Process optimization of IR detectors based on In(Ga)Sb QDs in an InAs matrix

Mina Rajabi
Master of Science Thesis
Stockholm, Sweden
September 2012

TRITA-ICT-EX-2012:271
Mina Rajabi
Master of Science Thesis
September 2012

Nanotechnology program
Royal Institute of Technology (KTH)
Stockholm, Sweden.
Supervisor at Acreo AB: Dr. Qin Wang
Examiner at KTH: Prof. Mats Göthelid
Contents

Abstract .................................................................................................................................................... i
Acronyms .................................................................................................................................................. ii
Acknowledgment ..................................................................................................................................... iii

1. Introduction ......................................................................................................................................... 1
  1.1 Background and motivation .......................................................................................................... 1
  1.2 Project goal .................................................................................................................................... 2
  1.3 Thesis outline ................................................................................................................................. 2

2. Infrared photodetectors ...................................................................................................................... 4
  2.1 Infrared detector technologies ...................................................................................................... 4
  2.2 Quantum structure based infrared photodetectors ..................................................................... 5
    2.2.1 Principles of quantum structures ........................................................................................... 5
    2.2.2 Quantum well/dot infrared photodetectors (QWIPs/QDIPs) ................................................ 6
    2.2.3 Intraband transitions in QWIP and QDIP ................................................................................ 7
    2.2.4 Interband transitions in D2B IR detectors .............................................................................. 7
  2.3. Figures of merit of infrared detectors .......................................................................................... 8
    2.3.1 Responsivity ............................................................................................................................ 8
    2.3.2 Dark current ............................................................................................................................ 8
    2.3.3 Detectivity .............................................................................................................................. 9
    2.4.4 Noise equivalent temperature difference .............................................................................. 9

3. IR detector fabrication techniques .................................................................................................... 10
  3.1 Material growth by epitaxy ......................................................................................................... 10
    3.1.1 Heterostructure growth ....................................................................................................... 10
    3.1.2 Quantum dot growth ............................................................................................................ 10
  3.2 Key device processing steps ........................................................................................................ 10
    3.2.1 Lithography ........................................................................................................................... 11
    3.2.2 Etching .................................................................................................................................. 11
    3.2.3 Passivation ............................................................................................................................ 11

4. Measurement techniques ................................................................................................................. 13
Abstract

This diploma project has been focused on optimization of the D2B IR detector fabrication process using different mesa sidewall treatments and passivation methods. X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and atomic force microscope (AFM) measurements have been carried out on samples treated by different wet etching methods, to analyze their surface chemical composition and roughness. The surface roughness has been improved by critic etching, annealing and NaClO sequential treatment steps. Then these results have been utilized to improve the process of the D2B IR detectors.

The dark current of the fabricated detectors passivated with various techniques have been characterized by I-V measurements at low (77 K) and room temperatures. The dark current mechanisms owing to surface shunt or bulk leakage are investigated by dark current temperature dependence analysis. By photoresist passivation devices with least leakage current are achieved.
Acronyms

AFM: Atomic Force Microscopy
D2B: Dot to Bulk
FPAs: Focal Plane Arrays
IR: Infrared
LWIR: Long Wavelength Infrared Radiation
MBE: Molecular Beam Epitaxy
MOVPE: Metal Oxide Vapour Phase Epitaxy
MWIR: Medium Wavelength Infrared Radiation
NIR: Near Infrared Radiation
QDs: Quantum Dots
QDIPs: Quantum Dot Infrared Photodetectors
QWIPs: Quantum Well Infrared Photodetectors
QWs: Quantum Wells
QWRs: Quantum Wires
S-K: Stranski- Krastanov
SEM: Scanning Electron Microscopy
SWIR: Short Wavelength Infrared Radiation
XPS: X-ray Photoelectron Spectroscopy
Acknowledgment

First of all, I would like to give my greatest thanks to my supervisor at Acero, Dr. Qin Wang, for entrusting me with this challenging project and for sharing her deep knowledge with me. I am also grateful to the trust she has in me, her kindness and her support in any other issues during these months.

I would like to thank my examiner at KTH, Prof. Mats Göthelid for helping me with XPS measurements and always keeping the door open for any technical discussions.

I am very grateful to Susanne Almqvist, for her support extended in fabrication and wire bonding of components, Amir Karim for helping me with SEM measurement and Shun Yu for extending help in XPS measurements and accompanying me for a week in Lund.

Thanks Reza Nikpars and Andy Zhang for introducing me with measurement equipments I needed.

Thanks to the IMAGIC centre for the financial support of this project and for giving me the opportunity to work in this research group especially Dr. Jan Andersson and Dr. Sussan Savage.

I would also like to thank all the people at Acero and IRnova for making so much of friendly environment and kind help whenever I needed specially Ingemar Peterman, my friend and officemate Milad.

And last but not least, I would like to give my heartfull thanks to my parents, my sister and my best friend Saveda for giving me all the support, courage and affection during my stay in Sweden.
1. Introduction

1.1 Background and motivation

During the past years many fields have undergone radical changes due to the emerging of quantum mechanical effects and one such field is photonic devices. Novel quantum materials with exceptional optoelectronic properties offering promising applications have been developed. Since the advancement of epitaxial growth, semiconductors with low dimensional structures have been enabled, and have attracted intensive interest to achieve high performance photonic devices. These quantum structures confine carriers which results in quantized energy levels and as a result widespread possibilities to adjust the optoelectronic properties of the materials. This becomes more important in optoelectronic applications such as lasers and infrared (IR) detection.

