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INSBN BASED PHOTODIODES FOR LONG WAVELENGTH INFRARED PHOTODETECTION

WANG YAN

School of Electrical and Electronics Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Master of Engineering

2009

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SCHOOL OF ELECTRICAL ELECTRONICS ENGINEERING

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Abstract

InSbN alloys are a potential candidate for the long wavelength infrared detection. By adding only small amount of nitrogen to the binary InSb, the bandgap can be significantly reduced due to the band anticrossing effect. In this research, a thin layer of $\text{InSb}_{1-x}\text{N}_x$ was fabricated by multiple-step nitrogen ion implantations into the InSb substrate materials. Secondary Ion Mass Spectroscopy (SIMS) was used to characterize the diffusion behavior of nitrogen atoms in the InSbN alloys. A migration of nitrogen towards the surface was observed which did not follow the Fick's second law. However, the diffusion behavior of nitrogen in the bulk area could be fitted well. The diffusion coefficient constant D_0 was around $10^{-10} \text{ cm}^2/\text{s}$ and an activation energy of 0.55 eV was derived, indicating an interstitial dominant diffusion mechanism. This diffusion mechanism was also concluded from the analysis of the nitrogen element's bond configurations in X-ray Photoelectron Spectroscopy (XPS) experiments. XPS results show that the dominant bonds are the In-N bonds in the middle area and the interstitial bonds in the deeper region, respectively. Hall Effect measurement was conducted to investigate the effect of annealing process on the temperature dependant electrical properties of the InSbN alloys. The dominant phonon scattering was found. Higher annealing temperature resulted in lower carrier concentrations possibly due to

the acceptor nature of nitrogen. An intrinsic behavior above ~ 180 K was observed. When the magnetic field increased, the resistivity did not change much, but the carrier concentration became higher and the mobility became lower. X-ray photoelectron spectroscopy (XPS) was used to qualitatively and quantitatively analyze the bonds configuration and the chemical composition. It was found that oxides were formed at the surface with a lot of carbon, oxygen and hydrogen contaminations. In the InSbN layer, the In-N bond (the substitutional nitrogen) was said to be the one which resulted in bandgap reduction. Therefore, the In-N bond over the entire incorporated N was treated as the activation efficiency. When the implanted nitrogen concentration increased, the activation efficiency would decrease. Based on the nitrogen bond configuration, the calculated bandgap according to the theoretical InSbN bandgap model was drawn out. The photocurrent measurement system was used to get the spectrum response. The measured peak wavelength was in good agreement with the calculated one in XPS. However, the activation efficiency was greatly related to the annealing process and the ion implantation condition. The best annealing condition was optimized at the temperature of 480°C for a duration of ten minutes by Rapid Thermal Process (RTP). The protection SiN layer was used to prevent decomposing of InSbN alloys. The ion implantation energy should not be very high to avoid serious damages.

InSbN photodiodes prepared by Magnesium implantation into the InSbN alloys for long wavelength infrared photodetection were realized. It was demonstrated that such photo-diode could detect middle to long wavelength infrared radiation and the absorption peak energies could be controlled by monitoring the implanted nitrogen dose. The measured photocurrent peak wavelengths ranging from 5000 nm to ~12000 nm were consistent with the bandgap ranging from 234.2 meV to 0 calculated using a 10-band $k\cdot p$ model.

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Chapter 1 Introduction

1.1 Motivation

"Infrared" (IR) refers to the region beneath the red end of the visible color spectrum. All objects radiate some energy in the infrared; even objects at room temperature and frozen objects such as ice. These infrared radiant energies can be detected by infrared detectors – a transducer converting radiant energy in the infrared light into a measurable form like current or voltage. Photon detectors are preferred rather than thermal detectors due to their poor response to high frequency modulation on the incident radiation. In photon detectors, absorbed radiation excites electronic transitions within the material, which can lead to the change in material conductivity (photoconductive detectors) or produce small potential difference across a p-n junction in the semiconductor (photovoltaic detectors) [1]. Long Wavelength IR band (8-12 μm) has attracted a lot of attention due to its high sensitivity to ambient temperature of objects, better transmission through mist and smoke and little effect of atmospheric conditions on transmission. Therefore, the LWIR detector has wide application in military, environment, medical and space industry. Some of its important applications are night vision aid or detecting many environmental gases and chemicals important to industrial process and indoor air quality monitoring, such as SO_2 ,

NH₃, O₃ and chlorofluorocarbon refrigerant compounds thanks to their unique IR absorption signatures in the long wavelength IR [2,3]. Nowadays, there are mainly three kinds of material available for LWIR detection: Mercury Cadmium Telluride (MCT), AlGaAs/GaAs quantum well (QW), strained supper lattice InAs/GaInSb.

Mercury Cadmium Telluride $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ (MCT) is currently most commonly used material because of its extreme flexibility for IR detector applications, i.e. by varying the composition of Cadmium, it is possible to obtain detector of any type for optimized detection at any region of IR spectrum including dual and multicolor devices. The proportion of Cadmium necessary to obtain the LWIR responses is 18-20%. Other advantages are close lattice matching between CdTe and HgTe, high optical absorption coefficient, high electron mobility and readily available doping techniques. The MCT currently provides the highest figure of merits compared with other detectors [4]. However, the weak bonding between Hg and Cd and high Hg pressure make a bad controllability of the composition as growing material. Hence, uniformity, reproducibility, yield and cost are the main motivation to replace the MCT material.

Superlattice materials by bandgap engineered can create artificial narrow gap, thus Quantum Well Infrared Photoconductor (QWIP) is another commonly used device for detecting the LWIR. And **AlGaAs/GaAs quantum well (QW)** is based on the mature GaAs processes and thus high material quality can be easily achieved in improving yield and cost issues. However, due to fundamental limitations associated with the intersubband transitions, Quantum Well Infrared Photoconductor (QWIP) has low quantum efficiency (less than 20%) and high thermal generation rate. Hence, detectivity and operating temperature of the QWIP are much lower than the MCT [5].

Strained supper lattice InAs/GaInSb in theory offers the possibility of high sensitivity and operating temperature of an intrinsic detector. Reduction of Auger recombination rate at room temperature in InAs/GaInSb superlattice by nearly 1 order of magnitude compared to the MCT with similar band gap, which results in detectivity of $1.3 \times 10^8 \text{ cmHz}^{1/2}/\text{W}$ at $11 \mu\text{m}$ wavelength at room temperature, has been claimed. However, the maturity of the detector technology is presently far from being comparable to MCT detectors.

Besides these materials, another potential candidate is **Indium Antimony Nitride Alloys**. InSb has the smallest bandgap of any of the binary III-V

semiconductors (about 175 meV at room temperature) and a cut off wavelength of 7 μm at 300 K and 5.3 μm at 30 K. It plays important roll on the mid, even far-infrared optoelectronics applications. By adding only small amount (<1%) of nitrogen to the binary InSb, the $\text{InSb}_{1-x}\text{N}_x$ alloys are able to show response in 8 to 12 μm range at room temperature [6,7]. Moreover, since small amount of nitrogen is required to produce large changes in the bandgap, the alloy InSbN can be almost lattice matched to existing substrate material, enabling high quality alloys to be grown and incorporated into the existing optoelectronics infrastructure. In addition, InSbN is attractive because of its inherent Auger suppression, since the concerning thermal generation and recombination in narrow gap semiconductors at near room temperature is determined by the Auger mechanism and thus auger recombination rate is the limiting factor in detector sensitivity and light emitting diode (LED) efficiency. Recent experiments reveal that Auger recombination rate of InSbN is only about one-third that of the MCT with equivalent bandgap due to the high electron mass and conduction band nonparabolicity of the InSbN alloys. Hence, it indicates that devices built with InSbN are likely the better choice for optoelectronic devices in the 8-12 μm range than the MCT.

This research will deal with development and micro fabrication of Indium Antimony Nitride materials for long wavelength infrared detector application.

1.2 Objectives

Driven by the above motivations, the objectives of this project are describe as below

- To achieve InSbN alloys using direct nitrogen ion implantation
- To optimize the annealing condition for defects elimination and nitrogen activation
- To characterize the properties of the InSbN alloys
- To fabricate and characterize InSbN infrared photodetectors

1.3 Major Contribution of the thesis

InSbN alloys were fabricated by direct nitrogen ion implantation. The optimal annealing condition was determined by comparing two types of annealing methods, furnace and rapid thermal process annealing. Electrical properties

and the effects of the annealing temperature were characterized using Hall Effect measurements. Subsequently, the behavior of the implanted nitrogen was studied and the diffusion coefficients were derived. A diffusion mechanism of interstitial diffusion was found with the supportive XPS results. Last but not least, the photoconductive and p-n junction photodetectors were fabricated and their optical properties were characterized.

1.4 Report Organization

The whole report is divided into six chapters:

Chapter 1: The general applications and classification of photodetectors were introduced in this chapter. Available materials for long wavelength infrared photodetectors were presented. After that, the motivation of fabricating InSbN based photodetectors, objectives and major contributions were described.

Chapter 2: In this chapter, literature review and fabrication methods of InSbN alloys were stated. Two types of theoretical band structure models were briefly elaborated.

Chapter 3: In this chapter, details of equipments used to characterize samples were described.

Chapter 4: In this chapter, properties of InSbN material were investigated. Firstly, sample details and the theoretical band edges as a function of nitrogen composition were given. After that, two types of annealing methods and their effects on the properties were studied. The optimal annealing condition was determined. Electrical characterization by Hall Effect system was performed and the diffusion behavior of the implanted nitrogen was examined.

Chapter 5: The growth, fabrication and characterization of photoconductive and P-N junction formed photodetectors were introduced in details. The conclusion for ion implantation energy for fabricating InSbN alloys was drawn.

Chapter 6: In this chapter, this report was concluded and some recommendations were given.

