably due to contribution from InPO4 compound, not simply In-O, because the heats of formation of In2O3 and P2O5 are high enough
to form the InPO$_4$. The spectra of In 3d and P 2p support the existence of InPO$_4$ on the passivated surface. Even though the width of FWHM and the peak shape of the Ga 3d state (of the substrate) in sample 2 seem to be one peak from the underlying InGaAs surface, the peak should be overlapped with the Ga 3d line of Ga-S because the heats of formation of the likely compound of Ga, As, and In with sulfur (Table 4.1) show that the Ga-S reactions are energetically favored over the As-S reactions. Also, published results showed that the Ga-S bonding is stronger than the As-S bonding. However, smaller spin orbit splitting and binding energy shift of Ga cannot resolve the Ga 3d$_{5/2}$ and 3d$_{3/2}$ levels on a clear sulfide peak. As shown in Fig. 6.4, the spectra of As 3d of sample 2 exhibit a clear peak of As-S bonding, which indirectly supports the existence of the Ga-S bonding on the passivated surface.

The photoemission spectrum for the As 3d is shown in Fig. 6.4, along with its decomposition into substrate and reacted component. In sample 1, the As 3d core level of substrate has a peak centered at 39.29 eV and another at 43.32 eV, which is at ~4 eV higher binding energy from the substrate peak, is due to As-O compound (probably As$_2$O$_3$) that is the main source of the surface or the interface states. Thomas et al.[68] observed that the peak of As 3d due to oxidized As on the InGaAs surface is shifted 4.4 eV toward the higher binding energy from the peak of substrate component, and the high binding energy component is most closely consistent with As in its +5 oxidation. The previously published results for As-O compound on the GaAs surface indicated two oxidation states for As atoms, one characterized by a 2.9 ~ 3.1 eV chemical shift (As$_2$O$_3$), and the second by a large shift of 4.6 eV (As$_2$O$_5$). However, there was no peak appearing on the high binding energy side (i.e., either 2.9 ~ 3.1 or 4.6 eV) of the As 3d unshifted peak from the spectra of the sample 2 as shown in Fig. 6.4. This is clearly showing that there is no arsenic oxide on the passivated surface. The absence of the As oxide peak from the spectrum of the P$_2$S$_5$/(NH$_4$)$_2$S treated
Figure 6.4 (a) As 3d expanded and curve fitted spectra at 15° take-off angle.
Figure 6.4 (b) As 3d expanded and curve fitted spectra at 45° take-off angle.
sample clearly demonstrates that, as speculated in Chapter 5, the phosphorus atoms in the vicinity of the arsenic oxide gradually extract oxygen from the arsenic oxide to form phosphorus oxide, while elemental arsenic atoms, which are the major cause of surface states, are bonded to sulfur. As a result, it is expected that the density of surface states is considerably reduced on the surface after passivation. A clear peak of As-S compound species (probably As$_2$S$_3$) has been shown from the spectra of sample 2 (Fig. 6.4). This chemical shift, which is $\sim$ 2 eV shift referenced to the peak of the substrate, is characteristic for an As-S compound because Spindt et al.[70] used surface sensitive synchrotron radiation photoemission spectroscopy and observed a chemically shifted component due to sulfur bonding at 1.7 eV toward higher binding energy from GaAs surface treated with sulfur compound. From the spectra of sample 3, it has been observed that the passivated surface becomes oxidized during the air-exposure. However, it is observed that there still exists As-S species close to the substrate, not air-exposed top surface.

The In 3d levels are a spin orbit split doublet (splitting $\sim$ 7.6 eV). As shown in Fig. 6.5, the spectra of In 3d level from the substrate of sample 2 have peaks of 444.93 and 452.41 eV at 15°, and 444.85 and 452.36 eV at 45°. The chemical shift of In 3d referenced to the substrate in the case of the 3d$_{5/2}$ of sample 2 is 1.25 eV at 15° and 1.32 eV at 45°. These 1.25 $\sim$ 1.32 eV shifted peaks are probably from either InPO$_4$, InPS$_4$, or an admixture of InPS$_4$ + In$_2$S$_3$ with at least some traces of the oxides. The component of the In 3d$_{5/2}$ peak approximately 1.3 eV higher in binding energy than the InGaAs component is consistent with that expected for InPO$_4$. The P 2p peak also supports the presence of the InPO$_4$ on the passivated surface. However, In$_2$O$_3$ is a wide bandgap (3.5 eV) conductive metal oxide that can have a high density of donors due to nonstoichiometry, and In$_2$S$_3$ is a low bandgap (2.03 eV) that can cause an increase in the reverse leakage current. As shown in the electrical characterization,
Figure 6.5 (a) In 3d expanded and curve fitted spectra at 15° take-off angle.
Figure 6.5 (b)  In 3d expanded and curve fitted spectra at 45° take-off angle.
most of the oxides formed on the surface by chemical passivation are, as suggested by Lucovsky [53], of a chemical structure that has a very high degree of chemical ordering, for example, InPO$_4$ or GaPO$_4$. It is possible that P$_2$O$_5$ + In$_2$O$_3$ can convert to InPO$_4$. In terms of thermodynamic stability, the equilibrium composition would appear to be either In$_3$O$_3$ + P$_2$O$_5$ or InPO$_4$, not In$_2$O$_3$ + In$_2$S$_3$. If the oxides on the surface are formed by the mixture of conductive In$_2$O$_3$ and low bandgap In$_2$S$_3$, then they are not expected to show the barrier height enhancement. The spectra of In 3d for sample 3 exposed in air for five months show almost no difference from that of sample 2. This strongly suggests the chemical stability of InPO$_4$.