High-performance IR cameras are needed for applications in defense and security, space technology, search and rescue, meteorology, astrophysical imaging and other industrial areas. Three generation IR systems can be categorized: 1st Gen scanning system (mid 50’s till 70’s), 2nd Gen staring system (mid 70’s till 90’s) and 3rd Gen multicolour functionality (since 1998 till present) [1]. Lower dark current, higher operating temperature and spatial uniformity over a large area are some of the prerequisites for the next generation photonic imaging applications [2]. Over a large research, at present $\text{HgCdTe}$ is the most dominantly used system though it provides high quantum efficiency but still suffers from basic material properties. Limited material quality generates large dark current and results in low device yield and high cost. An alternative system to answer this issue is quantum well infrared detector (QWIP) based on III-V semiconductors with mature processing techniques. Performance of the most advanced QWIP based on $\text{GaAs}/\text{AlGaAs}$ could compete with $\text{HgCdTe}$ IR detectors. These two systems still need to operate at low temperatures (lower than 77K), which requires costly cryogenic systems for cooling, namely high cost [1, 3].

Success with QWIPs led to the development of quantum dot infrared detector (QDIPs). They have promising features to outperform QWIPs by demonstrating lower dark current and higher operating temperatures [1]. This rapid progress in the last decade makes it a competitive technology for the third-generation imaging systems [4]. The other new
approach is type II strained layer super lattices (T2SLs) which has growth complexity and higher cost [5].

1.2 Project goal

This thesis project is focused on processing analysis and development of type-II quantum dot IR photodetectors utilizing a novel material system where the detection mechanism is based on transitions from bound hole states in In(Ga)Sb QDs to continuum states of InAs bulk material [3]. These detectors are referred to as dot-to-bulk (D2B) infrared photodetector, which is expected to provide performance levels similar to quantum well infrared photodetectors (QWIPs), but at operating temperature in excess of 200 K. It enables the use of less expensive thermoelectric coolers, thereby making them potentially attractive as a low-cost high-performance long wavelength infrared (LWIR) detector. However, surface leakage currents arising from the D2B detector mesa sidewalls, due to a large number of surface states, is still a challenge. When the material undergo etching process to form mesas, the periodic crystal structure ends abruptly leading to formation of dangling bonds most of which terminate to native oxides when the surface is exposed to the air [6]. Results presented in literatures show that Sb-based structures introduce unwanted surface leakage current especially in Focal Plane Arrays (FPA) as the device dimensions shrink [7]. These sources act as a conductive path parallel to the surface contributing in leakage current [8]. In fact, the device leakage current or dark current is not only caused by surface leakage current, but also induced by the defects in the bulk material [8].

The goal of this work is to remove the trap states from the device surface and then preserve the surface quality by passivation techniques to achieve high performance D2B IR detectors.

1.3 Thesis outline

This thesis is structured as following: chapter 2 illustrates the physics of infrared photodetector technology. Chapter 3 briefly explains the various device fabrication techniques used in this work. Measurement techniques are presented in chapter 4. In chapter 5 processing steps for the devices and test structures that are used for surface characterizations are discussed. Chapter 6 depicts the experimental results from samples with different surface treatments, in terms of surface composition and roughness of the corresponding samples. The dark current behaviour of the fabricated D2B detectors are also detailed in this chapter, which
allows us to investigate the suppression of the leakage current with different cleaning processes by wet etching and passivation techniques. In chapter 7 summary and future plan on this work is put forth.
2. Infrared photodetectors

2.1 Infrared detector technologies

Infrared (IR) radiation is electromagnetic radiation with a wavelength ranging between the visible and microwaves in the electromagnetic spectrum. Every object emits IR and the radiated spectrum depends strongly on the temperature of the object, as described by Planck’s radiation law as shown in eq.1. According to this law, the temperature can be found according to the color of the radiation, in other words \( \lambda \) or vice versa [9].

\[
E(\lambda) = \frac{2hc^2}{\lambda^5 \left( \exp\left(\frac{hc}{\lambda kT}\right) - 1 \right)} \quad \text{----------- (1)}
\]

Where \( \lambda \) is the wavelength, \( T \) is temperature and constants \( c, h \) and \( k \) corresponds to the speed of light, Planck’s constant and Boltzmann’s constant respectively.

The radiation of hot objects which are more than 1000 K is in the visible region while radiation of cold objects, such as human bodies, is in the infrared region. IR radiation can be subdivided into four regions according to the transmission properties of the atmosphere [9]:

- Near infrared (NIR): 700 nm -3um
- Medium wavelength infrared (MWIR): 3-5 um
- Long wavelength infrared (LWIR): 8-14 um
- Far infrared (FIR): 16 um-1 mm

The MWIR and LWIR transmissions are the mostly correlated with our surrounding objects making them the important window for thermal imaging applications. The NIR and FIR have applications in free-space optical communication and terahertz technology, respectively.

Thermal imaging is mainly based on two detecting technologies namely thermal detectors and photon detectors. Thermal detectors can operate at room temperatures but they suffer from low sensitivity and weak response while photon detectors are highly sensitive and have fast response but they require cryogenic temperature in order to reduce the dark current. However, importing new design structures enables wide possibilities for MWIR and LWIR detection. Type-II strained layer super lattices (T2SLs) and quantum dots and wires are some such examples for high temperature IR detections.
2.2 Quantum structure based infrared photodetectors

2.2.1 Principles of quantum structures

- **Semiconductor heterostructure**

  When two different semiconducting materials are deposited sequentially on each other they form a semiconductor heterostructure. For growing such structures several epitaxial growth techniques with possibility of growing layers as thin as a monolayer have been introduced such as Molecular Beam Epitaxy (MBE), Metal Organic Chemical Vapor Deposition (MOCVD) or Metal Organic Vapor Phase Epitaxy (MOVPE). Depending on the band alignment of any two adjoining semiconductors three different types of heterostructure can be formed as shown in Fig.2.1 [10, 11].