Chapter 2 Literature Review and Band models

2.1 Literature Review

$\text{InSb}_{1-x}\text{N}_x$ compounds with low nitrogen fractions x reveal interesting features as materials for optoelectronic devices. The replacement of a few percent of Sb element by small, highly electronegative, and isoelectronic nitrogen atoms results in a dramatic reduction of the fundamental band gap of approximately 100 meV per atomic percent of nitrogen. This phenomenon was first reported [8] in 2000 when a light emitting diode with active regions made up of high quality InSbN/InSb superlattice were grown by molecular beam epitaxy technique using an electron cyclotron resonance plasma source. After that, the Auger lifetime [9,10] and some band structure models [11,12,13] were investigated from 2001. It was found that the conduction band dispersion also had an enhanced nonparabolicity, which suppressed Auger recombination. Auger lifetime in alloys was measured with 11 and 15 μm absorption edges using a time-resolved pump-probe technique and was found to be longer at room temperature than equivalent band gap $\text{Hg}_{1-y}\text{Cd}_y\text{Te}$ alloys at the same quasi-Fermi level separation. The anticrossing model was associated with anticrossing between the localized resonant states of the nitrogen within the conduction band and the extended states of the conduction band itself. The

steady reduction in the band gap with increasing N composition was well described using a two-level band-anticrossing model. When more and more people were attracted to this potential material, different growth techniques like ion implantation [14,15,16], metalorganic vapor phase epitaxy [17] and molecular beam epitaxy [18,19,20,21,22,23,24] were employed to fabricate the InSbN alloys and study their properties. In the report written by I. Mahboob et al, a non-uniform electron concentration depth profile closed to the surface was found by low-energy nitrogen implanting into the InSb substrate with an ion energy of 2 KeV and a radiative annealing at 550 K for 3 hours. The electronic properties of the nitrogen-implanted InSb could not be explained by an InSb band structure as this fails to reproduce the temperature independence of the carrier concentration in an extrinsic semiconductor. Additionally, the reduction in the carrier density could be explained by the acceptor-type nature of the implanted nitrogen. In the publication of our groups, InSbN alloys were fabricated by two-step nitrogen ion implantation into InSb (111) wafers. X-ray photoelectron spectroscopy results indicated that most of the implanted nitrogen ions substitute Sb to form In–N bonds. The percentage of the In–N bonds was found to decrease with the increase of the implanted nitrogen. Such alloys could effectively detect long wavelength infrared radiation and the absorption peak energies could be controlled by monitoring the implanted nitrogen dose. The

measured photocurrent peak wavelengths from photocurrent measurement in chapter 5 were consistent with the band gaps of the alloys calculated using a ten-band $k \cdot p$ model. T. D. Veal et al. grew the InSbN alloys by molecular beam epitaxy using a mixed nitrogen and hydrogen plasma. The grown InSbN samples were investigated by X-ray photoelectron spectroscopy. A large proportion of the nitrogen in the alloy was contained within the neutral N–H complexes. Annealing at 300 °C removes hydrogen from these complexes, increasing the concentration of isoelectronic nitrogen acceptors. H. T. Pham et al. grew InSbN by radio frequency plasma-assisted molecular beam epitaxy. Varying the nitrogen plasma power (200–500 W) and growth temperature (330–420 °C) resulted in little increase in total N content but a significant change in lattice strain. A combined analysis involving x-ray diffraction, x-ray photoelectron spectroscopy, and secondary ion mass spectroscopy measurements indicated that the dominant defects were interstitial N–Sb. Increasing the plasma power resulted in increasing the interstitial N–Sb amount rather than the substitutional N–Sb amount. For fixed plasma power, decreasing the growth temperature helped to reduce the interstitial N–Sb defect. A photo-modulation system based on Fourier Transform spectrometer was developed [25], which permitted one to look further into the longer wavelength region. The new technique was applied to dilute-N InSbN in the wavelength

region of $\sim 6\text{-}9\ \mu\text{m}$. Another FTIR-based photo-modulated transmission Spectroscopic technique [26] was also reported. A $\sim 10\%$ red-shift in bandgap corresponding to a shift in bandgap of approximately 16 meV had been observed at room temperature for the InSbN ternary alloy. The intra- and inter-band transitions in InSbN/InSb quantum well (QW) were studied [27] theoretically using 10-band $k\cdot p$ model combined with envelope function Fourier expansion method. The results indicated that the InSbN/InSb system could be employed for QW infrared photodetection based on inter-conduction sub-band transitions since the related momentum matrix elements are much greater than those at usual III-V compound material systems such as GaAs/AlGaAs, InGaAs/GaAs etc. Quantum dots (QD) embedded on both InAs and GaAs substrate were also reported [28,29]. Strain induced, self-assembled quantum dots were grown using solid-source molecular beam epitaxy. Nitrogen incorporation during formation of quantum dots changed surface energy barrier and caused anisotropic distribution of strain energy, resulted in formation of closely coupled multiple quantum dots in $\langle 110 \rangle$ orientation. The QDs showed a mid infrared luminescence around $3.6\ \mu\text{m}$. The band structure calculation confirmed that the band-anticrossing occurred with localized nitrogen energy band, $E_N = 0.42\ \text{eV}$, and resulted in energy band gap reduction of 50 meV with adding 1% of nitrogen.

2.2 Fabrication methods

InSbN alloys can be grown by molecular beam epitaxy (MBE) technology. One advantage with MBE was that using forming gas (hydrogen and nitrogen) when growing dilute InSbN was able to maintain a low N_2 concentration. However, the bad effect was nitrogen induced defects such as interstitial N-Sb (which can be reduced by fixed power and decreasing the growth temperature). In general, MBE provides ultimate control growth parameters (to the monolayer level) in real time and is favorable for growing heterostructures requiring precise control of layer composition, doping profile, and sharp layer transition. But the process requires ultra-high vacuum, and for high quality deposition material, one needs a very expensive system.

Nitrogen ion implantation into InSb substrate can be used to fabricate InSbN alloys. This method is operated at low temperature of less than 400 °C, which is beneficial for InSb material since its melting point is quite low (530°C). Moreover, in ion implantation, the incorporated atoms can be introduced controllably and reproducibly and, dose can be controlled accurately to allow better process feature requirement with high accuracy of $\pm 1\%$. However, surface damages will be caused because of the high energies ion implanter is employed, so that high temperature annealing is required to remove the defects.

Another method of fabrication of InSbN is Metalorganic Vapor Phase Epitaxy (MOVPE). It is commonly used to grow complex multilayer structures of compound semiconductor materials from surface chemical reactions. Compared with MBE, it is a low temperature process, does not require high vacuum, and growth rate as well as throughput are both higher. But MOVPE has very little in situ control.

In this project, all the samples were fabricated by using a multiple-step ion implantation method to ensure a better uniformly nitrogen distribution.

2.3 Band anticrossing model

It has been found that when adding nitrogen to replace a small fraction of anion in semiconductor alloys, the band gap bows strongly with nitrogen content and electron effective mass arises, which lead to material inherit Auger suppression. Many theoretical models have been developed to explain the phenomenology of III-V nitrides. Band Anticrossing model is the most important theory to investigate the band structure of the III-N-V Alloys. This model assumes that

the conduction band of a III-V Nitride alloy splits into two energy bands E_+ and E_- due to the interaction between highly localized N states and the extended conduction band edge states of the host III-V semiconductor. Solutions for the two energy bands E_+ and E_- are found from the 2x2 determinant in equation (1), where $E_C(k)$ is the energy of the host semiconductor conduction band, E_N is the energy of the localized state nitrogen, V_{NC} is a matrix element describing the interaction between the two states E_C and E_N . And the lower eigen value E_- give the final conduction band edge energy.

$$\begin{vmatrix} E(k) - E_C(k) & V_{NC} \\ V_{NC} & E(k) - E_N \end{vmatrix} = 0 \quad (1)$$

V_{NC} depends on the nitrogen composition by equation (2), where β is a constant describing the coupling between localized N states and the extended states of the host semiconductor, x is the alloy composition.

$$V_{NC} = \beta x^{1/2} \quad (2)$$

Fig. 1 below shows the calculated conduction band minimum (CBM). It can be seen that the conduction band edge shifts down (E_-) and becomes flatter when it approaches the localized nitrogen state. The energy positions of the E_- and E_+ depend on alloy concentration x , the coupling parameter β and the location of E_N with respect to the conduction band edge E_C .

Fig. 1. Illustration of the effects of band anticrossing on the conduction band structure. (a) The highly electronegative isoelectronic N induced localized state resonant with the conduction band; (b) The localized state located below the conduction band. The solid curves are the reconstructed E_- and E_+ subbands resulting from the band anticrossing interaction between the localized states (dash-dotted line) and the extended states of the conduction band (broken line) [6].

2.4 Tight binding model and modified 10 band K• P model

The 10 band k.p model for calculating the bandgap iteration has been developed for $\text{GaN}_x\text{As}_{1-x}$ base on the BAC model by Linsay and O'Reilly employing a sp^3s tight binding Hamilton [30,31,32]. This model includes the interaction of the localized N level with the conduction band of III-V host in addition to the conduction and valence bands. The 10-band k-p Hamiltonian interaction can be expressed as

$$\mathbf{H} = \begin{bmatrix} \mathbf{H}_{ps} & \mathbf{H}_{ps-N}^* \\ \mathbf{H}_{ps-N} & \mathbf{H}_N \end{bmatrix} \quad (3)$$

Where $\mathbf{H}_{ps}$ is the 8-band Hamiltonian, $\mathbf{H}_N$ is the N band Hamiltonian, and $\mathbf{H}_{ps-N}$ consists of the coupling terms between different bands [33].

Considering the nitrogen compositional dependence of E_C and V_{NC} for $\text{GaN}_x\text{As}_{1-x}$

$$\begin{aligned} E_C &= E_0 - \alpha x \\ E_N &= E_{N0} - \gamma x \\ V_{NC} &= \beta x^{1/2} \end{aligned} \quad (4)$$

Where E_0 and E_{N0} are the energy of the unperturbed conduction band edge of the III-V alloy and nitrogen, respectively; α , β , γ are constants; x is nitrogen composition.

Hence, the 2×2 Hamiltonian describing the interaction between the conduction band edge and nitrogen resonant level is given by

$$H_{N.C} = \begin{bmatrix} E_{N0} - \alpha x & \beta \sqrt{x} \\ \beta \sqrt{x} & E_C - \gamma x \end{bmatrix} \quad (5)$$

The tight binding method plays important on investigating the influence of localized perturbations on the electronic structure. The analysis of sp^3 's calculation shows that the distorted lattice around nitrogen site due to the shorter III-nitrogen bond length and the large nitrogen electronegativity have key effect on determining the magnitude of V_{NC} . Moreover, the large electronegativity of N induces an increased charge transfer from the neighboring III atoms to the nitrogen site. They are the main causes of the enhanced band gap bowing.

Chapter 3 Characterization techniques

Several kinds of characterization equipments are used to investigate the electrical and optical properties of InSbN alloys in the work. They are Secondary ion mass spectroscopy, Hall Effect measurement system, X-ray diffraction, X-ray photoelectron spectroscopy and Photocurrent measurement system.