Representative spectrum of the P 2p level in Fig. 6.6 has one symmetric broad peak at $\sim 134$ eV, which indicates the presence of one oxidation state for phosphorus. Although there are many possible species during the passivation via the following chemical reactions, it seems unlikely that phosphorus oxides (P$_4$O$_6$, P$_4$O$_{10}$) would exist for any length of time on samples because P$_4$O$_{10}$ readily sublimes at ambient temperature under the conditions of the XPS experiment.

\[
\begin{align*}
2P_2S_5 + 2Ga_2O_3 & \rightarrow P_4O_6 + 2Ga_2S_3 + 4S \\ 
2P_2S_5 + 2As_2O_3 & \rightarrow P_4O_6 + 2As_2S_3 + 4S \\ 
2P_2S_5 + 2In_2O_3 & \rightarrow P_4O_6 + 2In_2S_3 + 4S \\ 
P_4O_6 + 4S & \rightarrow P_4O_6S_4 \\ 
Ga_2O_3 + P_2O_5 & \rightarrow 2GaPO_4 \\ 
In_2O_3 + P_2O_5 & \rightarrow 2InPO_4
\end{align*}
\]

Therefore, the peaks at $\sim 134$ eV for sample 2 and 3 may represent either GaPO$_4$ or InPO$_4$ due to the high heats of formation of Ga$_2$O$_3$ (-258 Kcal), In$_2$O$_3$ (-221 Kcal), and P$_2$O$_5$ (-356 Kcal). Nishitani et al.[71] observed a P 2p peak centered at 134.7
Figure 6.6 (a) P 2p expanded and curve fitted spectra at 15° take-off angle.
Figure 6.6 (b)  P 2p expanded and curve fitted spectra at 45° take-off angle.
eV and an O 1s peak centered at 532.7 eV from GaPO$_4$ formed on the GaP surface. If there is P-O bonding such as GaPO$_4$ or InPO$_4$, any such bonding should be seen by a peak near $\sim 134$ eV. Most published values for InPO$_4$ showed that P 2p and O 1s ranges about $133 \sim 134$ eV and $531 \sim 532$ eV, respectively. For example, Hollinger et al.[72] identified the peak at 531.8 eV as oxygen in an InPO$_4$ - like structure. According to Lucovsky [53], both InPO$_4$ and GaPO$_4$ are chemically stable and most probably diatomic analogs of SiO$_2$ in which all of the In and Ga atoms are incorporated into the covalent network and hence can not contribute to an ionic conductivity. He said that this type of network requires a very high degree of chemical ordering. However, it should be kept in mind that the phenomena involved in the oxidation are more complicated than these equations may suggest. Furthermore, the surface chemistry of oxides of phosphorus is somewhat complicated by the possibility of the presence of surface nitrogen-bonded species etc., because phosphorus pentoxide reacts with ammonia to give a white powdery solid of unknown structure containing both P-N-P as well as PONH$_4$ during treatment. An AES depth profile was taken from the passivated samples which has been exposed to the ambient environment for two days. Spectra of the surface after P$_2$S$_5$/(NH$_4$)$_2$S treatment are shown in Fig. 6.7 and Fig. 6.8. Several observations are immediately apparent from these profiles and correlate to the nature of the treatment. The profile shows that the surface still contained very low concentrations of arsenic with a gradual increase of arsenic towards the substrate, which is a promising result in terms of long term stability.