1. **Type I: Straddling**, in which the smaller bandgap material lies in between the larger bandgap material.
2. **Type II: Staggered**, in which one material’s bandgap offsets to the bandgap of the other material.
3. **Type III: Broken gap**, in which bandgap of one material is completely higher or lower than that of the other material.

These band alignments provide potential barriers and traps for the charge carriers and consequently result in limitation of carrier’s motion in some directions. Based on this confinement of carriers the structures can be classified into three different designs as shown in Fig.2.2 [10, 13].

- **Quantum well (QW):** Formation of a 2D quantum well is in such a way that it confines the motion of electrons/holes in one direction, while it is free to move in the other two directions.
- **Quantum wires**: Formation of a 1D quantum wire is in such a way that it confines the motion of electrons in two directions, while free to move in the third direction.

- **Quantum dots (QD)**: Formation of a 0D quantum dot is in such a way that it confines the motion of electrons in all three directions.

![Classification of semiconductors based on confinement of charge carries a) bulk semiconductor b) quantum well c) quantum wire d) quantum dot](image)

**Figure 2.2 Classification of semiconductors based on confinement of charge carries a) bulk semiconductor b) quantum well c) quantum wire d) quantum dot [12]**

### 2.2.2 Quantum well/dot infrared photodetectors (QWIPs/QDIPs)

Infrared absorption in a QWIP is based on utilizing the intrasubband transition of carriers confined in the ground state to various excited states in the conduction band. The QWIP structure is shown in Fig. 2.3a. Due to mature and low cost fabrication, they are commercially available in large format focal plane arrays (FPA) and have applications in medical imaging, gas sensors, surveillance and so on. However, they suffer from low quantum efficiency, lack of normal incidence absorption, high level of dark current and require cooling to cryogenic operation temperatures [1].

![Schematic layers of a) QWIP b) QDIP](image)

**Figure 2.3 Schematic layers of a) QWIP b) QDIP [1]**

QDIPs are conceptually similar to QWIPs but it is expected to solve the above issues of QWIPs by the virtue of zero-dimensional quantum confinement. Their main promising advantages over QWIPs are listed as follows:

- Enabling normal incidence absorption due to its three-dimensional confinement, so no need of extra light coupling techniques such as gratings.
- Reducing temperature dependency of carrier distribution by having density of states as series of delta functions in energy.
• Gain reduction in dark current level due to its longer carrier life time (10-100 times) in the excited state [1].

However interesting physical properties and the relative ease of fabrication have recently attracted researchers towards QDIPs. They have predicted that QDIPs will significantly outperform QWIPs and emerge as an important technology for infrared detection. But QDIPs suffers from low absorption (quantum efficiency) due to large inhomogeneous dot size and density with the Stranski-Krastanov (S-K) growth mode.

2.2.3 Intraband transitions in QWIP and QDIP

By incident photons to the IR detectors, electrons in the ground state of QW or QD in the conduction band will be excited to escape directly or indirectly out of the confining potential to the continuum [10]. These electrons then, under an applied bias, drift towards the collector contact as is shown in the Fig. 2.4. The electrons could be recaptured into another well/dot or continue their way reaching the contact and contributing to the photocurrent. This probability is defined by a parameter called gain [1, 14]:

\[ g = \frac{\text{carrier life time } (\tau)}{\text{carrier transit } (t)}. \]

![Figure 2.4 potential profile for QWIPs and QDIPs under bias [1]](image)

2.2.4 Interband transitions in D2B IR detectors

This structure utilizes the quantum confinement in 3D in the type II band alignment as “broken gap” as shown in Fig. 2.5. The interband transitions occur from bound hole states in \( \text{In(Ga)Sb} \) QDs to continuum states of \( \text{InAs} \) bulk material under IR irradiation.
2.3. Figures of merit of infrared detectors

2.3.1 Responsivity

The responsivity of a photodector is a merit of measuring the detector response as an electrical output per optical input (measured in V/W or A/W). It is defined to be:

\[ R = \frac{S}{P A} \quad [\text{V/W}] \quad (2) \]

- **S**: Signal output [V]
- **P**: Incident energy [W/cm²]
- **A**: Detector active area [cm²]

2.3.2 Dark current

The current that flows in a biased detector where photo excitation phenomenon doesn’t exist is called dark current [12]. Since this current is a non-photo related current it is called “dark current”. Dark current in intrasubband detectors are generated due to three predominant mechanisms as illustrated in Fig. 2.6. generation recombination current, tunneling current and surface leakage current (due to poor surface quality) provide different contributions to the dark current.

- **A. Thermionic emission** (thermally excited electrons from ground state jumps to the continuum)
- **B. Thermally assisted tunneling** (thermally excited electrons from second excited state tunnel to the continuum)
- **C. Sequential tunneling** (electrons in ground state directly tunnel between wells or dots)

Regarding photodetectors, mechanism A and B are the most prominent mechanisms which are strongly affected by applied voltage, operating temperature and energy level structure [15].
Figure 2.6. Dark current mechanisms in QWIPs and QDIPs. (A) Thermionic emission (B) Thermally assisted tunneling (C) Sequential tunneling [12]

2.3.3 Detectivity

Detectivity $D^*$, is a merit to evaluate the performance of a detector considering both responsivity and thermal noise. It is defined as

$$D^* = \frac{\sqrt{A \cdot \Delta f}}{NEP} \text{ [cmHz}^{1/2}\text{W}^{-1}]$$ \hspace{1cm} (3)

$A$ : Area of the photosensitive region
$\Delta f$ : Effective noise bandwidth
$NEP$ : Noise equivalent power