3.1 Hall Effect measurement system

The Hall Effect measurement system is used to determine the electrical properties of materials, such as the net carrier density in a sample, the carrier resistivity and the mobility of the carriers [34]. The Hall Effect comes about due to the nature of the current in a conductor put inside magnetic field. Current consists of the movement of many small charge carriers, typically electrons, holes, or both. Moving charges experience a force, called the Lorentz Force, when a magnetic field is present that is not parallel to their motion. The Lorentz Force is given by the following equation in terms of the electric and magnetic fields:

$$\mathbf{F} = q (\mathbf{E} + \mathbf{v} \times \mathbf{B}) \quad (6)$$

where F is the force, $\mathbf{E}$ is the electric field, $\mathbf{B}$ is the magnetic field, q is the electric charge of the particle, $\mathbf{v}$ is the instantaneous velocity of the particle, $\mathbf{x}$ is the vector cross product.

When such a magnetic field is absent, the charges follow an approximately straight path. However, when a perpendicular magnetic field is applied, their path is curved so that moving charges accumulate on one side of the material. This leaves equal and opposite charges exposed on the other side, where there is a scarcity of mobile charges. The result is an asymmetric distribution of charge density across the Hall element that is perpendicular to both the straight path and the applied magnetic field. The separation of charge establishes an electric field that opposes the migration of further charge, so a steady electrical potential builds up for as long as the charge is flowing. In semiconductors where the carriers are generally both electrons and holes which may be present in different concentrations and have different mobilities, the formula for the Hall coefficient is

$$R_H = \frac{-n\mu_e^2 + p\mu_h^2}{e(n\mu_e + p\mu_h)^2} \quad (7)$$

where n is the electron concentration, p is the hole concentration, μ_e is the electron mobility, μ_h is the hole mobility and e is the absolute value of the electronic charge.

3.2 X-Ray Diffraction (XRD)

X-ray diffraction is a non-destructive standard analytical technique for analyzing the crystallographic structure, chemical composition, and physical properties of materials and thin films. This technique is based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy. Crystals are regular arrays of atoms, and X-rays can be considered waves of electromagnetic radiation. Atoms scatter X-ray waves, primarily through the atoms' electrons. An X-ray striking an electron produces secondary spherical waves emanating from the electron. This phenomenon is known as elastic scattering, and the electron is known as the scatterer. A regular array of scatterers produces a regular array of spherical waves. Although these waves cancel one another out in most directions through destructive interference, they add constructively in a few specific directions, determined by Bragg's law:

$$2d \sin \theta = n\lambda \quad (8)$$

where d is the spacing between diffracting planes, θ is the incident angle, n is any integer, and λ is the wavelength of the beam.

These specific directions appear as spots on the diffraction pattern, often called reflections. Thus, X-ray diffraction results from an electromagnetic wave (the

X-ray) impinging on a regular array of scatterers (the repeating arrangement of atoms within the crystal).

Fig. 2. The incoming beam (coming from upper left) causes each scatterer to re-radiate a small portion of its energy as a spherical wave. If scatterers are arranged symmetrically with a separation d , these spherical waves will be in synch (add constructively) only in directions where their path-length difference $2d \sin \theta$ equals an integer multiple of the wavelength λ . In that case, part of the incoming beam is deflected by an angle 2θ , producing a reflection spot in the diffraction pattern.

3.3 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy is a quantitative spectroscopic technique that measures the elemental composition of a alloy, empirical formula, chemical state and electronic state of the elements that exist within a material. XPS spectra are obtained by irradiating a material with a beam of aluminum or magnesium X-rays while simultaneously measuring the kinetic energy (KE) and number of electrons that escape from the top 1 to 10 nm of the material being analyzed. XPS requires ultra-high vacuum (UHV) conditions. Because the energy of a particular X-ray wavelength equals a known quantity, we can determine the electron binding energy (BE) of each of the emitted electrons by using an equation that is based on the work of Ernest Rutherford (1914):

$$E_{\text{binding}} = E_{\text{photon}} - E_{\text{kinetic}} - \Phi \quad (9)$$

where E_{binding} is the energy of the electron emitted from one electron configuration within the atom, E_{photon} is the energy of the X-ray photons being used, E_{kinetic} is the kinetic energy of the emitted electron as measured by the instrument and Φ is the work function of the spectrometer (not the material).

A typical XPS spectrum is a plot of the number of electrons detected (Y-axis) versus the BE of the electrons detected (X-axis). Each element produces a characteristic set of XPS peaks at characteristic BE values that directly identify each element that exist in or on the surface of the material being analyzed. These characteristic peaks correspond to the electron configuration of the electrons within the atoms, e.g., 1s, 2s, 2p, 3s, etc. The number of detected electrons in each of the characteristic peaks is directly related to the amount of element within the area (volume) irradiated. To generate atomic percentage values, each raw XPS signal must be corrected by dividing its signal intensity (number of electrons detected) by a "relative sensitivity factor" (RSF) and normalized over all of the elements detected. In this research, XPS analysis is performed using a Kratos AXIS spectrometer with monochromatic Al Ka (1486.71 eV) X-ray radiation. The survey spectra in the range of 0~1200 eV are recorded in 0.1 eV step for each sample, followed by high-resolution spectra over different element peaks in 0.1 eV steps, from which the peak shift and detailed compositions were calculated. Curve fitting is performed after a background subtraction by a Lorentzian-Gaussian method.

3.4 Secondary Ion Mass Spectrometry (SIMS)

Secondary ion mass spectrometry (SIMS) is a technique to analyze the composition of solid materials, especially semiconductors and thin films, by sputtering the surface of the specimen with a focused primary ion beam and collecting and analyzing emitted secondary ions from the sample. A high vacuum with pressures below 10^{-6} torr is required to ensure that secondary ions do not collide with background gases on their way to the detector and it also prevents surface contamination by adsorption of background gas particles during measurement. In this project, caesium primary ions generated from the surface ionization source are used when highly electronegative nitrogen element is investigated. These caesium atoms vaporize through a porous tungsten plug and are ionized during evaporation. After that, the primary ions are accelerated and focused on to the target sample to sputter some atoms off the surface. These secondary ions are then collected by ion lensed and filtered according to atomic mass, then projected onto a CCD screen. Continuous analysis while sputtering produces information as a function of depth, called a depth profile.

3.5 The photocurrent measurement system

The photocurrent measurement system is the most important setup to characterize the photo-detectors. The spectrum response, responsivity, and the peak detection wavelength can be conveniently measured by such a system. The photocurrent measurement system used in this work consists of an infrared source, a monochromator, a lock-in amplifier, a cryostat and temperature controller, and a series of optical components such as lens, chopper, mirror, etc. Fig. 3 shows the schematic diagram of the photocurrent measurement system.

Fig. 3. Schematic diagram of the photocurrent measurement system

In order to achieve the maximum output of the photocurrent measurement system from IR source, the light coupling should be optimized. The basic design rules demand all the optical number ($f/\#$) of relevant component to be matched. The filament of the infrared lamp should be conjugated to the position of the entrance slit and its image must cover the input slit. A Jobin Yvon Triax 320 monochromator offers wavelength scanning in our system. The input and output optical numbers of the monochromator are 4.1. We use KRS-5 lens to focus the light from the radiation source on the input slit of the monochromator. The off-axis parabolic mirror pair is used to collect the output light from the exit slit of the monochromator and focus the light normally on the 45° facet of the sample fixed on a copper holder inside the cryostat. The IR source used in our system is an Oriel 6575 ceramic element mounted in a lamp house. The element has a cylindrical ceramic core with a platinum resistance wire wound around it. The irradiation is similar to that of the blackbody at the same temperature of 1450K.

To calibrate the spectral non-uniformity of the system and the power of the IR source, an Oriel pyroelectric detector (Model 70124) is employed as the reference detector.

When monochromatic light comes out from the monochromator and is focused to the sample's surface or the pyroelectric detector, the photocurrent signal of the device are pre-amplified by the current pre-amplifier and then fed into the lock-in amplifier. A computer is employed to control the monochromator and collect data.

Chapter 4 Properties of InSbN alloys

4.1 Sample Preparation and annealing

4.1.1 Three batches of samples with different ion implantation

conditions

Three batches of $\text{InSb}_{1-x}\text{N}_x$ samples were prepared by N^+ ion implantation into n-type InSb (111 and 100) substrates. The implantation details are shown below. The “nitrogen concentration” row of each table indicates the proposed nitrogen values we want to get. From these proposed nitrogen concentrations, implantation process details are determined including the dose and energy used. In order to obtain a uniform nitrogen profile over a certain depth in the InSb substrate, a multi-step N^+ ion implantation scheme with different energies was used for the formation of InSbN layers.

Table 1. Conditions of nitrogen ion implantation into InSb (111) substrates

Batch 1	1-1	1-2	1-3	1-4	1-5	1-6
Nitrogen concentration	0.2%	0.4%	0.6%	0.7%	1.0%	6.0%
Total dose	1.0E15	2.0E15	2.95E15	3.45E15	4.95E15	2.95E16
Implantation energy(KeV)/dose(cm^{-2})	33/2x10 ¹⁴ 150/8x10 ¹⁴	33/4x10 ¹⁴ 50/1.6x10 ¹⁵	33/5.5x10 ¹⁴ 150/1.4x10 ¹⁵	33/6.5x10 ¹⁴ 150/2.8x10 ¹⁵	33/ 9.5x10 ¹⁴ 150/4.0x10 ¹⁵	33/5.5x10 ¹⁵ 150/2.4x10 ¹⁶

Table 2. Conditions of nitrogen implantation into InSb (100) substrates

Batch2	2-1	2-2	2-3	2-4	2-5	2-6
Nitrogen concentration	4%	5%	6%	7%	8%	20%
Total dose	2.2E16	2.1E16	2.7E16	3.1E16	4.0E16	4.8E16
Implantation energy(KeV)	30/4.0 x10 ¹⁵	30/5.0 x10 ¹⁵	30/6.0 x10 ¹⁵	30/7.0x10 ¹⁵	30/8.0x10 ¹⁵	30/2.0x10 ¹⁶
/dose(cm ⁻²)	120/1.2x10 ¹⁶	120/1.5x10 ¹⁶	120/1.8x10 ¹⁶	120/2.1x10 ¹⁶	120/2.4x10 ¹⁶	120/6.0x10 ¹⁶
	500/2.8x10 ¹⁶	500/3.5x10 ¹⁶	500/4.2x10 ¹⁶	500/4.9x10 ¹⁶	500/5.6x10 ¹⁶	500/1.4x10 ¹⁷

Table 3. Conditions of nitrogen implantation into InSb (111) substrates

Batch 3	3-1	3-2	3-3	3-4	3-5
Nitrogen concentration	0.6%	0.7%	0.8%	0.9%	2.0%
Implantation energy(KeV) / dose(cm ⁻²)	30/74.0x10 ¹⁴	30/ 8.0x10 ¹⁴	30/8.5x10 ¹⁴	30/1.0x10 ¹⁵	30/2.2x10 ¹⁵
	90/1.0x10 ¹⁵	90/125x10 ¹⁵	90/1.4x10 ¹⁵	90/1.5x10 ¹⁵	90/3.4x10 ¹⁵
	240/3.8x10 ¹⁵	240/4.4x10 ¹⁵	240/5.0x10 ¹⁵	240/5.6x10 ¹⁵	240/1.3x10 ¹⁶

4.1.2 Furnace annealing

Fig. 4 shows the depth profiles of the as-implanted three samples of batch one with 0.2%, 1% and 6% nitrogen. The total implanted doses were found to be about 1×10^{15} , 5×10^{15} and 2×10^{16} ions/cm² by integrating the area of the implantation profile, respectively, which were closed to the proposed nitrogen concentration shown in Table 1. Fig. 5 shows the nitrogen depth profiles of the three samples simulated using TRIM94. The nitrogen concentrations from the simulation and the experiment are at almost the same level except at surfaces of the wafers. Two peaks originated from the two implantations were obvious in the two profiles. To remove the damage introduced by the ion implantation, activate the implanted nitrogen and form InSbN alloys, annealing process was necessary.