6.4. Summary and Conclusion

Changes in InGaAs surface chemistry were observed as a result of P$_2$S$_5$/(NH$_4$)$_2$S passivation. In order to determine how the P$_2$S$_5$/(NH$_4$)$_2$S treatment causes such improvements in the electrical quality of the surface, XPS has been used to examine
Figure 6.7 Auger Electron Spectroscopy (AES) depth profiles after 1 day in air (top) and after 1 min. sputtering (bottom).
Figure 6.8 Auger Electron Spectroscopy (AES) depth profile for the passivated sample which was exposed in air for 1 day.
InGaAs surfaces following an acid etch and $\text{P}_2\text{S}_5/(\text{NH}_4)_2\text{S}$ treatment. Angle-resolved spectra of As 3d and Ga 3d levels exhibit the existence of As-S and Ga-S species on the surface. Formation of As-S compound contributes to the reduction of surface states caused by mostly $\text{As}_{\text{Ga}}$ antisite defects. From the spectra of Ga 3d and P 2p, it has been observed that there exist oxygen species such as GaPO$_4$, InPO$_4$, and P$_2$O$_5$. According to Lucovsky, the chemical structure of GaPO$_4$ and InPO$_4$ formed by the reaction of $\text{Ga}_2\text{O}_3$, $\text{In}_2\text{O}_3$, and P$_2$O$_5$ is a highly ordered nonconductive species which implies the chemical stability of GaPO$_4$ and InPO$_4$, and that these oxides are responsible for the barrier height enhancement on InGaAs surface after chemical passivation, whereas native oxides, $\text{Ga}_2\text{O}_3$ and $\text{As}_2\text{O}_3$, are very unstable, volatile, and inhomogeneous. When the passivated samples are exposed to air, the oxygen and moisture react slowly with the sulfur to form volatile SO$_x$ compounds. Therefore, the degradation of the passivation with time in air results from the breaking of the As-S and Ga-S bonds and their replacement by bonds to oxygen at the surface, and this leads to the formation of arsenic because, as shown in Table 4.1, the heats of formation of As and Ga sulfides are far less than the heats of formation of the As and Ga oxides. Another possible degradation mechanism is that exposure to the atmosphere results in the change of chemical structure of GaPO$_4$ and INPO$_4$ owing to the absorption of moisture. Once the passivation layer is disrupted by these reactions, its electrical characteristics deteriorate.
7.1. Introduction

The wavelength multiplexing/demultiplexing technique involves the transmission of multiple optical signals with different wavelengths via a single fiber and detecting each optical signal with different wavelengths by the demultiplexing circuit and the detectors through the output fibers at the receiver end. This is a viable technique for making full use of the low-loss characteristics of optical fibers between 0.8 and 1.5 μm wavelength regime. The technique provides an useful means for increasing the capacity of optical fiber transmission systems. The conventional technique has used classical optical components such as lenses, prisms, gratings, and interference filters to separate and recombine optical signals at different wavelengths. There have been increasing interest in developing the demultiplexing devices using III-V compound semiconductors for use in optical fiber communications. For example, several types of active wavelength-selective demultiplexers, which perform both demultiplexing and detection, have been reported. Campbell et al.[73] has used stacked epitaxial InGaAsP layers having different band gaps and compositions to detect and demultiplex two-wavelength bands. However, the device has a poor wavelength selectivity and an unsatisfactory degree of crosstalk suppression. Larsson et al.[74] reported results on a high-speed dual wavelength demultiplexing experiment using a monolithic linear array of superlattice p-i-n photodetectors in a waveguide configuration. The detectors can be tuned to different wavelengths using the electro-absorption effect,
and the wavelength-multiplexed optical signals can be demultiplexed directly into different electrical channels with an improved wavelength selectivity and an increased crosstalk attenuation. More recently, Johnson et al.[75] and Miyazawa et al.[76] have demonstrated two-wavelength detectors using disordering of multiquantum well structure by Zn diffusion or by rapid thermal annealing. The wavelength range of these devices was in either the short-wavelength (600 ~ 900 nm) or the long-wavelength (1100 ~ 1300 nm) region.

In this chapter, a new planar high-speed, dual-wavelength InAlAs/InGaAs Schottky barrier photodiode with graded superlattice structure is reported. The detector is capable of detecting and demultiplexing in both the short- and long-wavelength (0.8 - 1.3 μm) simultaneously without the complication of additional optical components is demonstrated.