2.4.4 Noise equivalent temperature difference

Noise equivalent temperature difference (NETD) is a merit of FPA performance regarding signal-to-noise ratio of the detector. It determines the minimum temperature difference the detector can distinguish for a given bias, input irradiance and temperature, in other words it is the sensitivity of the detector. It’s the temperature change of a scene required to produce a signal equal to the rms noise [7]. It is defined as:

$$NETD = (\pi C \eta_{BLIP} \sqrt{N_w})^{-1}$$

$\tau$ : Optics transmission spectrum
$C$ : Thermal contrast
$N_w$ : Number of photogenerated carriers integrated for one integration time

$$\eta_{BLIP} = \left(\frac{N_{\text{photon}}^2}{N_{\text{photon}}^2 + N_{\text{FPA}}^2}\right)$$ is the percentage of background-limited performance.
3. IR detector fabrication techniques

3.1 Material growth by epitaxy

3.1.1 Heterostructure growth

High quality material growth is essential for any device technology. The two main growth techniques for semiconductor heterostructures are molecular beam epitaxy (MBE) and metal organic vapour phase epitaxy (MOVPE) [11].

- MBE is a high vacuum technique. Crucibles containing desired materials are heated up in order to evaporate atoms or molecules to the hot substrate. The slow growth rate together with programmed shutters provides good control of growth direction and thickness [16].
- MOVPE is another important growth technique similar to MBE but the gases here are complex molecules of metal-organic, and the deposition takes place by chemical reaction of atomic species on the hot substrate. This technique is more preferred in industry due to its higher growth rate and lower vacuum resulting in lower processing cost [16].

3.1.2 Quantum dot growth

One interesting way of growing quantum dots is using Stranski-Krastanow growth mode. Whenever a film of a certain material is deposited on the substrate of a different material, it will induce strain into the crystal. When the thickness of the grown film exceeds a certain limit (critical thickness) it relaxes by spontaneous formation of islands, the quantum dots [17]. This method is an energy driven process (mainly the chemical interaction energy, wetting energy and elastic energy) and utilizes the lattice mismatch for creation of QDs with high density and rather uniform shape and size [18].

3.2 Key device processing steps

IR photodetectors processing steps can be divided in major steps as shown below

- Mesa formation by lithography and etching
- Surface polishing by wet chemical etching
- Passivation using dielectric film or polymers
- Contacts by metal deposition and lift-off
3.2.1 Lithography

Lithography plays a key role in success of semiconductor device technology. Lithographic techniques are needed for patterning devices on large-scale wafers [16]. The general process involves following steps:

- Spin coating photoresist
- Exposure (Optical image through a photomask)
- Developing the resist
- Baking

3.2.2 Etching

- **Wet chemical etching:**
  
  Wet etching is usually isotropic (vertically and horizontally). It is a simple and inexpensive method but requires choosing a proper chemical agent. This choice depends on the chemical composition of the structure material i.e. number of bonds between atoms, their binding energy and type of atoms to be removed [34]. The etching process could be utilized for:
  
  - Providing clean surface, free of oxides and residual contamination
  - Etching of surface patterns
  - Revealing crystallographic planes and dislocations
  - Polishing or homogenous surface removal without surface damage
  - Removing surface damages resulting from surface cutting or polishing

- **Plasma etching:**
  
  This method provides a more efficient etching process over wet etching. The plasma is produced by passing an RF electrical discharge through a gas at low temperature creating ions and electrons. These ions bombard the surface with controlled energy then interact with the elements on the surface and etch them away. Depending on the purpose the ion energy can be varied either high to have anisotropic etching with no undercutting or low when selective etching is required [16].

3.2.3 Passivation

It is believed that an optimal passivation is needed to get a leak-free diode based on narrow bandgap semiconductor materials and it becomes more important for the device operating in the LWIR region [8]. The efficiency of an optoelectronic device is strongly
affected by common issues of III-V semiconductors such as high surface state densities, surface Fermi level pinning and a residual oxide layer on the surface [19]. So recent decade’s passivation processes have been developed aiming to:

- Prevent unwanted reactions with the atmosphere during the whole device operation life time (chemical passivation).
- Remove interfacial states from the band gap and prevent their formation (electrical passivation).
- Block transferring of electrons from semiconductor surface to the passivating layer.

Well known relevant passivation techniques in this field are [8]:

- Depositing a thick insulator layer/dielectric on the surface after removing native oxide for example SiO$_2$, SiN, cured BCB or photoresist
- Chalcogenide passivation which is surface modification by V or VI group elements such as ammonium sulphide, zinc sulphide.
- Overgrowth with larger bandgap material.
4. Measurement techniques

4.1 X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) is one of the most powerful surface analytical techniques which can provide precise information of qualitative elemental analysis (except Hydrogen and Helium), quantitative composition and chemical state of elements on the surface. This is a very surface-sensitive and non-destructive method with typical “sampling depth” of only a few nanometers. [20]

➢ How XPS works?

Schematic of the basic working principal of XPS is shown in Fig. 4.1. The sample is exposed to monochromated soft X-rays, in order to provoke the photoelectric effect, and then the energy spectrum of the emitted photoelectrons is detected by a high-resolution electron spectrometer called the electron energy analyser. This detector records the kinetic energies of the electrons associated with these atoms revealing the elements composition. This is shown in eq.1:

\[ E_k(e) = \frac{h\nu}{2} - E_B - \phi_{\text{spec}} \]  

Where

- \( E_k(e) \): kinetic energy of electron
- \( h\nu \): energy of incident photon
- \( E_B \): binding energy of electron
- \( \phi_{\text{spec}} \): work function of spectrometer

\[ \text{K.E.} = \frac{h\nu}{2} - \text{B.E.} - \phi_{\text{spec}} \]

Figure 4.1 schematic of XPS principle [21].