Fig. 4. SIMS results of the as-implanted three samples which were implanted twice with an ion energy of 33 KeV and 150 KeV, respectively. The total doses are 1×10^{15} , 5×10^{15} and 2×10^{16} ions/cm², respectively, for the three samples.

Fig. 5. Nitrogen depth profiles of 0.2%, 1% and 6% N InSbN samples simulated using TRIM94.

To effectively activate the nitrogen without further dissociation of the host material, the annealing conditions should be carefully considered, including the annealing temperature and the time. Since the melting temperature of InSb is about 530 °C, the annealing temperature should be lower than it. The annealing temperature was tested increasing from the room temperature with a step of 50 °C. When the temperature was adjusted above 300 °C in furnace (a furnace is a device used for heating) annealing, small bubbles appeared at the surface. Therefore, a furnace annealing at low temperature (550K) but for a long time (5 hours) was chosen referring to other publications [14,20]. During the annealing process, the samples were encapsulated between two silicon plates to avoid contamination and release of nitrogen atoms.

Fig. 6. SIMS results of the 0.2%, 1% and 6% N InSbN samples in batch one after being annealed for 5 hours at 550K.

By comparing the above graph with the as-implanted one, several phenomena could be observed. First, the two nitrogen peaks are flattened so that a film of InSbN alloy near the wafer surface is formed. Second, the nitrogen concentration level dropped and the distribution depth increased. Third, there was an accumulation of nitrogen at the surface of the sample, and the concentration of the accumulated nitrogen increased with the annealing period of time. Such nitrogen accumulation was also reported in other materials [35,36].

After that, XPS measurement was carried out. One example of analyzing the bond configurations of the InSbN sample with the nitrogen composition of 6% in batch 1 was shown in

Fig. 7. At the surface, a lot of oxygen and carbon contaminated the material. According to

Table 4, Sb and In atoms were found to exist in their oxides forms-SbO_x (Sb₂O₃ and Sb₂O₅) and In₂O₃, all had a higher binding energy. Nitrogen atoms were bonded with carbon, oxygen and hydrogen atoms. After argon bombardment, most of Sb anions were bonded with In cations. Nitrogen element had three contributions: In-N, In-N-Sb and Sb-N. The In-N bond took effect on the bandgap bowing. Therefore, the percentage of In-N peak over all the nitrogen contributions was treated as the nitrogen activation efficiency.

Fig. 7. (a) In the Sb 3d XPS lines of the 6% N InSbN sample scanned before argon etching, Sb-O and Sb-In bonds are found. The shaded area represents O 1s XPS line. (b) In the In 3d XPS lines of the 6% N InSbN

sample scanned before argon etching, In-O bond is dominant. (c) In the N 1s XPS lines of the 6% N InSbN sample scanned before argon etching, N-O bond is the main one. (d) In the Sb 3d XPS lines of the 6% N InSbN sample scanned after etching for a depth of 100 nm, only Sb-In bond is found. (e) In the In 3d XPS lines of the 6% N InSbN sample scanned after etching for a depth of 100 nm, In-Sb bond is observed instead of In-O bond. (f) In the N 1s XPS lines of the 6% N InSbN sample scanned after etching for a depth of 100 nm, N element is mainly contributed by three components: In-N, In-N-Sb and Sb-N bonds.

Table 4. Binding energies of In and Sb in InSb and corresponding oxides in XPS.

	In lines (eV)		Sb lines (eV)		Reference
	3d _{3/2}	3d _{5/2}	3d _{3/2}	3d _{5/2}	
InSb	452.05	444.55	537.4	528.1	[37]
In ₂ O ₃	452.20	444.70			[37]
Sb ₂ O ₃			539.4	530.1	[38]
Sb ₂ O ₅			540.2	531.0	[38]

Similar analysis was applied to the batch 1 samples except the first one because of the poor detectivity limit of XPS machine to nitrogen element. The summarized XPS results were shown in

Table 5. When the ion implanted nitrogen concentration increased, the nitrogen activation efficiency decreased. They were plotted in Fig. 8 and the well fitted curve could be expressed by a first order exponential decay equation,

$$y = 19.9 \exp (-x/1.4)+60.0 \quad (10)$$

Table 5. Summarized N-related bonds components for batch 1 samples

Sample no.	Implanted N conc.(%)	Incorporated N conc.(%)	In-N/ N (%) (activation efficiency)	Activated N (%)
1-2	0.4	0.388	75.0	0.291
1-3	0.6	0.575	73.0	0.420
1-5	1	0.903	69.8	0.630
1-6	6	5.875	60.3	3.618

Fig. 8. Plot of nitrogen activation efficiency via the implanted nitrogen concentration (solid square) and the fitted exponential curve.

Batch 2 samples, grown by three-step ion implantation with a higher implantation energy compared to batch 1 samples, were annealed and characterized in the same way as above. The results obtained from the XPS measurement were shown in Table 6. It was found that the activation efficiency was much lower (<10%) even for the same incorporated nitrogen level. In other words, the furnace annealing is insufficient to activate nitrogen atoms in high damaged samples. To improve the activation efficiency, Rapid Thermal Processing (RTP) at a higher annealing temperature for a short time was considered.

Table 6. Summarized N-related bonds components for batch 2 samples

Sample no.	Implanted N conc.(%)	Incorporated N (%)	In-N / all N (%)	Activated N (%)
2-2	5	4.13	9.2	0.38
2-3	6	5.28	8.9	0.47
2-4	7	5.95	8.6	0.51
2-5	8	7.21	8.6	0.62

4.1.3 Rapid Thermal Process (RTP)

During the RTP annealing, four temperatures 410°C, 450 °C, 480 °C and 500 °C for ten minutes were chosen. Si₃N₄ protection layer was deposited onto the surface to avoid the escape of nitrogen and the decomposition of alloys at high annealing temperature. XRD technique was used to analyze the crystal structure. Fig. 9 showed one example. It was found that an obvious left shoulder appeared beside the main substrate peak (23.78°). Therefore, the curve can be divided into two peaks corresponding to the layer peak (23.72°) and the substrate peak, respectively. A negative peak separation was calculated by

subtracting the substrate angle from the layer angle. From this, a positive experimental mismatch was computed according the equation below,

$$M = - \cot \theta \cdot \delta\theta \quad (11)$$

where θ is the angle of the substrate peak, $\delta\theta$ is the peak separation between the layer peak and the substrate peak.

After annealing, right shoulder came out. When the temperature increased, the right shoulder got higher except that for the 500 °C one as shown in Fig. 10.

Fig. 9. XRD result of the 0.4% N InSbN sample in batch one before annealing (open circle) and two fitted peaks (solid lines).

Fig. 10. XRD results of 0.4% sample in batch 1 as implanted, annealed at 410 °C, 450 °C, 480 °C and 500 °C for 10 minutes.

Table 7. Experimental mismatch calculated from Fig. 10 based on formula (12)

#1-2 (0.4%) (111)	-ve m (ppm)	+ve m (ppm)
Before annealing		1918
410C 10m+450C 5m	-962	
450C 10m	-2552	
480C 10m	-2774	
500C 10m	-844	

Table 7 summarized all the mismatches. The negative mismatch could only be caused by In-N bonds. Therefore, the temperature 480°C, which had the most negative mismatch as well as the highest nitrogen activation efficiency, was considered as the optimal annealing temperature. With this new annealing temperature, XPS were performed again. The the activation efficiency was improved a little bit, which was shown in Table 8.

Table 8. Comparison of activation efficiency from two different annealing conditions

Sample no.	In-N / N (%)	
	550K 5hrs	480C 10m
2-2	9.2	11.2
2-3	8.9	10.9
2-4	8.6	10.4
2-5	8.6	10.4

4.2 Energy bandgap

The band structure of $\text{InN}_x\text{Sb}_{1-x}$ is predicted using the modified 10 band k.p Hamiltonian developed for $\text{GaN}_x\text{As}_{1-x}$. In the case of $\text{InN}_x\text{Sb}_{1-x}$, E_c changes with the composition x following the equation (4). $E_c = 0.177$ eV (at 300K) when $x=0$, which is the bandgap of InSb. Calculated result of E_{N0} is 470 meV above the conduction band edge, and α , γ and β are calculated to be 0.77 eV, 0.77 eV, 2.2 eV respectively [9]. Moreover, the bandgap of InSb is depends on the temperature. It can be described as below, in which $a = 0.6$ meV·K⁻¹ and $b = 500$ K.

$$E_g(T) = E_g(0) - aT^2 / (b + T) \quad (12)$$

Hence the band gap of 243.3 meV at 30 K is used as a starting point in the calculation, as we can experimentally verify the band gaps of the $\text{InN}_x\text{Sb}_{1-x}$ alloys with different N composition by directly measuring the optical absorption at this temperature.

Base on equation (5), the calculated energies of E_+ and E_- subband edges resulted from the band anticrossing effect between the localized N states and the conduction band of the InSb host as a function of N composition up to 3% are shown in Fig. 11. From this bandgap model, the simulated bandgap values

were able to be computed based on the activated nitrogen percentage obtained in XPS results.

Fig. 11. Calculated E_+ , E_- and N level (E_N) in $\text{InN}_x\text{Sb}_{1-x}$ at 30 K as a function of N composition, using the ten-band k-p model. The energy band gap is 234.2 meV at 0 N composition and becomes 0 at 3% N.

Table 9. Simulated bandgap data for batch 1 and 2 samples based on the XPS results and calculated bandgap model.