7.2. Design and Experiment

The ternary compound semiconductors such as In₀.₅₃Ga₀.₄₇As and In₀.₅₂Al₀.₄₈As, which are lattice matched to InP substrate, are materials of considerable interest for applications in 1.3 to 1.6 μm lightwave communications. The n-In₀.₅₃Ga₀.₄₇As has high electron mobility (∼ 13800 cm²V⁻¹s⁻¹ at 300 K) and high saturation velocity (∼ 2.5 × 10⁷ cm/s) and low band gap energy (0.74 eV). However, low Schottky barrier height (∼ 0.2 eV) on the n-In₀.₅₃Ga₀.₄₇As causes excessive leakage current [59] in such devices. The reverse leakage current is critical in determining the performance of a photodetector for optical communication systems since shot noise generated by the reverse leakage current can limit the detector sensitivity. Thus, InGaAs photodiodes are usually fabricated with PIN diode structure to minimize the reverse-bias dark current. To overcome this problem, various approaches have been sought to enhance the effective barrier height on n-In₀.₅₃Ga₀.₄₇As. For example, it has been demon-
strated that the reverse leakage current can be greatly reduced by growing a thin $p^+ - In_{0.52}Al_{0.48}As$ layer on $n-In_{0.53}Ga_{0.47}As$ to enhance the Schottky barrier height. Ohno et al. [77] have reported Schottky barrier height of 0.8 eV for aluminum contact on $In_{0.52}Al_{0.48}As$. Hsieh et al. [78] also found that gold contacts on $In_{0.52}Al_{0.48}As$ resulted in Schottky barrier height of 0.64 eV. Lin et al. [79] have investigated composition dependence of $Au/In_{x}Al_{1-x}As$ Schottky barrier heights in details and found Schottky barrier height of 0.82 eV for $x = 0.52$, which is sufficient for many device applications. Thus, the incorporation of a lattice matched wide band gap $In_{0.52}Al_{0.48}As$ epilayer on a low band gap $In_{0.53}Ga_{0.47}As$ layer would result in barrier height enhancement and reduction of reverse leakage current. In addition, a highly resistive undoped $InAlAs$ layer prevents edge breakdown of the photodiode. Since the band gap energy of the $In_{0.52}Al_{0.48}As$ ($E_g = 1.45$ eV) is close to that of GaAs ($E_g = 1.43$ eV), the photoresponse of an $In_{0.52}Al_{0.48}As$ Schottky diode should resemble to that of a GaAs photodiode (i.e., $0.4 < \lambda < 0.9 \mu m$). Therefore, in our detector structure, the two-wavelength response is achieved by using a wide band gap $In_{0.52}Al_{0.48}As$ as top layer to absorb short-wavelength photons and a lower band gap $In_{0.53}Ga_{0.47}As$ bottom layer to absorb the long-wavelength photons.

However, as shown in Fig. 7.1, the direct band gap heterostructure between the $In_{0.52}Al_{0.48}As$ and the $In_{0.53}Ga_{0.47}As$ layers has a valence band discontinuity of $\Delta E_v = 200$ meV. As a result, charge trapping at the $InAlAs/InGaAs$ interface is expected to limit the speed of the photodiode. Introduction of a grading layer between $InAlAs$ and $InGaAs$ can reduce the deleterious effects of carrier trapping (Fig. 7.2). It is well known that the band gap of $InGaAs/InP$ graded superlattice can change gradually from the band gap of $InP$ to that of $InGaAs$ by controlling the thickness of $InP$ and $InGaAs$ layers. We used $InAlAs$ instead of $InP$ for barrier height enhancement since Schottky barrier height on $InP$ is still too low for detec-
Figure 7.1  Energy band diagram of an InAlAs/InGaAs heterostructure under reverse-bias condition.
Figure 7.2  Energy band diagram of an InAlAs/graded superlattice/InGaAs heterostructure under reverse-bias condition.
The graded-superlattice on top of n-In_{0.53}Ga_{0.47}As (0.8 μm, 5 ×10^{15} cm^{-3}) consists of alternate ultra-thin multilayers of undoped In_{0.53}Ga_{0.47}As (n ~ 5 ×10^{15} cm^{-3}) and In_{0.52}Al_{0.48}As (n ~ 5 ×10^{15} cm^{-3}). The duty factors of In_{0.52}Al_{0.48}As and In_{0.53}Ga_{0.47}As layers are spatially varied by changing the thickness of the InGaAs layers from 5 to 55 Å and InAlAs layers from 55 to 5 Å while keeping the period of superlattice constant (= 60 Å). The resultant effective band gap of the graded superlattice can be expressed as

\[
E_{\text{eff}} = \frac{E_g(\text{In}_{0.53}\text{Ga}_{0.47}\text{As}) \cdot L(\text{In}_{0.53}\text{Ga}_{0.47}\text{As}) + E_g(\text{In}_{0.52}\text{Al}_{0.48}\text{As}) \cdot L(\text{In}_{0.52}\text{Al}_{0.48}\text{As})}{L(\text{In}_{0.53}\text{Ga}_{0.47}\text{As}) + L(\text{In}_{0.52}\text{Al}_{0.48}\text{As})}
\]

(7.1)