In this thesis the XPS experiments were carried out at MAX-lab in Lund (Sweden) using beamline I4. A schematic of the setup is illustrated in Fig. 4.2 and the specific information about the beamline is listed in Table 4.1
4.2 Atomic Force Microscopy

Atomic Force Microscopy (AFM) is a technique to analyze the surface topography, measuring, imaging and manipulating objects in the order of nanometers at higher resolution than other scanning microscopy.

How AFM works?

The schematic of AFM operation is shown in Fig 4.4a. The principle of operation of AFM measurements mainly depend on short range inter-atomic force-based interactions between the sample and the probe tip. In this thesis all the measurements are done under
tapping mode. This mode has become an important AFM technique, since this mode overcomes some of the limitations of both contact and non-contact AFM by eliminating lateral forces that can damage soft samples and reduce image resolution. Also this mode provides high resolution without damaging the sample or the tip. In this mode the piezoelectric crystal makes the cantilever oscillates very close to its resonance frequency. Any changes in surface will induce force due to Van der Waals interaction between a sharp tip mounted on a cantilever and the surface. The position of a laser spot reflected from the cantilever on a position sensitive photodetectors gives the structure of the surface. Surface roughness strongly affects properties of thin films like optical scattering, resistivity due to grain boundary, thickness and interfacial properties. This can be due to various reasons such as growth process, surface treatment, etc.

Figure 4.4 Schematic view of a) AFM [23] and b) SEM [24]

4.3 Scanning Electron Microscopy

The scanning electron microscopy (SEM) is a method for high-resolution imaging of surfaces, and consists of a microscope which uses electrons instead of light. This technique combines of several ranges of advantages such as higher magnification, larger depth-of-field, greater resolution and ease of sample observation, which makes SEM to count as one of the useful tools in all fields of characterization of solid materials.

- How SEM works?

The schematic of SEM operation is shown in Fig. 4.4b. When the sample is placed inside the microscope's vacuum column where air is pumped out, it will be targeted by the high energy electron beams produced by a thermal emission source coming from a filament to
the electron gun located at the top of the column. The beam passes through a series of electromagnetic lenses to focus these electrons to a very fine spot on the sample. When this beam hits the surface electrons scatter and generate secondary electrons which give the topographical information. Backscattered electrons can reveal crystallographic orientation and different phases in many materials while X-rays display thickness and composition information.

4.3 Dark current measurement

Dark current measurements can be used to study the effective quality of the etching and passivation steps of IR detectors. Since dark current is the only dominant current at low temperature when no excitation is available [19], it is necessary to reach cryogenic temperature for dark current measurements [26]. This condition can be achieved by cooling down the device in liquid nitrogen environment. In this work I-V measurement is performed for unpassivated devices by arranging a cooled set up with probe station and semiconductor analyzer HP 4156A, while passivated devices are dipped into a liquid nitrogen container (shielded dewar) equipped with electrically wire-bonded holder to the HP 4156A as shown in Fig. 4.5.

Figure 4.5 I-V set up; left, liquid nitrogen container with HP 4156A and right, probe station
5. D2B photodetector processing

5.1 D2B structures

In this project wafers with D2B structures were grown with S-K method by MOVPE at KTH [27]. Corresponding reference samples without dots were also grown for comparison. One example D2B structure shown in Fig. 5.1 includes 10 stacks of \textit{InSb} quantum dots with 80 nm spacer, which embedded into a pin \textit{InAs} diode structure.

![Schematic D2B structure](image)

5.2 Mask set to fabricate single pixel D2B detectors

The mask set used in this project is designed to fabricate single pixel D2B detectors specifically for the purpose of achieving an effective surface passivation. It includes various single pixel detectors in different shapes and sizes, also with small format FPA in different angles with 28 µm mesa and 30 µm pitch. Some test structures for optical and electrical characterization of the detectors are included as well. Each 2” wafer ensures 38 chips with size of approximately 7 cm by 5 cm. To explore the shape dependency on performance, there are mainly 2 types of single pixel detectors; square and round shape with or without metal pad on it for ensuring wire bonding contact as shown in Fig. 5.2. Also to explore the passivation effect, two different test structures with the same area but longer in perimeter were designed as shown in Fig 5.3.

![Schematic of single photodetectors](image)
5.3 Device processing

The device processing is done through the following steps: initially the surface is cleaned by solvent to make it ready for the processing. Then Optical lithography has been performed to pattern the devices on the wafer by using a mask. After developing the resist, wafers have been etched by wet chemical process. The main etchant for mesa formation is a solution of orthophosphoric acid ($H_3PO_4$), citric acid, hydrogen peroxide ($H_2O_2$) and DI water ($H_2O$) at a ratio of 1:1:2:20 where $H_2O_2$ oxidises III-V surfaces while $H_3PO_4$ etches III-V oxides ($In_2O_3$). The Citric acid based solution is a mixture of monohydrate citric acid crystals ($C_6H_8O_7$) dissolved in DI $H_2O$ using an ultrasonic bath. Then $H_2O_2$ was added to the etchant mixture in order to prevent outgassing [28]. III-V compounds are based on the covalent bonding which requires an oxidising agent to break their bonds [7]. Most often $HNO_3$ and $H_2O_2$ are used for this purpose and to prevent solution from total dissociation complex agents such as tartaric or citric acid would be added [28]. Etching solutions used in this work are listed in table 5.1.