Sample no.	In-N/ N (%) (activation efficiency)	Activated N (%)	Simulated bandgap (meV)	Sample no.	In-N/ N (%) (activation efficiency)	Activated N (%)	Simulated bandgap (meV)
1-2	75.0	0.291	203.8	2-2	9.2	0.38	197
1-3	73.0	0.420	193.3	2-3	8.9	0.47	187
1-5	69.8	0.630	175.2	2-4	8.6	0.51	184
1-6	60.3	3.618	- Eg	2-5	8.6	0.62	173

4.3 Electrical Characterization

Hall Effect system was used to characterize the electrical properties of the InSbN alloys. Fig. 12 - Fig. 14 showed the effect of annealing process on the temperature dependant electrical properties. First, it indicated that the formed InSbN alloys were n-type. Second, in the temperature range (180–300 K) the temperature dependent resistivity exhibited an exponential behavior ($\rho(T) \propto \exp(E_0/2KT)$). The calculated slope leaded to an activation energy $E_0=0.25\pm0.2$ eV. The activation energy could also be calculated from the slope of temperature dependent carrier concentration, which gave a value $E_0=0.26\pm0.1$ eV. The two slopes were measured with experimental errors. Therefore, the activation energy E_0 was around 0.25 eV or 0.26 eV, which was quite closed to the activation energy of the intrinsic InSb wafers. The intrinsic carrier concentration of InSb was given as $n_i = 5.76 \times 10^{14} T^{3/2} \exp(-(E_0=0.26)/2KT) \text{ cm}^{-3}$ [39,40,41]. Below 180 K, the resistivity tended to decrease as the temperature dropped and the measured carrier concentration was almost independent of temperature. The InSbN alloys were said to present an intrinsic behavior with approximately equal numbers of electrons and holes above 180 K. Since the electrons were much lighter, they would dominate the conductivity and give the sign of the Hall constant. When the temperature was lowered, the intrinsic carriers freezed out and the extrinsic properties of the

semiconductor came into play. However, the activation energy of the extrinsic behavior could only be calculated from the low temperature range (15-77 K) slope, which was not realized in this study. [42] The temperature dependence of the hall mobility given in Fig. 14 exhibited an increase with decreasing temperature, limited by the polar optical phonon scattering. Third, higher annealing temperature would result in lower electron carrier concentration below 180K. One of the reasons was because that higher annealing temperature would reduce more donor-type defects such as antimony vacancies, which were formed during the ion implantation. After annealing process, induced damages were recovered and the electron concentration dropped. This phenomenon was also able to be explained by the acceptor-type nature of the highly electronegative nitrogen [43,44]. More nitrogen impurities were activated at higher annealing temperature and acted as acceptors, lowering the carrier concentration.

Similar analysis had been applied to another set of InSbN samples with different doping level, shown in Fig. 15 - Fig. 17. The calculated activation energy E_0 was also quite closed to 0.26 eV, which was in agreement with the intrinsic one. The sample with higher doping level exhibited a similar behavior as the one annealed at a higher temperature.

Fig. 12. Variation of electron carrier concentration (open symbol) of the atomic 6% N InSbN sample annealed at different temperatures for 3 hours with temperature. The intrinsic carrier concentration slope (solid line) is indicated.

Fig. 13. Variation of Hall resistivity (open symbol) of the atomic 6% N InSbN sample annealed at different temperatures for 3 hours with temperature. The intrinsic carrier concentration slope (solid line) is indicated.

Fig. 14. Variation of Hall mobility (open symbol) of the atomic 6% N InSbN sample annealed at different temperatures for 3 hours with temperature.

Fig. 15. Variation of electron carrier concentration (open symbol) of atomic 0.4%, 0.6% and 1% N InSbN samples annealed at 550K for 3 hours with temperature. The intrinsic carrier concentration slope (solid line) is indicated.

Fig. 16. Variation of Hall resistivity (open symbol) of atomic 0.4%, 0.6% and 1% N InSbN samples annealed at 550K for 3 hours with temperature. The intrinsic carrier concentration slope (solid line) is indicated.

Fig. 17. Variation of Hall mobility (open symbol) of atomic 0.4%, 0.6% and 1% N InSbN samples annealed at 550K for 3 hours with temperature.

Fig. 18. The Hall Effect results of 6% N (top) and 1% N (bottom) samples in batch one annealed at 480°C for 10 minutes at different magnetic fields.

The effect of the magnetic field on the electrical properties was also studied. All the samples exhibited the same trend and Fig. 18 showed one example. It was found that the resistivity did not change much, but the carrier concentration became higher and the mobility became lower when the magnetic field increased.

To conclude, Hall Effect measurement was conducted to investigate the electrical properties of InSbN alloys. When the temperature went down, the electron carrier concentration decreased first and then kept almost constant, the resistivity increased first and then decreased, the mobility kept increasing. The dominant scattering mechanism was found to be phonon scattering. Higher annealing temperature resulted in lower carrier concentrations due to the recovery of donor-type defects and the acceptor nature of nitrogen. An intrinsic behavior above ~ 180 K was observed. The InSbN alloys with higher nitrogen concentration showed the same electrical behavior as the one annealed at a higher temperature. When the magnetic field increased, the resistivity did not change much, but the carrier concentration became higher and the mobility became lower.

4.4 Behavior of the implanted nitrogen

The behavior of nitrogen atoms in InSbN alloys was studied with the aids of SIMS and XPS techniques. Fig. 19 showed the nitrogen profiles of the sample with a dose of 2×10^{16} ions/cm² after being annealed for 3, 5 and 10 hours at 277 °C. There was fast nitrogen diffusion in the InSb wafer and the diffused depth was proportional to the annealing time.

Fig. 19. Nitrogen distributions of the 6% N InSbN sample in batch one after being annealed for various periods of time at 550k obtained by SIMS. The solid lines are the fittings using the Fick's second law equation.

Fig. 20 showed the SIMS results for the same sample but annealed at different temperatures for 3 hours. It was seen that the nitrogen accumulation at the surface and nitrogen diffusion in InSb wafer were also proportional to the annealing temperature. However, the nitrogen concentration in the InSbN layer was not uniform anymore if the annealing temperature is too high. Therefore, it was important to find the detailed diffusion coefficient so that one could accurately control the thickness of the InSbN layers which were of uniform nitrogen distribution.

Fig. 20. Nitrogen distributions of the 6% N InSbN sample in batch one after being annealed at various temperature for 3 hours measured with SIMS. The solid lines are the fittings using the fick's second law equation.

It was well known that the diffusivity of nitrogen could be determined by applying the Fick's second law to the profiles, assuming that the diffusion coefficient was independent of concentration. The depth and time dependent concentration $N(x, t)$ was written as [45]

$$N(x, t) = \frac{Q}{\sqrt{2\pi(\Delta R_p^2 + 2Dt)}} \exp\left(-\frac{(x - R_p)^2}{2\Delta R_p^2 + 4Dt}\right) \quad (13)$$

where Q is the dose, R_p is the projected range, ΔR_p is the standard deviation, D is the diffusion coefficient, and t is the annealing time. In our case, since each sample was implanted twice with different energies, we proposed the following equation to describe the profile,

$$N(x, t) = \frac{Q_1}{\sqrt{2\pi(\Delta R_{p1}^2 + 2Dt)}} \exp\left(-\frac{(x - R_{p1})^2}{2\Delta R_{p1}^2 + 4Dt}\right) + \frac{Q_2}{\sqrt{2\pi(\Delta R_{p2}^2 + 2Dt)}} \exp\left(-\frac{(x - R_{p2})^2}{2\Delta R_{p2}^2 + 4Dt}\right) \quad (14)$$

The first and second terms of the equation correspond to the implanted nitrogen concentrations contributed by the first and second implantation, respectively. Q_1 is the dose of the first implantation and Q_2 is the dose of the second implantation.

By fitting equation (14) with the measured nitrogen profiles showed in Fig. 19 and Fig. 20, parameters like the diffusion coefficient, projected range and standard deviation could be extracted and they were listed in Table 10.

Table 10. Extracted diffusion coefficients from Fig. 19 and Fig. 20

D(cm ² /s)	T(K)	t(hour)
8.9×10 ⁻¹⁶	550	3
		5
		10
5.8×10 ⁻¹⁶	523	3
1.5×10 ⁻¹⁵	573	
2.3×10 ⁻¹⁵	598	
4.2×10 ⁻¹⁵	623	

With the diffusion coefficient data derived, we plot $\ln D$ versus $1/T$ in Fig. 21. The diffusion coefficient extracted can be described by the expression,

$$D = D_0 \exp\left(\frac{-E_a}{k_b T}\right) \tag{15}$$

where the E_a is the activation energy with a value of 0.55 ± 0.03 eV, k_b is the Boltzmann constant and D_0 is the pre-exponential factor with a value of $1.09 \pm 0.6 \times 10^{-10}$ cm²/s.

Fig. 21. Diffusion coefficients plotted versus the temperature.

To verify the diffusion coefficient, we did the same fitting to other samples. The diffusion coefficients extracted were in good agreement with each other. Fig. 22 shows one example of the nitrogen distribution of the samples with a dose of $5 \times 10^{15} \text{ cm}^{-2}$ after being annealed for 5 hours at 550K.

Fig. 22. Nitrogen distribution of the 1% InSbN sample with a dose of $5 \times 10^{15} \text{ cm}^{-2}$ after being annealed for 5 hours at 550K obtained by SIMS.

Basic diffusion mechanisms in crystals include two species, defect independent processes and defect dependent processes [46]. Generally, the latter processes were easier to happen because of lower activation energy, which included interstitial, vacancy and dislocation mechanisms. Especially the interstitial mechanism was the most probable one, since it usually had the lowest activation energy compared to others. For example, the activation energy values for the interstitial diffusion model were found to be between 0.5 and 1.5 eV, and between 3 and 5 eV for the vacancy diffusion in both silicon and gallium arsenide [36].

For the nitrogen diffusion in GaAs, Stolwijk's group reported an activation energy of 2.27 eV and a pre-exponential factor of $6.58 \times 10^{-3} \text{ cm}^2/\text{s}$, and proposed a kick-out model for the diffusion mechanism, which involved the virtually immobile nitrogen on the arsenic sublattice, interstitial nitrogen and interstitial arsenic elements [47]. The diffusion of the implanted nitrogen in Si was studied by Jones' group. They reported that the peak of the nitrogen profiles moved towards Si surface and the whole profile shrank, which could not be explained by the conventional Fickian theory [18]. As far as the nitrogen diffusion in the InSb, the activation energy of $0.55 \pm 0.03 \text{ eV}$ indicated an interstitial dominate diffusion. With this mechanism, nitrogen diffused towards both surface and bulk. The accumulation at the surface was mainly due to the discontinuity of the wafer.

