Study of Improved Optical Properties of Nitrogen Implanted GaAs by Active Screen Cage

By

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(147-FBAS/MSPHY/S13)

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INTERNATIONAL ISLAMIC UNIVERSITY, ISLAMABAD

FACULTY OF BASIC AND APPLIED SCIENCES

DEPARTMENT OF PHYSICS

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A Thesis submitted to

Department of Physics, Faculty of Basic and Applied Science, International Islamic University, Islamabad (IIUI) for the Award of Degree of

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Chairman Department of Physics 23/5/16

International Islamic University Islamabad

Dean Faculty of Basic and Applied Science

International Islamic University, Islamabad

INTERNATIONAL ISLAMIC UNIVERSITY, ISLAMABAD
FACULTY OF BASIC AND APPLIED SCIENCES
DEPARTMENT OF PHYSICS

Dated ____________

Final Approval

It is certified that the work presented in the thesis entitled **"Study of Improved Optical Properties of Nitrogen Implanted GaAs by Active Screen Cage"** by **Muhammad Saddique Akbar Khan** bearing **Registration No.147-FBAS/MS PHY/S13** is of sufficient standard in scope and quality for award of degree of MS Physics from International Islamic University, Islamabad.

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Internal Examiner:
Dr. Wiqar Hussain Shah
Assistant Professor IIUI.

بسم الله الرحمن الرحيم

DEDICATED

to

My beloved

Mother

Grand Father

Father

and

My

Respected teachers

Declaration

I, **Muhammad Saddique Akbar Khan** (Registration # 147-FBAS/MSPHY/S13), student of MS Physics hereby declare that the work presented in the thesis entitled **"Study of Improved Optical Properties of Nitrogen Implanted GaAs by active screen cage"** in partial fulfillment of MS degree in Physics from International Islamic University Islamabad, is my own work and has not been published or submitted as research work or thesis in any form in any other university or institute in Pakistan or aboard.

Muhammas Saddique Akbar Khan
(147-FBAS/MSPHY/S13)

Dated: ____________________

Forwarding Sheet by Research Supervisor

The thesis entitled “**Study of Improved Optical Properties of Nitrogen Implanted GaAs by active screen cage**” submitted by Muhammad Saddique Akbar Khan (Registration # 147-FBAS/MSPHY/S13) in partial fulfillment of MS degree in Physics has been completed under my guidance and supervision. I am satisfied with the quality of his research work and allow him to submit this thesis for further process to graduate with Master of Science degree from Department of Physics, as per IIUI Islamabad rules and regulations.

Dr. Waqar Adil Syed
Chairman Department of Physics
International Islamic University Islamabad

Dated: ______________________

ACKNOWLEDGEMENTS

I have really no words to express the deepest sense of gratitude to Almighty **ALLAH** the most merciful and compassionate, the Creator of the universe for giving me the strength and perseverance for completing the research. I offer my humblest and sincerest words of thanks to the **Holy Prophet** (P.B.U.H) who is always a source of guidance and knowledge for humanity. It is a matter of great pleasure and honor for me to express my deep sense of devotion and deepest gratitude to Dr. Waqar Adil Syed, Chairman Department of Physics International Islamic University as supervisor. Finally, I acknowledge the help, the encouragement, endless love, support and prayers of my family and my colleagues which have always been a source of inspiration and guidance for me all the way.

Muhammad Saddique Akbar Khan
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ABSTRACT

GaAs is a group III-V compound semiconductors in which Gallium belong to 3rd group and Arsenic belong to 5th group. It is used in high speed, high frequency and low resistive and low power electronic devices. It has low noise and maximum electron mobility. The main motivation for using GaAs compound semiconductors for device applications is found due to the optical properties. The band gap of GaAs can be change from 1.1 to 1.42 eV for low dose or dilute nitrogen and 1.42 to 3.4 eV for high dose of nitrogen. When dose is high then Arsenic is totally replaced by nitrogen. The band gap varies from 3.2 to 3.5 eV. The nitrogen is implanted by plasma nitriding technique. The samples were treated for 30 min,, 45 min 60 min,90 min and 130 min. The value of current was 0.8 Amp. The samples were annealed to remove the defects. The annealing temperature was 650°C and time was 30 min. After implantation the followings characterizations were performed. XRD was studied to investigate the crystal structure. Rutherford back scattering (RBS) was used to find out the nitrogen composition as compared to Ga and As. Film thickness and depth was also calculated by RBS. Diffused reflectance spectroscopy was used to calculate the band gap. By Tauck plot and Munk function, the band gap was calculated