The detector structure as shown in Fig. 7.3 is grown by molecular beam epitaxy (MBE) on the Fe-doped semi-insulating InP substrate, which consists of an n^- (5 ×10^{15} cm^{-3}) InAlAs absorption layer of 0.5 μm thick, a 10 periods 600 Å of undoped InAlAs/InGaAs graded superlattice layer, an undoped n-type (5 ×10^{15} cm^{-3}) InGaAs absorption layer of 0.8 μm thick, and an n^+ (2 ×10^{18} cm^{-3}) InGaAs layer of 0.3 μm thick to facilitate for ohmic contact. The device fabrication procedure is discussed as follows. The sample was first degreased in trichloroethan (TCE), acetone, methanol, and de-ionized water, and were then blown dry with nitrogen gas. A mesa defining the active area was formed by etching with 1 H₃PO₄ : 1 H₂O₂ : 38 H₂O up to the n^+ InGaAs layer. Another larger mesa was defined to reach the semi-insulating substrate. For surface passivations, polyimide was spin-coated onto the wafer. The contact pads were positioned on the polyimide to minimize the parasitic capacitances. The ohmic contacts were formed by using a standard lift-off process. The ohmic contact on n^+ InGaAs was formed by electron-beam deposition of Au-Ge/Ni/Au (1000/200/2000 Å) metals, and by subsequent annealing at 450 °C for 1 min in a forming gas ambient (H₂-N₂, 5-95 percent). A 100 Å of gold film for the transparent Schottky barrier
Figure 7.3 Cross-sectional view of the InAlAs/graded superlattice/InGaAs layers grown by MBE for Schottky barrier photodiode.
contact and a 200 /3000 Å Cr/Au film for the bonding pad were deposited on the InAlAs by electron-beam evaporation at a deposition rate of 2 Å/s at a pressure of \(8.5 \times 10^{-7}\) torr. Prior to metal contact evaporation, a wet chemical etching was performed in a solution of buffered HF (BOE) to remove native oxide from the surface of the contact areas. Figure 7.4 shows the cross sectional view of the planar Schottky barrier photodiode used in this study.

### 7.3. Results and Discussion

The current-voltage (I-V) characteristics of the Schottky barrier photodiodes were measured by using an HP4140B pA Meter/DC voltage source (see Fig. 7.5). The devices exhibit reverse leakage currents of less than 1.2 nA at 5 V bias, and their breakdown voltages exceed 15 V. The leakage current of this detector is comparable to that of a GaAs Schottky barrier photodiode reported earlier by us [80]. We attribute this low leakage current to: (1) high Schottky barrier height on InAlAs, (2) good polyimide dielectric passivation, and (3) high-quality of InAlAs/InGaAs epitaxial layers. The ideality factor, determined from the slope of the forward-bias I-V characteristics, is found equal to 1.2. The capacitance-voltage (C-V) characteristics were measured by using HP4280A C-Meter/C-V plotter. The total (junction and parasitic) capacitances of the photodiode, with an area of \(9.8 \times 10^{-5}\) cm\(^2\), were found equal to 0.1 pF at zero bias. The spectral response was measured by using a Digikrom 240 monochromator and tungsten light source (Fig. 7.6). The optical power of the incident radiation, divided by a beam splitter, was focused on a reference detector and on the photodiode. The source was chopped at a 750-Hz rate to eliminate the effects of background noise and ambient variations. The detected signals were recorded as a function of wavelength with a phase-sensitive lock-in amplifier. The measured photocurrent was calibrated with a germanium photodetector.
Figure 7.4  Cross-sectional view of the InAlAs/graded superlattice/InGaAs planar Schottky barrier photodiode.
Figure 7.5  Current-voltage (I-V) characteristics for the InAlAs/graded superlattice/InGaAs Schottky barrier photodiode.
Figure 7.6  Schematic diagram for the spectral response measurement.
The external quantum efficiency of the detector measured at - 5 V (i.e., the n\textsuperscript{−} region is fully depleted) is shown in Fig. 7.7. A responsivity of 0.42 A/W was measured at 1.3 μm, which corresponds to a quantum efficiency of 38 percent. As shown in Fig. 7.7 and Fig. 7.8, the crosstalk between the two wavelength bands, which measures the amount of overlap between two curves, has been calculated and plotted from the extrapolated responsivity curves. The decrease of the quantum efficiency for wavelength close to \( \sim 0.9 \) μm, which contributes to lower the crosstalk between the short- and long-wavelength bands, can be explained as follows. The short-wavelength cut-off corresponds approximately to the band gap energy of the top InAlAs layer. For wavelengths longer than the cutoff wavelength of InAlAs, the value of the absorption coefficient is too small to give appreciable absorption. Since the values of absorption coefficients near \( \sim 0.4 \) μm for the short-wavelength regime of InAlAs and \( \sim 0.9 \) μm for the long-wavelength regime of InGaAs are very large (> \( 10^5 \) cm\(^{-1}\)), the photocarriers are generated at the top edge of the InAlAs active layer and not created uniformly across the active layer. According to Shockley, an inversion layer is present in a metal/n-type semiconductor diode if the barrier height is greater than one-half of the band gap energy of the semiconductor. The experimental results showed that \( \Phi_{\text{Bn}} \) of Au/In\(_{0.52}\)Al\(_{0.48}\)As is \( \sim 0.8 \) eV which is greater than one-half of In\(_{0.52}\)Al\(_{0.48}\)As bandgap (1.45 eV). Li et al.[81] derived a theoretical expression for the quantum yield of a metal-semiconductor Schottky barrier photodiode which takes into account the effect of the presence of an inversion layer. This can be expressed by

\[
\eta(\lambda) = \left[ \frac{\alpha L_n}{\alpha L_n + (\epsilon/\epsilon_c)} \right] \left[ -e^{-\alpha x_i} + \left( \frac{1}{\alpha x_i} \right) [1 - e^{-\alpha x_i}] \right] + \left[ e^{-\alpha x_i} - \frac{e^{-\alpha W}}{(1 + \alpha L_p)} \right] \tag{7.2}
\]