To study the behavior of nitrogen, XPS was employed to exam the bond configurations of configurations of nitrogen in the samples. The result was shown in Fig. 23. At the surface, most of nitrogen atoms were bonded with carbon (399.5 eV), hydrogen (400.7eV) and oxygen (401.8 eV) atoms. There are small amount of interstitial nitrogen (403.8 eV) moving from the bulk area to the surface. After argon etching (around tens of nanometers), the nitrogen peak shifted to the lower binding energy region. In-N-Sb (397.5 eV) bond was the main dominants. There were also some In-N (396.5 eV) bonds by substitution and interstitial nitrogen (403.8 eV). The intensity was relatively low, which was in agreement with the low nitrogen concentration in SIMS distribution in Fig. 24. Sometimes the N-C and N-O bonds would still exist due to the insufficient etching time. To get the real bond configurations, samples were

further etched to around 300 nm. During the uniform distributed nitrogen area (300 nm), the main contribution to the nitrogen peak was the In-N bond. Some of the Sb-N (399.0 eV) bonds [12] which were formed during the ion implantation might be remained with insufficient annealing. There also were small amount of interstitial nitrogen (403.8 eV). (403.8 eV). While in the bulk region (500 nm), the signal was very weak since the nitrogen nitrogen concentration was almost one order less. The dominant bonds were In-N-Sb, In-N-Sb, molecular N₂ (400.7 eV) and interstitial nitrogen. The molecular N₂ and interstitial interstitial nitrogen were also reported by J. D. Hecht et al. [48,49]. The increased interstitial interstitial peak at about 500 nm proved the interstitial diffusion mechanism, which can be which can be clearly seen in

Table 11.

Fig. 23. The X-ray photoelectron spectroscopy (XPS) results (black lines) of nitrogen element demonstrate the change of nitrogen bonding configurations with the depth of samples. The gray lines are the split and fitted peaks. (a) The nitrogen bond configurations at surface. N is bonded with C, H and O. Interstitial N is found. (b) The nitrogen bond configuration after argon etching for 10 nm. In-N and In-Sb-N bond appear. (c) The nitrogen bond configuration after argon etching for 210 nm. In-N bond is the dominant one. (d) The nitrogen bond configuration after argon etching for 300 nm is similar with the one in (c) except a bigger area under the In-N peak. (e) The nitrogen bond configuration after argon etching for 500 nm. Signal is weak. In-N-Sb bond, molecular nitrogen N_2 and the interstitial N are dominant.

Table 11. Nitrogen bond configurations at different depths obtained from the XPS results.

	Total Area (N)	In-N(%)	Interstitial(%)
Surface	3358	-	-
10 nm	2160	22.2	-
210 nm	2351	61.6	26.1
300 nm	2321	62.2	37.8
500 nm	496	-	34.8

Fig. 24. Nitrogen concentration distribution obtained by SIMS with the inset showing the nitrogen distribution near the surface.

To conclude, the diffusion behavior of implanted nitrogen into InSb substrates was studied by SIMS. Annealing progress led to the redistribution of nitrogen impurities making the sample better uniformity. At the same time, it also activated the incorporated nitrogen atoms to perform the band-reduction function. A migration of nitrogen towards the sample surface was observed which did not follow the Fick's second law. However, the diffusion behavior of nitrogen in the bulk area could be fitted well. The diffusion coefficients at different temperatures were plotted, and the corresponding activation energy for nitrogen in InSb was around 0.55 eV, indicating an interstitial dominant diffusion. XPS results showed the nitrogen bond configurations at different depths. The dominant bonds were the In-N bond in the middle area and the interstitial bond in the deeper region, respectively. It supported the interstitial diffusion mechanism.

Chapter 5 InSbN alloys for infrared photodetection

5.1 Photoconductive photodetection optical characterization

After material properties' characterization, photoconductive photodetector devices were fabricated, by adding Indium electrodes on to the InSbN alloys, to examine their optical responses. Photocurrent measurement technique was then used to characterize the optical spectra. From Fig. 25, it is seen that the highest photocurrent peak in all the samples appears at about $5.3\ \mu\text{m}$ (at 30K) which originated from the binary InSb ($6.8\ \mu\text{m}$ at 300K). The photocurrent spectra are extended to a longer wavelength with the incorporation of nitrogen. For the 6% N sample, there was not any reaction from the photocurrent experiment. By splitting the curve into two main peaks- InSb peak and InSbN peak, the InSbN bandgap values were derived from the InSbN peak position in the longer wavelength region. These results were in excellent agreement with the theoretical one calculated from XPS results in chapter 4.1.2. It meant that the InSbN based photodetector was successfully realized, and the detected wavelength of which could be controlled by monitoring the concentration of the implanted nitrogen.

(a)

(b)

(c)

(d)

Fig. 25. (a) Photocurrent spectra of InSb substrate at 30K (solid line) with a fitted sharp peak around 5.3 μm (dash line). (b) (c) and (d) Photocurrent spectra of the 0.4%, 0.6% and 1% N InSbN samples at 30K (solid line). Two fitting curves (dash line) represent one sharp InSb peak, came from the substrate, and the other one broad InSbN peak, came from the layer. The broadness is due to the non-uniform distribution of nitrogen over a depth, leading to a range of bandgap values. As the N percentage increases, the broad peak shifts to the longer wavelength.

Table 12. Comparison of bandgap values obtained from photocurrent and XPS measurements.

Sample No.	Peak for InSbN	Bandgap (meV)	Simulated bandgap (meV)
1-2 (0.4% N)	6142 nm	201.9	203.8
1-3 (0.6% N)	6291 nm	197.1	193.3
1-5 (1% N)	7080 nm	175.1	175.2
1-6 (6% N)	No photocurrent observed	--	-E _g

Similarly, the photocurrent results for batch 2 samples were shown in Fig. 26. They proved the poor activation efficiency withdrawn from previous XPS results. This low value of activation efficiency was due to the high implantation energy, which induced a lot of defects. To reduce the defects of ion implantation, low implantation energy should be used.

(a)

(b)

(c)

(d)

Fig. 26. (a) (b) (c) and (d) Photocurrent spectra of the 5%, 6%, 7% and 8% N InSbN samples at 30K (solid line). Two fitting curves (dash line) represent one sharp InSb peak, came from the substrate and the other one broad InSbN peak, came from the layer. The broadness is due to the non-uniform distribution of nitrogen over a depth, leading to a range of bandgap values. As the N percentage increases, the broad peak shifts to the longer wavelength.

Table 13. Comparison of bandgap values obtained from photocurrent and XPS measurements.

Sample No.	Peak for InSbN	Bandgap (meV)	Simulated bandgap (meV)
2-2 (5% N)	6307 nm	196.6	197
2-3 (6% N)	6608 nm	187.6	187
2-4 (7% N)	6800 nm	182.4	184
2-5 (8% N)	7103 nm	174.5	173

To conclude, low ion implantation energy (<250 KeV) should be applied to avoid huge damages to the material. The optimal annealing temperature was around 480 °C in RTP. By adjusting the ion implantation and annealing conditions, the activation efficiency as well as the bandgap could be controllable.

5.2 P-N junction formation and photodetection

Magnesium (Mg) was implanted into three different samples (2-7, 2-8 and 2-9) after N implantation to form a p layer so that a simple p-n junction could be formed. Sample details were shown in Table 14.

Table 14. N⁺ and Mg⁺ ion implantation conditions used for formation of photodiodes.

Batch 2 (100)	2-7	2-8	2-9
Nitrogen concentration	5%	6%	7%
N: Implantation energy (KeV)	90/ 8.0 x10 ¹⁵	90/ 9.6 x10 ¹⁵	90/ 10.1 x10 ¹⁵
/	180/ 1.8 x10 ¹⁶	180/ 2.2 x10 ¹⁶	180/ 2.5 x10 ¹⁶
dose (cm ⁻²)	530/ 3.7 x10 ¹⁶	530/ 4.4 x10 ¹⁶	530/ 5.2 x10 ¹⁶
Mg: Implantation energy (KeV)/ Dose (cm ⁻²)	40/ 2.0 x10 ¹⁵	40/ 2.0 x10 ¹⁵	40/ 2.0 x10 ¹⁵

After annealing, mesa structures were fabricated by using standard photolithographic process. The standard device fabrication process chart is schematically shown in Fig. 27 and is explained in details in the following.

Fig. 27. Flow chart of Photo-diode fabrication process

- ◆ **Wafer cleaning:** put the samples into Acton and then IPA, boiling the solution at 200 °C for about 15 minutes to clean the sample surfaces.
- ◆ **Mask cleaning:** clean the surfaces of masks with Acton and then IPA.
- ◆ **Photolithography step one for mesa fabrication:** drop 1518 photoresist glue onto the positive surface of samples and then spin them for 30 seconds to form a uniform thin photoresist layer → dry the samples at 105°C for 1 minute and 45 seconds to get rid of H₂O → expose the samples covered with the mesa mask under ultraviolet (UV) for 30 seconds.
- ◆ **Developing:** Put AZ solution and H₂O in the proportion of 1:2 into a beaker. Develop for 1-2 minutes and then dry the samples at 110 °C for about 15 minutes.

-
- ◆ **Mesa wet etching:** The etch solution is lactic acid: nitric acid=10:1 [50]. The etching should be stopped in the p-type layer.
 - ◆ **Photolithography step two for metal electrode fabrication and developing:** Spin 5214 photoresist glue on the surface of samples → dry the samples at 105°C for 1 minute and 45 seconds → expose the samples covered with the metal-contact mask under ultraviolet (UV) for 5 seconds → dry the samples at 110°C for 8-10 minutes → expose the samples without mask covering under ultraviolet (UV) for 25 seconds → develop the samples using solution of AZ:H₂O = 1:2 for 1-2minutes.
 - ◆ **Clean oxide:** remove the oxide in the sample surfaces using solution of HCL (37%): H₂O = 1:10 for about 20 seconds and then rinse the samples.
 - ◆ **E-beam evaporation:** coat the surfaces of samples with gold, nickel and germanium alloy. The evaporation order is Ti (60nm) + Au (200nm).
 - ◆ **Rapid thermal annealing to form ohmic contact:** rapid thermal annealing processing of the samples at 300°C for 10 seconds.
 - ◆ **Wafer bonding:** cut the samples into proper small pieces, and then bond it onto a package with several metal pins by proper glue.
 - ◆ **Wire bonding:** connect the metal contacts of the diode to the metal pins of the package with fine gold wires using wire bonding machine.