<table>
<thead>
<tr>
<th>Type</th>
<th>Purpose</th>
<th>Chemicals</th>
<th>ratio</th>
<th>Processing time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>etchant I</td>
<td>Mesa etching</td>
<td>$H_3PO_4$; $C_6H_8O_7$; $H_2O_2$; $H_2O$</td>
<td>1:1:2:20</td>
<td>143</td>
</tr>
<tr>
<td>etchant II</td>
<td>Acid treatment</td>
<td>$C_6H_8O_7$; $H_2O_2$</td>
<td>5:1</td>
<td>60</td>
</tr>
<tr>
<td>etchant III</td>
<td>polishing</td>
<td>NaClO</td>
<td>1:100</td>
<td>10</td>
</tr>
</tbody>
</table>

Since oxidizing is unavoidable after any chemical reaction, it is expected to have unpurified surface after mesa etching. The material used in this work is composed of $InAs$ and $InSb$, the possible oxides of these compounds [19] are shown in table 5.2.
It was claimed in chapter 2 that the main sources of dark current are oxides and elemental radicals such as As, In$_2$O$_3$ and As$_2$O$_3$. It is important to remove these sources as much as possible. In order to do so we treated the device surface by citric acid. Here the wafers are held in citric acid agent for 1 min and then rinsed in DI water and blown with nitrogen. In next step metal contact deposition is done. First optical lithography is performed to make a pattern for contacts. After developing the resist, a stack of Ti+Pt+Au is deposited by metal evaporation. Finally, we lift off the remaining resist with metal on top to achieve the desired structures. Post metal annealing in vacuum is done for 5 min at 275°C. This step is immediately followed by surface polishing and passivation. First, sodium hypochlorite solution was used in order to polish the probable roughness after mesa etching. The treatment is for 10 seconds and is followed immediately by passivation of the mesa side walls. Here we have explored three different passivation materials to preserve the quality of the surface after these chemical treatments. The passivation is utilized to suppress the leakage current coming from the mesa sidewalls of the detectors based on narrow bandgap materials. Fig. 5.4 is showing the microscopic image of one chipset after the above detailed processing.

<table>
<thead>
<tr>
<th>III-V comp.</th>
<th>Equilibrium</th>
<th>Air/chemical oxide</th>
<th>Thermal oxide</th>
<th>Anodic oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>InAs</td>
<td>In$_2$O$_3$+As</td>
<td>-</td>
<td>In$_2$O$_3$+As/In$_2$O$_3$+As$_2$O$_3$</td>
<td>In$_2$O$_3$+As$_2$O$_3$</td>
</tr>
<tr>
<td>InSb</td>
<td>In$_2$O$_3$+Sb</td>
<td>In$_2$O$_3$+Sb$_2$O$_3$</td>
<td>In$_2$O$_3$+Sb</td>
<td>In$_2$O$_3$+Sb$_2$O$_3$</td>
</tr>
</tbody>
</table>

5.4 Sample preparation for structural surface charaterization

The wafer with structure shown in Fig.5.5 was cleaved into 6 small samples as illustrated in Fig.5.6; each of them was used in wet chemical etching process steps as below:
First, all 6 samples were cleaned with sequential immersion in acetone, isopropanol and DI water and blown with nitrogen. One sample is kept as “Reference sample” in order to have the original surface to compare for other treated samples. Then, the other 5 samples have been etched with etchant I by approximately etching rate of 295 nm/min for about 143 sec reaching to the p-InAs layer as shown in Fig. 5.5. The etched thickness was measured to be 820 nm by Tencor assuring to be on the epi layer. Again one of the samples is kept as “Mesa sample”. In order to improve the surface by removing oxides and elemental radical formed after mesa etching, surface treatment was followed by three more steps. First, these 4 samples were treated with etchant II for about 60 sec and one sample is kept away to be taken as “Citric sample”. Then last 3 samples were annealed in thermal vacuum machine in temperature of 275°C for 5 min and one sample is kept away to be count as “Thermal sample”. Finally 2 samples treated with sodium hypochlorite for 10 sec one freshly before measurement. This sequence is also depicted in the table 5.3.

![Figure 5.5 Schematic structure of measured samples](image1)

![Figure 5.6 Sample’s positioning on the wafer](image2)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Surface treatment</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>Reference</td>
</tr>
<tr>
<td>2- 6</td>
<td>S1</td>
<td>Mesa etched</td>
</tr>
<tr>
<td>3- 6</td>
<td>S1+S2</td>
<td>Citric acid</td>
</tr>
<tr>
<td>4- 6</td>
<td>S1+S2+anneal</td>
<td>Annealed</td>
</tr>
<tr>
<td>5</td>
<td>S1+S2+anneal+S3</td>
<td>NaClO</td>
</tr>
<tr>
<td>6</td>
<td>S1+S2+anneal+S3(fresh)</td>
<td>NaClO fresh</td>
</tr>
</tbody>
</table>
6. Results and discussions

6.1 XPS characterization

This section elucidates the results obtained from the XPS measurements. These experiments were carried out at MAX-lab in Lund (Sweden) using beamline I4. The measurement of the survey spectra were done with binding energy in the range of 0 to 120 eV using photon beam of 140 eV. Whereas \( \text{In}4d \) spectrum was done at photon of energy 75 eV and 145 eV, and \( \text{As}3d \) at 110 eV and 160 eV, respectively.

The survey spectrum as shown in Fig. 6.1 consists of \( \text{SiO}_2 \), As, In and Na on some sample’s surface. In all spectra \( \text{SiO}_2 \) is observed, its origin is not clear. Since it is observed even in reference spectrum one can believe that it is due to the contamination of this element inside the chamber. Small peak of Na in mesa spectrum could be attributed to the contamination in mease formation processing which disappears after citric acid treatment.