Chapter 1

Introduction

The modern semiconductors [1] brought a great revolution in the field of electronics industry while having enormous applications in transistors, processors, solar cells, light emitting diodes, laser diodes and in optical windows, owing to their striking physical and electronic properties. Semiconductors can be divided into a number of classes out of which III-V semiconductors especially GaAs is the most studied material. The large electron mobility at low electric field of GaAs, as shown in Figure 1.1, opens new window for the applications in low power, high speed and high frequency electronic devices.[2]

1.1 Properties of III-V semiconductors

The interesting physics behind the striking properties of semiconductors, especially III-V semiconductors, can be discussed on the basis of followings properties.

I-Crystal structure

Wurtzite and Zincblende are the most commonly available crystal structures in semiconductors. Wurtzite, as shown in Figure 1.2, is a two dimensional hexagonally closed packed lattice of tetrahedral shape. While Zincblende and rock salt crystal structure have face centred lattice in cubic form, with coordination number of four and six respectively. GaAs is commonly available in Zinc Blende while GaAsN can have both wurzite as well as zinc blende crystal structure. On the other hand GaN exists in wurtzite crystal structure [3]. If Arsenic is completely replaced by nitrogen in GaAsN, the crystal structure takes the form of Wurtzite crystal structure; on the other hand, nitrogen remaining in interstitial position reproduces the crystal structure of GaAs i.e zinc blende.

II- Variable conductivity

Owing to filled valance bands at room temperature while having covalent bonding with neighbouring atoms, a pure semiconductor has poor electrical conductivity. In order to enhance their conductivity, semiconductors are doped with either tri-valent or penta-valent materials creating p-type or n-type materials respectively with improved conductivity. At the higher temperatures, the breaking of covalent bonds creates free electrons as well as vacant spaces known as electron hole pairs, responsible for the flow of current in semiconductors. Upon further increase in temperature the resistance of the material increases due to collisions.