The devices had a diameter of 250 μm . The schematic structure and photograph of the diode were shown in Fig. 28 and Fig. 29.

Fig. 28. Schematic structure of photo-diode (side view)

Fig. 29. Photograph of the device (top view). The round ones are mesa islands and upper contact metal. The boundary is bottom contact metal and the cross is the align symbol. The diameter of the biggest round mesa is about 200 μm .

After fabrication, a plot of current versus voltage for the diodes is shown below. From this characteristic IV curve, the PN junction is said to be formed.

Fig. 30. I-V curve of the PN junction diode

XPS and photocurrent measures were performed again and results are shown in the following tables and figures. Although the activation efficiencies in the diodes (~10%) were slightly higher than the one in the conductive alloys with the same implanted N (< 9%), the detected wavelength peak extension was still smaller due to a stronger escape of nitrogen from the surface.

Table 15. Summarized N-related bonds configurations for Mg implanted samples obtained from the XPS measurement

Sample no.	Implanted N conc.(%)	N over all atoms (%)	In-N/ all N (%)	Activated N (%)	Simulated bandgap (meV)
2-7	5	3.25	11.1	0.36	198
2-8	6	3.8	10.5	0.4	194
2-9	7	4.34	9.9	0.43	192

(a)

(b)

(c)

Fig. 31. (a) (b) and (c) Photocurrent spectra of the 5%, 6%, 7% N and Mg implanted InSbN samples at 30K (solid line). Two fitting curves (dash line) represent one sharp InSb peak, came from the substrate and the other one broad InSbN peak, came from the layer. The broadness is due to the non-uniform distribution of nitrogen over a depth, leading to a range of bandgap values. As the N percentage increases, the broad peak shifts to the longer wavelength.

Table 16. Comparison of bandgap values obtained from photocurrent and XPS measurements

Sample No.	Peak for InSbN	Measured bandgap (meV)	Simulated bandgap (meV)
2-7	6305 nm	196.7	198
2-8	6332 nm	195.5	194
2-9	6468 nm	191.7	192

To conclude, the photodiodes fabricated by subsequently ion implantation of nitrogen and magnesium into the InSb substrates gave a response to the region ~6 μm . The performance was not as good as the one with pure nitrogen implantation. Further improvement was required.

Chapter 6 Summary and Recommendation

From 2000, $\text{InSb}_{1-x}\text{N}_x$ alloys have attracted great attention due to its potential capability in long wavelength infrared detection. InSb has the smallest bandgap of any of the binary III-V semiconductors (about 175 meV at room temperature) and a cut off wavelength of 6.8 μm at 300 K and 5.3 μm at 30 K. It played an important role on the mid, even far-infrared optoelectronics applications. Due to the band anti-crossing effect, by adding only small amount (<2.5%) of nitrogen to the binary InSb, the $\text{InSb}_{1-x}\text{N}_x$ alloys were able to show a response in 8 to 12 μm range at room temperature. The small lattice mismatch and low auger recombination rate were the other two advantages.

In this report, a thin layer of $\text{InSb}_{1-x}\text{N}_x$ had been fabricated by multiple-step nitrogen ion implantations into the InSb substrate materials. SIMS was used to characterize the diffusion behavior of nitrogen after furnace annealing at different temperatures (from 250 °C to 400 °C) for different periods of time (from 30 minutes to 10 hours). During the annealing process, the nitrogen atoms were redistributed, making the sample better uniformity. They were activated to bond with host materials performing the band reduction function. At the same time, damages induced by ion implantation were repaired. The SIMS indicated that nitrogen atoms in the InSbN alloys were not stable but diffused significantly during annealing. The flatted distributed nitrogen region was around 0.4 μm depth. An accumulation of nitrogen at the sample surface was observed which did

not follow the Fick's second law. However, the diffusion behavior of nitrogen in the bulk area could be fitted well. The diffusion coefficient was determined and it was expressed by an exponential relation with a constant D_0 of $10^{-10} \text{ cm}^2/\text{s}$ and an activation energy of 0.55 eV, indicating an interstitial dominant diffusion process. This diffusion mechanism was also concluded from the analysis of the nitrogen element's bond configurations in XPS experiments. XPS results of nitrogen element at different depths showed that the dominant bonds were the In-N bonds in the middle area and the interstitial bonds in the deeper region, respectively.

Hall Effect measurement was conducted to investigate the temperature dependant electrical properties of the InSbN alloys such as the resistivity, the average carrier concentration and mobility. First, it indicated that the InSbN alloys are n-type. Second, when the temperature changed from 300K to 90K, the resistivity increased first and then dropped down after certain temperature marked as CT. The electron carrier concentration decreased fast and then kept almost constant. The increasing mobility indicated a dominant phonon scattering. Third, it was found that the annealed samples had a lower resistivity, higher concentration and lower mobility compared with the one before annealing. However, for the same sample the higher annealing temperature resulted in a lower carrier concentration probably due to the acceptor-like nature of nitrogen. Fourth, the temperature dependant resistivity and concentration above the CT region exhibited an exponential relationship with an activation energy $E_0=0.25 \text{ eV}$, indicating an intrinsic behavior. Last, the effect of

the magnetic field on the properties was also studied. The resistivity did not change much, but carrier concentration became higher and the mobility became lower as the magnetic field increased.

X-ray photoelectron spectroscopy (XPS) was used to qualitatively and quantitatively analyze the bond configuration and chemical compositions. It was found that In_2O_3 and Sb_2O_x were formed at the surface. Meanwhile, most of nitrogen atoms were bonded with carbon, oxygen and hydrogen atoms forming contaminations. Inside the InSbN layer, In-N bond (the substitutional nitrogen), In-N-Sb and Sb-N bond were the main contributions. Higher annealing temperature eliminated more defects and activated larger percentage of In-N bonds, which resulted in bandgap bowing. When the implanted nitrogen increased, less percentage of them would occupy the anion lattice sites, but the total substitutional nitrogen atoms still steadily increased. Based on the nitrogen bond configuration, the calculated bandgap according to the theoretical InSbN bandgap model was drawn out. The photocurrent measurement system is used to get the spectrum response. The measured peak wavelength was in great agreement with the calculated one using XPS data.

By comparing the results of batch one and batch two samples obtained from XPS and photocurrent measurements, the annealing and the ion implantation conditions were compared. The InSbN layer formed in batch 2 samples with higher energy

was thicker than that in batch one. However, the activated nitrogen, In-N bond, was just around 10% of the total implanted ones. Rapid thermal annealing was used replacing the furnace annealing. The optimal annealing temperature was found around 480 °C from the XRD analysis. Due to the higher annealing temperature, the protection SiN layer was used to prevent decomposing of InSbN alloys. These measures helped improve a little due to the big damage induced by the high energy ion implantation. The low ion implantation energy should be used to achieve better activation efficiency. By controlling the ion implantation energy and the incorporated nitrogen concentration, the activation efficiency as well as the bandgap was controllable.

P-N junction formed photodetectors prepared by Magnesium implantation into the InSbN alloys for long wavelength infrared photodetection were fabricated. It was demonstrated that such photo-diode could effectively detect middle to long wavelength infrared radiation and the absorption peak energies could be controlled by monitoring the implanted nitrogen dose. The measured peak wavelengths were consistent with the bandgap calculated using a 10-band $k \cdot p$ model.

In the future, InSbN thin layers on top of other substrate materials instead of the InSb substrate should be fabricated to avoid the high response from the InSb

material. Further work still need to be done to improve the activated nitrogen percentage as well as the efficiency of the photodetectors.

Publication List

1. Wang, Y.; Zhang, D.H.; Huang, Z.M.; Liu, W.; Li, J.H.; Liu, C.J.; Wee, A.T.S., "Study of ion-implanted in $\text{Sb}_{1-x}\text{N}_x$ alloys using secondary ion mass spectroscopy", *IEEE Conference on Electron Devices and Solid-State Circuits 2007*, 677-680.
2. Wang, Y.; Zhang, D.H.; Chen, X. Z.; Zhang, Sam S. Y.; Liu, C.J.; Wee, A.T.S., "Behavior of nitrogen implanted into InSb wafers", *Submitted for publication*.
3. Wang, Y.; Zhang, D. H.; Liu, W., "The temperature dependence of electrical properties in N-doped InSb", *IEEE PhotonicsGlobal International Conference in Photoincs 2008*.
4. Zhang, D.H.; Liu, W.; Wang, Y.; Chen, X.Z.; Li, J.H.; Huang, Z.M.; Zhang, Sam S. Y., "InSbN alloys prepared by two-step ion implantation for infrared photodetection", *Applied Physics Letters*, **93**, 131107-9 (2008)
5. Liu, W.; Zhang, D.H.; Huang, Z.M.; Wang, Y.; Yoon, S.F.; Fan, W.J., "Studying of intra-band and inter-band transitions in InSbN/InSb quantum well using 10-band k-p model", *2006 6th International Conference On Numerical Simulation of Optoelectronic Devices (IEEE Cat. No. 06EX1456)*, 2006.
6. Li, J. H.; Zhang, D. H.; Wang, Y., Zhao, M.; Zheng, W. F.; Yuan, N. Y., "In-N co-doped P-type ZnO films electrical prepared by modified ion beam enhanced deposition", *IEEE PhotonicsGlobal International Conference in Photoincs 2008*.
7. Li, J. H.; Zhang, D. H.; Wang, Y., Zhao, M.; Zheng, W. F.; Yuan, N. Y., "Property comparison between tantalum and tungsten doped polycrystalline VO₂ thin films", *IEEE PhotonicsGlobal International Conference in Photoincs 2008*.