![Overview spectra of all samples with 140 eV photon energy](image)

Different photon energy provides useful approach to study sample’s chemical composition in different depth from the surface owing to their different electron escape depth. \( \text{As}3d \) and \( \text{In}4d \) spectra have been obtained at different photon energy in Fig. 6.2 and Fig. 6.3 respectively. \( \text{As}3d \) spectra have been measured at 110 eV and 160 eV. There is a strong and broad peak of \( \text{AsO}_2 \) at 45 eV. A small shoulder near 43 eV corresponds to radical As or other...
chemically shifted arsenic which is more visible in Mesa and Ref spectrum. Also the doublet peak at 41 eV corresponds to As bonded to In. The peak at 42 eV is dominant by As doublet on top. The relative difference between two peaks differs in each case. There has been an improvement in this regards with the Fresh and Citric treatment. The As shoulder has been totally disappeared after citric etching. It can be predicted that citric acid have oxidised the elemental arsenide. Later on NaClO seems to decrease this oxide.

![Figure 6.2 XPS spectra of As3d for all samples measured at 110 eV and 160 eV, respectively.](image)

In4d spectra depicted in Fig. 6.3 have been recorded at 75 eV and 145 eV, respectively. A main doublet peak at 18 eV corresponds to In-O and In-As. The In-O is dominant at 23 eV than that of In-As [30]. But this difference becomes more distinguishable in Citric and Fresh spectra. This confirms the probable improvement by these two cases. In addition, there is a “bump” between 27 and 30 eV that could be raised due to plasma excitations of the photoemitted electron on its way out from the sample. The relatively higher intensity of this bump at higher photon energy (145 eV) proves possibility of excitations of electrons below the surface.
6.2 AFM characterisation

6.2.1 Investigating the effect of uniformity of surface roughness

Three reference samples are chosen from different quarter in different position for AFM measurement as shown in Fig 6.4.

Interestingly the results indicate the roughness didn’t vary much for the reference samples located on different positions on the wafer, namely the surface roughness is position independent for untreated wafer. The AFM measurement for these samples are illustrated in Fig 6.5.
6.2.2 Effect of different treatments on surface roughness

In this part all 6 samples chosen from Fig 5.6 according to the etching plan in table 5.3 have been characterized and compared in terms of their surface roughness. The results can be seen in Fig 6.6.

Figure 6.5 3D AFM micrographs of reference samples in different positions, 1a with roughness of 0.35 nm, 1b with roughness of 0.89 nm, and 1c with roughness of 0.55 nm
Figure 6.6 3D and top view AFM micrographs, 1a) Reference with roughness of 0.89 nm, 1b) Mesa etched with roughness of 2.05 nm, and 1c) Citric acid with roughness of 1.16 nm, 1d) Thermal annealing with roughness of 1.17 nm, 1e) Sodium hypochlorite with roughness of 1.09 nm and 1f) Fresh sodium hypochlorite with roughness of 1.07 nm.

Table 6.1 shows the surface roughness of the samples after each chemical treatment. The roughness analysis reveals that Citric acid etching improves the surface roughness. It is also observed that thermal annealing didn’t vary the surface much, but fresh NaClO further decreased the roughness to the reference sample’s roughness level.
6.2.3 Effect of different treatments on surface roughness of the same sample

In order to confirm the results described in 6.2.2, the AFM measurement is performed for one specific sample after each process step listed in table 6.1. The results are illustrated in Fig. 6.7.

<table>
<thead>
<tr>
<th>No</th>
<th>Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Reference</td>
</tr>
<tr>
<td>2</td>
<td>Mesa etched</td>
</tr>
<tr>
<td>3</td>
<td>Citric acid</td>
</tr>
<tr>
<td>4</td>
<td>Annealed</td>
</tr>
<tr>
<td>5</td>
<td>NaClO</td>
</tr>
<tr>
<td>6</td>
<td>NaClO fresh</td>
</tr>
</tbody>
</table>

Table 6.1 Roughness estimation of all samples
6.3 SEM characterisation

Achieving good mesa sidewall profile including desired anisotropy and smooth etched surface is another challenge for reducing surface leakage current of the D2B detectors. SEM measurements are performed to investigate detector’s mesa sidewall profile. A device from wafer 25717 with the structure shown in Fig. 5.5 has been used for SEM measurement. In addition, D2B structure numbered as 25838 without quantum dots and No.25839 with quantum dots have been also measured to verify the effect of QD layers on the mesa sidewall roughness after wet chemical etch. The results are shown in Fig. 6.8.

It is clear from Fig. 6.8 that the QD structure suffers from poor anisotropy and surface roughness formed after wet etching. In order to overcome/improve these effects, investigation
of surface treatment using different wet chemical etchant on the mesa sidewall is the field of interest. In order to do so, the wafer was cleaved into 4 pieces after mesa etching, each has followed etching with citric acid, thermal annealing and NaClO. SEM images in Fig. 6.9 and 6.10 are presenting square and circular mesa’s sidewalls.

![Figure 6.9 SEM images of mesa sidewalls of photodiodes a) after mesa etching and b) after mesa etching and citric acid.](image)

![Figure 6.10 SEM images of mesa sidewalls of square shape photodiodes a) after thermal annealing and b) NaClO polishing.](image)

As we can see in Fig. 6.9 left the etched surfaces of InAs layer are full of tiny droplets which could be attributed to elemental As caused by the mesa etching process according to XPS studies reported in former XPS section [31]. Citric acid treatment was seen to enable for volatilising them to form a cleaner surface as shown in Fig. 6.9 right. Vacuum thermal annealing and Fresh NaClO shown in Fig. 6.10 present some roughness improvement on the sidewall though slight changes in roughness peaks could present different elemental case. This effect became stronger for the round shape detectors as shown in Fig. 6.11.
6.4 Dark current measurement

Different passivation techniques with polymer based and dielectric material have been studied in large extent to investigate how passivating step plays role in the level of dark current.