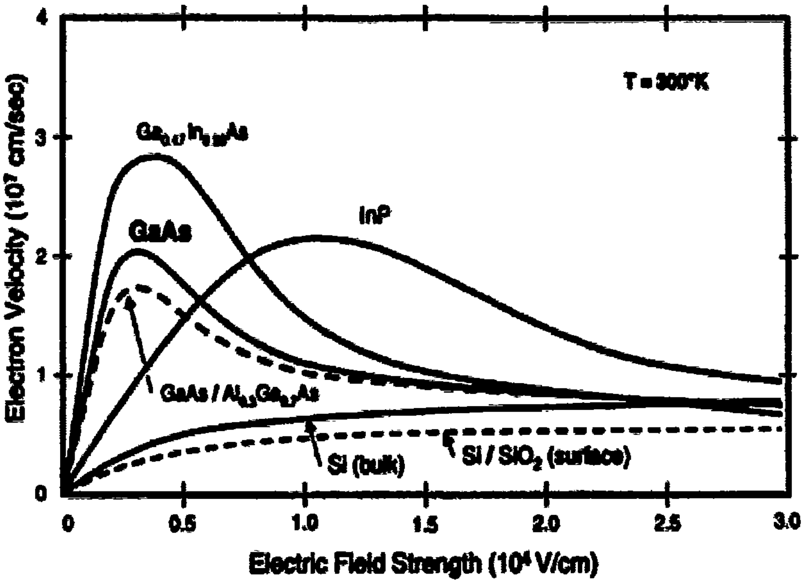
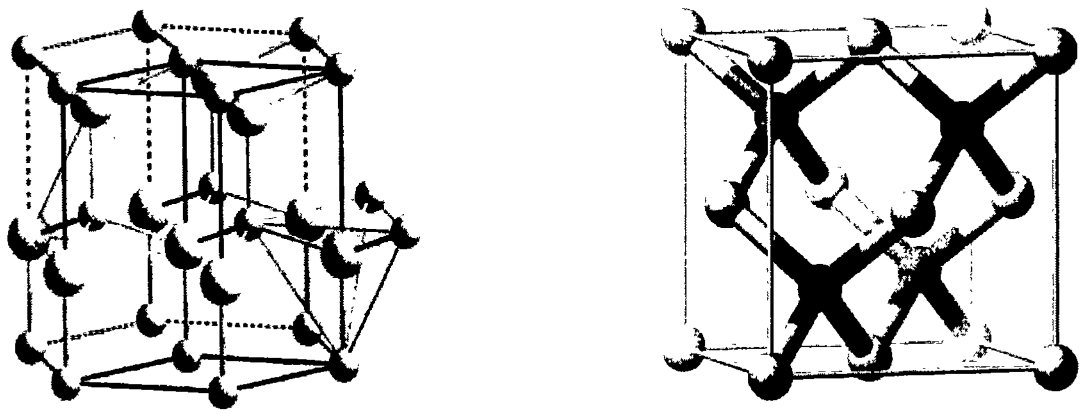


Figure 1.1 Velocity of electrons in semiconductors as a function of electric field strength [2]



Wurzite

Zincblende [3,4]

Figure 1.2 Wurzite and Zincblende crystal structure

III- Light emission

In some semiconductors, the de-exciting electrons produce EM radiation in the visible region of the spectrum making the material worthy of applications like light emitting diodes and fluorescent quantum dots. .The direct band gap of the semiconductors as dominant in GaAs, is usually attributed to this phenomenon as well as maximum absorption of light. The inclusion of dopant in the semiconductors materials modifies the light emission and absorption characteristics of semiconductors as indicated in GaAsN in which the Nitrogen reduces the reflection losses in the absorption of light .

1.2 Introduction of GaAs

The billion dollars worldwide industry of high speed and high frequency devices, having their base on transistors, strongly relies on semiconductors for fabrication of electronic devices. Initially the Silicon and Germanium based semiconductor devices were deployed. However with the passage of time, new and improved semiconductor material occupied the market .The new semiconductors have tuned various properties for different practical applications [5,6]. Soon after the discovery of laser in 1962, a new search for semiconductor materials with light emitting properties started. For improved light emitting properties, the material should incorporate a direct band gap in visible region which the then dominant semiconductor Silicon lacked. Silicon also lacked the capacity to act as a light emitter.[7,8] The light emitting properties as well as the direct band gap of GaAs got readily noticed to fill the gap of materials in the applications like lasers and LEDs .

Properties and applications

Gallium Arsenide (GaAs) is III-V compound semiconductor having Zinc Blende Crystal structure with high saturated electron velocity which enables it to operate at low resistance. Due to direct band gap, the absorption and emission of light as well as its tolerance to radiation damage is quite high. On the other hand, it can combine with materials of high dielectric constant and provide best isolation for the circuit . It has low noise to signal ration with high electron mobility which makes it a potential candidate for applications like microwave frequency, integrated circuits, infrared emitting circuits, laser diodes, optics and optical windows .

Devices based on GaAs are classified as electronic or photonic devices [9,10]. Electronic devices include bipolar transistor, field effect transistor, diodes, hetero-junction, bipolar transistor etc. While the useful photonic devices based on GaAs are LEDs, photo detectors and laser diodes. The utilization of GaAs in such a large number of applications and devices proves its worth as a useful material for the future applications as well.