References

- 1 Peter Caper and C.T Elliott. "Infrared detectors and emmitters: Materials and devices". Kluwer Academic Publishers 2001
- 2 A. Rogalski, Opt. Eng. 33, 1392 (1994)
- 3 See, for example, P. R Norton, Opt. Eng. 30, 1649 (1991)
- 4 J. Piotrowski, W. Gawron. "Ultimate performance of infrared photodetectors and figure of merit of detector material". *Infrared Physics & Technology* **38**, 63-68 (1997)
- 5 J. D. Kim, D. Wu, J. Wojkowski, J. Xu, and M. Razeghi, *Appl. Phys. Lett.* **68**, 99 (1995)
- 6 W. Shan, W. Walukiewicz and J. W. Ager. "Band anticrossing in GaInNAs". *Phys. Rev. Lett.* **82**, 1221 (1999)
- 7 C.W. Tu, *J. Phys. Condens. Matter* **13**, 7169 (2001)
- 8 A. D. Johnson, R. H. Bennett, J. Newey, G. J. Williams, T. M. Burke, et al, *Mater Res Soc Symp Proc.* 607, **23** (2000)
- 9 B. N. Murdin; M. Kamal-Saadi; A. Lindsay; E. P. O'Reilly; A. R. Adams; G. J. Nott; J. G. Crowder; C. R. Pidgeon; I. V. Bradley; J.-P. R. Wells; T. Burke; A. D. Johnson and T. Ashley, "Auger recombination in long-wavelength infrared In_NxSb_{1-x} alloys", *App. Phys. Lett.* **78**, 1568-1570 (2001)
- 10 L. Bhusal and A. Freundlich, " Assessment of electronic properties of In_NxSb_{1-x} for long-wavelength infrared detector applications", *Appl. Surf. Sci.* **255**, 703-5 (2008)

- 11 B. N. Murdin, A. R. Adams, P. Murzyn, C. R. Pidgeon, I. V. Bradley, J. P. R. Wells, Y. H. Matsuda, N. Miura, T. Burke, and A. D. Johnson, "Band anticrossing in dilute $\text{In}_x\text{Sb}_{1-x}$ ", *App. Phys. Lett.* **81**, 256-258 (2002)
- 12 I. Mahboob; T. D. Veal and C. F. McConville, " Electron dynamics in $\text{In}_x\text{Sb}_{1-x}$ " *Appl. Phys. Lett.* **83**, 2169-71 (2003)
- 13 T. D. Veal, I. Mahboob, and C. F. McConville," Negative Band Gaps in dilute $\text{In}_x\text{Sb}_{1-x}$ Alloys", *Phys. Rev. Lett.* **92**, 136801 (2004)
- 14 I. Mahboob; T. D. Veal and C. F. McConville, "Low-energy nitrogen ion implantation of InSb", *J. Appl. Phys.* **96**, 4935-8 (2004)
- 15 Y. Wang; D. H. Zhang; Z. M. Huang; W. Liu; J. H. Li; C. J. Liu and A. T. S. Wee, " Study of ion-implanted $\text{InSb}_{1-x}\text{N}_x$ alloys using secondary ion mass spectroscopy", *IEEE Conference on EDSSC*, 677-680 (2007)
- 16 D. H. Zhang; W. Liu; Y. Wang; X. Z. Chen; J. H. Li; Z. M. Huang and S. S. Y. Zhang,, "InSbN alloys prepared by two- step ion implantation for infrared photodetection", *Appl. Phys. Lett.* **93**, 131107 (2008)
- 17 T. Ishguro; Y. Kobori; Y. Nagawa; Y. Iwamura and S. Yamaguchi, "Crystal growth and electrical characterization of InSbN grown by metalorganic vapor phase epitaxy", *Progress in Compound Semiconductor Materials III-Electronic and Optoelectronic Applications Symposium*, 45-9 (2004)
- 18 T. Ashley; T. M. Burke; G. J. Pryce; A. R. Adams; A. Andreev; B. N. Murdin; E. P. O'Reilly and C. R. Pidgeon, " $\text{InSb}_{1-x}\text{N}_x$ growth and devices", *Solid-State Elec.* **47**, 387-94 (2003)

-
-
- 19 P. H. Jefferson; L. Buckle; D. Walker; T. D. Veal; S. Coomber; P. A. Thomas; T. Ashley and C. F. McConville, " Growth and characterization of high quality MBE grown $\text{In}_x\text{Sb}_{1-x}$ ", *Phys. Status Solidi-Rapid Res. Lett.* **1**, 104-6 (2007)
- 20 T. D. Veal; I. Mahboob; C. F. McConville; T. M. Burke and T. Ashley, "Effect of hydrogen in dilute $\text{In}_x\text{Sb}_{1-x}$ alloys grown by molecular beam epitaxy", *App. Phys. Lett.* **83**, 1776-1778 (2003)
- 21 I. Mahboob; T. D. Veal and C. F. McConville, "Determination of the substitutional nitrogen content and the electron effective mass in $\text{In}_x\text{Sb}_{1-x}(001)$ epitaxial layers", *IEE Proceedings-Optoelectronics*, **150**, 102-104 (2003)
- 22 T. D. Veal; I. Mahboob; L. F. J. Piper; T. Ashely; M. Hopkinson; C. F. McConville, "Electron spectroscopy of dilute nitrides", *J. Phys. Condensed Matt.* **16**, 3201-3214 (2004)
- 23 H. T. Pham; S. F. Yoon; K. H. Tan and D. Boning , "Effects of nitrogen incorporation in $\text{InSb}_{1-x}\text{Nx}$ grown using radio frequency plasma-assisted molecular beam epitaxy", *Appl. Phys. Lett.* **90**, 92115-13 (2007)
- 24 K.P. Lim; S. F. Yoon; H. T. Pham and S. Tripathy, " Defect characterization of $\text{InSb}_{1-x}\text{Nx}$ grown using radio frequency nitrogen plasma-assisted molecular beam epitaxy", *J. Phys. D: Appl. Phys.* **41**, 165301-4 (2008)

-
-
- 25 T. J. C. Hosea; M. Merrick; B. N. Murdin, "A new Fourier transform photo-modulation spectroscopic technique for narrow band-gap materials in the mid- to far-infra-red", *Phys. Status Solidi A*, **202**, 1233-1243 (2005)
- 26 M. Merrick; T. J. C. Hosea; B. N. Murdin; T. Ashley; L. Buckle and T. Burke, "Bandgap bowing in $\text{InSb}_{1-x}\text{Nx}$ investigated with a new fourier transform modulated spectroscopy technique for the mid-infrared", *A/P conference proceedings* **772**, 295-6 (2005)
- 27 W. Liu; D. H. Zhang; Z. M. Huang; Y. Wang; S. F. Yoon; W. J. Fan, "Studying of intra-band and inter-band transitions in InSbN/InSb quantum well using 10-band k.p model", *6th International conference on numerical simulation of optoelectronic devices*, (2006)
- 28 S. M. Kim; F. Hatami; H. B. Yuen and J. S. Harris, "Investigation of nitrogen induced closely coupled Sb based quantum dots for infrared sensors application", *Materials Research Society Symposium Proceedings*, **959**, 106-111 (2007)
- 29 S. M. Kim; H. B. Yuen; F. Hatami; A. Chin and J. S. Harris, "Optical properties of dilute nitride $\text{InN}(\text{As})\text{Sb}$ quantum wells and quantum dots grown by molecular beam epitaxy", *J. Elec. Materials* **37**, 1774-9 (2008)
- 30 A. Linsay, E. P O' Reilly. "Theory of enhanced bandgap non parabolicity in GaNxAs_{1-x} and related alloys". *Solid State Communication* **112**, 443-447 (1999)

-
-
- 31 E. P O'Reilly and A Linsay. "k.P model of ordered GaN_xAs_{1-x}". *Phys, Status Solidi B* **216**, 131 (1999)
- 32 E P O'Reilly, A Linsay et al. "Tight binding and k.p models for the electronic structure of Ga(In)NAs and related alloys". *Semicond. Sci. Technol.* **17**, 870-879 (2002)
- 33 D. H. Zhang, W. Liu, L. Sun, W.J. Fan, S.F. Yoon, S.Z. Wang, and H. C. Liu, *J. Appl. Phys.*, **99** (043514), 1-4 (2006)
- 34 J.-D. Hecht, F. Frost, D. Hirsch, H. Neumann and A. Schindler, A. B. Preobrajenski and T. Chasse, *J. Appl. Phys.* **90**, 6066 (2001).
- 35 J.Likonen, K.Vakevainen, T.Ahlgren, J.Raisanen, E.Rauhala, J.Keinonen, " Annealing behaviour of high-dose-implanted nitrogen in InP", *Appl. Phys. A* **62**, 463-468 (1996)
- 36 Lahir Shaik Adam, Mark E. Law, Kevin S. Jones, Omer Dokumaci, C.S.Murthy, and Suri Hegde, " Diffusion of implanted nitrogen in silicon", *J. Appl. Phys.* **87**, 5 (2000)
- 37 P. Legare; L. Hilaire and G. J. Maire, *Microsc. Spectrosc. Electron.* **5**, 771 (1980)
- 38 W. E. Morgan; W. J. Stec and J. R.van Wazer, *Inorg. Chem.* **12**, 953 (1973)
- 39 R. W. Cunningham and J. B. Gruber, *J. Appl. Phys.* **41**, 1804 (1970)
- 40 O. Madelung (Ed.), *Semiconductors-Basic Data*, (Springer-Verlag, Heidelberg, New York, Berlin, 1996)

-
-
- 41 J. R. Soderstrom, M. M. Cumming, J-Y Yao and T. G. Andersson, "Molecular beam epitaxy growth and characterization of InSb layers on GaAs substrates", *Semicond. Sci. Technol.* **7**, 337-343 (1992)
- 42 M. Kasap and S. Acar, " The temperature dependence of electron and magneto transport properties in Te-doped InSb", *Phys. Stat. Sol. (a)* **201**,14,3113-3120 (2004)
- 43 J. J. Hopfield, D. G. Thomas, and R. T. Lynch, *Phys. Rev. Lett.* **17**, 312 (1966).
- 44 K. M. Yu, W. Walukiewicz, J. Wu, D. E. Mars, D. R. Chamberlin, M. A. Scarpulla, O. D. Dubon, and J. F. Geisz, *Nat. Mater.* **1**, 185 (2002).
- 45 H.Ryssel, and I.Ruge, *ION IMPLANTATION* (Wiley, Chichester, 1986)
- 46 D. Shaw, *Atomic Diffusion in Semiconductors* (New York: Plenum, 1973)
- 47 G. Bosker, N.A. Stolwijk, J.V. Thordson, U. Södervall and T.G Andersson, *Phys. Rev. Lett.* **81**, 3443 (1998)
- 48 J. D. Hecht, F. Frost, D. Hirsch, H. Neumann, A. Sidorenko, A. Schindler, S. Krasnikow, L. Zhang and T. Chasse, " Influence of preparation parameters for low-energy ion beam nitridation of III-V semiconductor surfaces", *Solid State Elec.* **47**, 413-418 (2003)
- 49 J. D. Hecht, F. Frost, D. Hirsch, H. Neumann, A. Schindler, A. B. Preobrajenski and T. Chasse, "Interstitial nitrogen induced by low-energy ion beam nitridation of AIII-BV semiconductor surfaces", *J. Appl. Phys.* **90**, 12 (2001)

50 Kow-Ming Chang, Jiunn-Jye Luo, Cheng-Der Chiang and Kou-Chen Liu.

“Wet etching characterization of InSb for thermal imaging applications”. *Jpn.*

J. Appl. Phys. **45**, 1477-1482 (2006)