6.4.1 Comparing dark current of devices with and without quantum dots

The structural design of both the sets used in this section for measurement is the same except that one includes quantum dot layers in intrinsic layer. In both sets the surface after mesa etching is treated with citric acid and polished with NaClO and finally passivated with photoresist. Fig. 6.12 shows the I-V characteristics of the detectors with above explained structure. It could be observed that the dark current of the detectors without QDs is more uniform and lower in comparison with the corresponding devices with the QDs. This refers to probable presence of tunnelling from dots or defects have been introduced by them.

Figure 6.12. I-V characteristic for photoresist passivated detectors of a) with b) without QD
6.4.2 Influence of citric treatment on the detector dark current

From XPS, AFM and SEM measurements we observed that citric acid has significant improvement on the surface. So in this step after mesa etching the surface is treated only with citric acid and not annealing nor NaClO and passivated by photoresist. Dark current measurement of this group devices are shown in Fig. 6.13. By comparing their results with previous figure (Fig. 6.12a) it can be noticed that the dark current level is higher.

![Figure 6.13 I-V characteristic for photoresist passivated detectors with only citric acid treatment](image)

6.4.3 Photoresist passivation

The device fabrication is involving all the three-step treatment after mesa etching, citric acid, annealing and NaClO. The surface is then passivated with photoresist. Results of dark current are depicted in Fig. 6.14a. In Fig 6.14b the temperature dependenc of the dark current density of some good devices are presented.

![Figure 6.14. Dark current characteristic of InSb D2B detectors with photoresist passivation a) I-V and b) temperature dependency](image)
6.4.4 BCB passivation

The device processing steps are the same as described before except that polymer based-BCB has been used to passivate the detector’s surface instead of photoresist. The results of dark current are shown in Fig. 6.15a. As we can see only two device gained low dark current but still not low enough. The temperature dependency of the dark current density is measured and plotted in Fig 6.15b.

![Figure 6.15 dark current characteristic of InSb QD based D2B detectors with BCB passivation a) I-V and b) temperature dependency](image)

6.4.5 Effect of photoresist passivation for InGaSb QDs based D2B detectors

The device processing follows the same pattern as before including InGaSb QDs with small changes in material design. The results illustrated in figure below depict lower dark current comparing with InSb QDs results in Fig. 6.14a. Also higher yield was obtained as shown in Fig. 6.16a. Their temperature dependency was measured and summarized in Fig. 6.16b

![Fig 6.16 dark current characteristic of InGaSb QDs detectos with photoresist passivation a)I-V and b) temperature dependency](image)
6.4.6 Effect of SiO$_2$ passivation for InGaSb QDs based D2B detectors

Here again the device processing steps are the same as described before except SiO$_2$ has been utilized for device passivation. The results are illustrated in Fig. 6.17, which presents the dark current of SiO$_2$ passivated devices are higher than that passivated by photoresist. The temperature dependency of dark current density for three of such devices have been measured and compared in Fig. 6.17b.

![Results of devices with SiO$_2$ passivation](image)

Figure 6.17 dark current characteristic for InGaSb QDs detectors with SiO$_2$ passivation a) I-V and b) temperature dependency

6.4.7 Comparison of different passivations

Fig. 6.18 indicates the effect of different passivation techniques in suppressing the leakage current. “Red curve” shows the highest dark current when there is no applied passivation while “light blue” is for the SiO$_2$ passivation and “dark blue” is the passivation with polymer based BCB both of which show comparable dark current with signal of tunnelling effect. “Green curves” belong to photoresist passivation dark current, the dark with InSb and the light with InGaSb QDs.

![Comparison of different passivation](image)

Figure 6.18 Comparison of different passivation techniques
Good passivation system has to be reliable and stable during the device performance. In order to evaluate this merit we have measured the dark current for the second and more times as shown in Fig. 6.19 and Fig. 6.20. The second time measurement of such devices are depicted in Fig. 6.19 which shows that unpassivated devices faced to high degradation of one order of magnitude, and BCB also degraded. The dark current of InSb QD based detectors passivated by photoresist shows slightly degradation while InGaSb QD based detector’s degradation is almost negligible and shows the lowest level of dark current.

![Figure 6.19 Comparison of different passivation techniques and repeat measurements](image)

This is more significant in the next figure which shows the five times repeating of a current measurement on one single device of InGaSb.

![Figure 6.20 Five times repeat measurement of a InGaSb device](image)
7. Summary and future work

- The origin of leakage current in terms of device surface roughness has been studied using the samples treated by different process steps by AFM and SEM measurements. The surface roughness has been improved by critic etching, annealing and NaClO sequential treatment steps.
- XPS measurement results indicate the surface states generated during mesa etch have been reduced by chemical treatments with citric acid and NaClO.
- Polymer-based passivation has been given better result among all regarding dark current.
- These results have been utilized to improve fabrication process of the D2B detectors.

In future more detail series process tests are needed as follows:
- Optimization process parameters by adjusting critic and NaClO concentration and etching time, also annealing tempartures and time.
- Investigation of passivation mechanism by study the interface between the D2B detector and passivation material.
- Fabrication of LWIR D2B detectors and FPAs utilizing optimized process parameters.
Bibliography


[21] R. Smart, et al., X-ray Photoelectron Spectroscopy, Department of physics and materials science, City University of Hong Kong.

[22] [online] https://www.maxlab.lu.se/beamlines/I4.