where the inversion layer width \( x_i \) is given by

\[
x_i = \left( \frac{\epsilon_0 \epsilon_s}{2q N_D V_D} \right)^{1/2} \left( \Phi_{\text{Bn}} - \frac{1}{2}(E_g/q) \right) \tag{7.3}
\]
Figure 7.7  The spectral response of the InAlAs/graded superlattice/InGaAs planar Schottky barrier photodiode.
Figure 7.8  The crosstalk between two wavelength regimes for the Schottky barrier photodiode.
where $\bar{e}$ is the mean electric field strength in the inversion layer, $\epsilon_c (= kT/qL_n)$ is the critical field, $N_D$ is the donor density, $N_V$ is the effective density of the valence band states, and $V_t$ is the thermal voltage ($=kT/q$). Li et al.[81] has shown that the sharp decrease of the quantum yield in the short wavelength regime can be attributed to the photocarriers generated in this inversion layer which recombine near the surface before they can be collected at the contact. Results of the spectral response measurements for the In$_{0.53}$Ga$_{0.47}$As photodiodes showed that the responsivity decreased rapidly for wavelengths shorter than 0.9 $\mu$m or greater than 1.6 $\mu$m [82,83,84]. The graded superlattice serves as a barrier to prevent diffusion of the photogenerated carriers from one absorption layer to the other. Therefore, the crosstalk between the two absorption layers can be effectively reduced by the graded superlattice between the top InAlAs and bottom InGaAs layer. In the response speed measurement, the photodiode was mounted on a 50-ohm microstrip transmission line, which was fabricated on the Cr-Au metallized alumina (Al$_2$O$_3$) substrate, and was connected to a bias tee through OSSM subminiature coaxial connector. The response speed of the photodiodes was measured by using the impulse response method. An argon pulsed laser with a full width at half maximum (FWHM) of 30 ps with a pulse repetition rate of 25 Hz was used as the optical source, and the response time was measured with an S-4 head sampling oscilloscope (Tektronix S24-11802) at a wavelength of 0.53 $\mu$m. The sampling oscilloscope introduces pulse broadening with a rise time of 25 ps. The measured response speed is a convolution of the true impulse response of the detector and the measurement system including the sampling gate width, the laser pulse width, and pulse broadening due to transmission lines and connectors. Since the response is primarily limited by the laser pulse and the rise time of the sampling oscilloscope, we can estimate a true response by deconvolution. The response speed of the Schottky barrier photodiode measured by the impulse response method is shown in Fig. 7.9; a
full width at half maximum of 180 ps was obtained at zero bias, which corresponds to a response speed of around 3 GHz. Further reduction in the rise time can be obtained by operating the detector at a higher bias voltage so that the active layer is fully depleted and the undesirable diffusion time delay can be avoided. To analyze the effects of the extrinsic circuit elements on the detector bandwidth, the SPICE simulation of the equivalent circuit of the photodiode was performed, and the result was plotted in Fig. 7.10, which showed a 3 dB cutoff frequency of around 10 GHz, a value which is significantly larger than the value obtained from the impulse response measurement.

7.4. Summary and Conclusion

A novel planar dual wavelength InAlAs/graded superlattice/InGaAs Schottky barrier photodiode has been designed, fabricated, and characterized. An InAlAs layer has been used to increase the Schottky barrier height, and to reduce the reverse leakage current to less than 1.2 nA at 5 V. Furthermore, an InAlAs/InGaAs graded superlattice layer of 600 Å has been introduced to reduce carrier trapping at the heterointerface of InAlAs/InGaAs layers. Using this novel structure, a double peak photoresponse for the detector was obtained with peak responsivity of 0.34 A/W at 0.8 µm and 0.42 A/W at 1.3 µm, respectively. Absence of an extended tail in the impulse response curve indicates that no significant charge trapping occurs at the InAlAs/InGaAs heterointerface. The measured FWHM of 180 ps for the photodiode may be attributed to the undesirable packaging parasitics such as large inductance of the bond wires and parasitic capacitances of the sample holder. This FWHM corresponds to a bandwidth of 3 GHz for the detector. Optimization of the device structure such as adjusting the absorption layer thickness and device packaging can further improve the responsivity and speed of the detector reported here.
Figure 7.9  The impulse response of the Schottky barrier photodiode measured by the impulse response method.
Figure 7.10 (a) Equivalent circuit model of the Schottky barrier photodiode to determine the 3-dB cutoff frequency by SPICE simulation.

\[ R_L = 50 \, \Omega \quad L_b = 0.9 \, \text{nH} \]
\[ R_S = 162 \, \Omega \quad C_p = 0.1 \, \text{pF} \]
\[ R_i = 10 \, \text{M\Omega} \quad C_j = 0.1 \, \text{pF} \]
Figure 7.10 (b)  The 3-dB cutoff frequency of the InAlAs/graded superlattice/InGaAs Schottky barrier photodiode.
CHAPTER EIGHT
SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

8.1. Summary and Conclusions

This dissertation describes the development of a new passivation technique using P$_2$S$_5$/(NH$_4$)$_2$S and of a novel high-speed broad-wavelength InAlAs/InGaAs Schottky barrier photodetector. The effects of P$_2$S$_5$/(NH$_4$)$_2$S surface treatment on the diode characteristics of Al- and Au-Schottky contacts formed on n-type GaAs have been investigated and compared with that of (NH$_4$)$_2$S$_x$ and NH$_4$OH/HF treatment. The Schottky contact formed on the P$_2$S$_5$/(NH$_4$)$_2$S-treated surface showed a higher barrier height than that of (NH$_4$)$_2$S$_x$-treated and unpassivated surface. The increase of the effective barrier height is attributed to phosphorus which enhances the compensation of As$_{Ga}$ antisite defect at the GaAs surface. Also, the P$_2$S$_5$/(NH$_4$)$_2$S and (NH$_4$)$_2$S$_x$ treatment on the MSM GaAs Schottky photodiodes have shown an improved spectral responsivity.

In order to determine how the P$_2$S$_5$/(NH$_4$)$_2$S treatment causes such improvements in the electrical quality of the GaAs surface, XPS was used to examine GaAs surfaces following an acid etch and P$_2$S$_5$/(NH$_4$)$_2$S treatment. Angle-resolved spectra of As 3d and Ga 3d levels exhibit the existence of As-S and Ga-S species on the surface. Formation of an As-S compound contributes to the reduction of surface states caused by mostly As$_{Ga}$ antisite defects. From the spectra of Ga 3d, P 2p, and O 1s, it has been observed that there exist oxygen species such as GaPO$_4$. The chemical structure of GaPO$_4$, formed by the reaction of Ga$_2$O$_3$ and P$_2$O$_5$, is highly ordered, which implies the chemical stability of GaPO$_4$. The degradation of the passivation
with time in air results from the breaking of the As-S and Ga-S bonds and their
replacement by bonds to oxygen at the surface, and leads to the formation of arsenic
because the heats of formation of As and Ga sulfides are far less than the heats of
formation of the As and Ga oxides. Another possible degradation mechanism is that
exposure to the atmosphere will result in a change of the chemical structure of GaPO₄
owing to the absorption of moisture. Once the passivation layer is disrupted by these
reactions, its electrical characteristic will deteriorate. It has been also demonstrated
that the barrier height enhancement on n-In₀.₅₃Ga₀.₄₇As can be made with a simple
chemical passivation. The Schottky contact formed on the P₂S₅/(NH₄)₂S-treated sur-
face showed a higher barrier height than that of (NH₄)₂S₂ and NH₄OH/HF-treated
surfaces. The increase of the effective barrier height is attributed to the MIS like
structure formed by the phosphorus oxide which has the most negative free energy
compared to Ga₂O₃, In₂O₃, and As₂O₃.

Angle-resolved spectra of As 3d and Ga 3d levels on the P₂S₅/(NH₄)₂S treated
n-type In₀.₅₃Ga₀.₄₇As surfaces also shows the existence of As-S and Ga-S species on
the surface. It has been observed that there exist oxygen species such as GaPO₄,
InPO₄, and In(PO₃)₃. The chemical structure of GaPO₄ and InPO₄ is known to be a
highly ordered nonconductive species which implies the chemical stability of GaPO₄
and InPO₄, and that these oxides are responsible for the barrier height enhancement
on InGaAs surface after chemical passivation.

In view of the higher barrier height, lower reverse leakage current, and the simple
process, the P₂S₅/(NH₄)₂S chemical passivation on GaAs and n-In₀.₅₃Ga₀.₄₇As reported
here is a viable and promising technique for improving stability and performance of
GaAs and InGaAs devices.

A novel high-speed dual-wavelength InAlAs/InGaAs Schottky barrier photo-
diode for 0.8 and 1.3 μm detection has been demonstrated employing band gap
engineering. The detector structure consists of a Au-Schottky contact on the n-In$_{0.52}$Al$_{0.48}$As/undoped n-In$_{0.52}$Al$_{0.48}$As/In$_{0.53}$Ga$_{0.47}$As graded superlattice (GSL)/n-In$_{0.53}$Ga$_{0.47}$As epilayers grown on a semi-insulating InP substrate by molecular beam epitaxy (MBE). The top wide bandgap n-In$_{0.52}$Al$_{0.48}$As epilayer absorbs photons in the visible to near infrared spectrum (i.e., 0.4 to 0.9 $\mu$m) with peak response occurred around 0.8 $\mu$m, whereas the bottom n-In$_{0.53}$Ga$_{0.47}$As epilayer absorbs photons in the 1.0 to 1.6 $\mu$m wavelength regime with peak response occurred at 1.3 $\mu$m. The effect of charge trapping due to the bandgap discontinuity ($\Delta E_c = 550$ meV, $\Delta E_v = 200$ meV) at the heterointerface, which may limit the speed of heterostructure photodiode, is significantly reduced by introducing a graded-superlattice of undoped n-In$_{0.52}$Al$_{0.48}$As/In$_{0.53}$Ga$_{0.47}$As (10 periods, 600 Å). Excellent dark I-V characteristics with low reverse leakage current and junction capacitance ($< 1.2$ nA and $< 0.1$ pF at 5 V, respectively) have been achieved in this new photodetector structure.

8.2. Recommendations for Future Study

The P$_2$S$_5$/(NH$_4$)$_2$S passivated GaAs and InGaAs surfaces showed the improved electrical and optical characteristics. However, the improved characteristics degrade with time when the passivated devices were exposed in ambient environment, possibly due to the oxidation. One approach to protect the passivated surface from the oxidation is to combine the chemical treatment with a dielectric passivation. The dielectric film deposited on the top of the chemically passivated surface will probably lead to the better stability of the P$_2$S$_5$/(NH$_4$)$_2$S passivated surface.

Even though a fair amount of information about the chemical composition of the passivated surface could be obtained from the XPS spectra, due to the limited resolution of the XPS analysis it is better to employ some other surface characterization techniques such as X-ray diffraction, synchrotron radiation, and SIMS in addition to the XPS study. Then it will be much easier to understand the surface physics and
chemistry related to the chemical bonding within the passivation layer formed on the GaAs and the InGaAs, and the interfacial structure between the passivation layer and the semiconductor surface.

Although n-type InGaAs is a very attractive material for the high-speed electronic and photonic devices due to its excellent properties, the low Schottky barrier height presents problems in forming Schottky barrier devices. In chapter 5, it has been shown that the chemical passivation on n-InGaAs is very effective method to reduce surface states and increase the barrier height. Therefore, it is very interesting to apply the chemical passivation technique on active devices such as metal-insulator-semiconductor field-effect transistor (MISFET).

The spectral response of the developed novel high-speed dual-wavelength Schottky photodetector has shown two separate photoresponse. If the crosstalk can be suppressed to almost zero, then the device can be used for wavelength demultiplexing/multiplexing (WDM).

The wavelength demultiplexing/multiplexing (WDM) technique, which transmits multiple optical signals with different wavelengths through a single optical fiber, is a useful means of making full use of the low-loss characteristics of optical fibers over a wide-wavelength region, and can also increase the capacity of optical fiber transmission systems. Although WDM technique is not fully matured at present, it has been gradually introduced into practical systems because this technology will play a major role in future optical communication. There are two basic configurations for WDM transmission systems, i.e., one-way and two-way transmission. Either requires a single optical fiber, several light sources and photodetectors, and optical multi/demultiplexing devices. At the transmitter, the input fibers are attached to optical sources whose emission wavelengths are $\lambda_1, \lambda_2, \ldots, \lambda_n$, respectively. Optical carriers are guided to a multiplexing circuit by input fibers. These carriers are
coupled to the signal transmission fiber after passing the multiplexing circuit. At the receiver, each optical carrier is selected by the demultiplexing circuit and is guided to detectors through output fibers. The advantage of WDM systems are: transmission capacity increase per fiber, system cost reduction, simultaneous transmission of different modulation-scheme signals, and service channel expandability after fiber installation. These are the reason WDM technology is expected to be widely applied to systems in various fields of communications. As a result, active wavelength-selective demultiplexers, which perform both demultiplexing and detection, are important since they simplify system configurations.
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BIOGRAPHICAL SKETCH

Kiuchul Hwang was born in Taegu, Korea, on June 25, 1953. He received the degree of Bachelor of Engineering in metallurgical engineering from the KyungPook National University in 1978. From 1978 to 1981, he worked with the Quality Control Division of a steel company where he was engaged in the improvement of products. He attended the University of Cincinnati for the degree of Master of Science in electrical engineering from 1984 to 1985, where he was a research assistant. Since Aug. 1986, he has been working toward the degree of Doctor of Philosophy at the University of Florida.

In September 1990, he joins the HEMT process group at General Electric Laboratory. His present interests include the development of novel passivation techniques for III-V compound semiconductor devices and new IR photodetector using superlattice and quantum well structures.
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Sheng S. Li, Chairman
Professor of Electrical Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Peter S. Zory
Professor of Electrical Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Dorothea E. Burk
Professor of Electrical Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Gys Bosman
Professor of Electrical Engineering
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Murali Rao  
Professor of Mathematics

This dissertation was submitted to the Graduate Faculty of the College of Engineering and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December 1990

Winfred M. Phillips  
Dean, College of Engineering

Madelyn M. Lockhart  
Dean, Graduate School