1.3 Selection of nitrogen for implantation

Large electro-negativity and small size of nitrogen are the main reasons for the selection of nitrogen for implantation. The electro-negativity of nitrogen i.e. 3.1eV, is much more than rest of group V element like P, As and Sb which average around 2 eV. The nitrides of semiconductors like GaAsN, GaN, GaPN, InPN and InAsN are amongst the highly studied materials for band gap applications [11,12]. The dilute nitride alloys such as GaAsN are used for wide band gap application. Therefore, GaAsN thin film and hetro-structure are best for broad range of optoelectronic applications, and provides the chance to investigate the nitrogen induced perturbation caused by parameters such as doping concentration, annealing temperature, pressure, voltage, time of nitriding and type of substrate [13,14]. Due to the difference of electro-negativity and size between N and As, there is possibility of formation of defects. Our aim is to study the effect on optical properties of GaAs with nitrogen implantation thus the emphasis will be given to the variation in the band gap of compound semiconductor.

1.4 Introduction about nitriding

Nitriding is an effective technique to provide surface hardening as well as wear and corrosive resistance for the different materials in industrial area. Normally thermal and thermo chemical method are adopted in the industry for this purpose in which the nitrogen is bombarded at the surface of material to fill up avoids and empty spaces between atoms and provide a better resistance against corrosion and wears [15].

Nitriding technique was developed J. Georges [16]. At that time this technique was limited only in industry. Bernard Berghaus introduced the ions or plasma nitriding. This technique was used for all possible material. After some years the salt bath nitriding was introduced. But this technique was failed because of side effects. After some time General Electric wrote about the plasma nitriding in full scale production. Later on pulse dc was introduced to improve these methods [17]. Post discharge was introduced in 1987. Georges developed the active screen cage nitriding.

Application of nitriding

- It is used for doping of semiconductors.
- It is used in the industry to improve the hardness and fatigue resistance of materials.
- It is also used to form a thin film at the surface of semiconductors.

1.5 Nitrogen based compounds of GaAs

Nitrogen implantation of the GaAs may lead to the formation of GaAsN with nitrogen at interstitial positions of the crystal structure. However, the substitution of arsenic by nitrogen may lead to formation of GaN [18]. GaN is also a III-V compound semiconductor. The sensitivity of GaN against the ionization radiation is very low which makes it suitable for operations at high temperature. It has large heat capacity and high thermal conductivity. The GaN has high break down voltage, high saturation velocity and high electron velocity. The melting point of GaN is 2500°C. GaN holds both Wurtzite and Zinc Blende crystal structure with energy gap of 3.4 eV. It is used in high printing, microwave radio-frequency, high power amplification, solar cell, single crystal nano tube, normally ultraviolet radiators and laser printing.

Table 1.1 Physical properties of GaAs and GaN

Physical properties	**GaAs**	**GaN**
Melting point	1238°C	2500°C
Mobility at 300K	-	1245cm^2/Vs
No atoms in 1cm^3	4.42×10^{22}	8.9×10^{22}
Effective electron Mass	$0.20m_0$	$0.063m_0$
Dielectric constant at 300K	12.9	8.9
Density	5.317(g/cm^3)	6.15(g/cm^3)
Reflractive index	3.8	2.33
Thermal conductivity	0.55(W/cmK)	2.1(W/cmK
Lattice constant	5.65A	a=3.189,c=5.185
Thermal expansion($\times10^6$K)	δa/a=5.59,δc/c=3.17	
Band gap	1.42 eV	3.4 eV
Molar mass	144.64(g/cm)	83.73
Crystal structure	Zinc Blende	Cubic and wurtzite

Dilute GaAsN has got a high attention for technological application at fundamental area with adding 5% concentration. Since both GaAsN and GaN have direct band gap having value 3.4 to 1.43 eV. They have the visible spectrum in infrared and ultraviolet region.

1.6 Optical properties

I -Band gap as a function of lattice constant

The Figure 1.3 shows the band gap energy as a function of lattice constant for some selected III-V semiconductor. A desired band gap may be engineered by creating alloy of different III-V semiconductors with changing the composition of nitrogen.

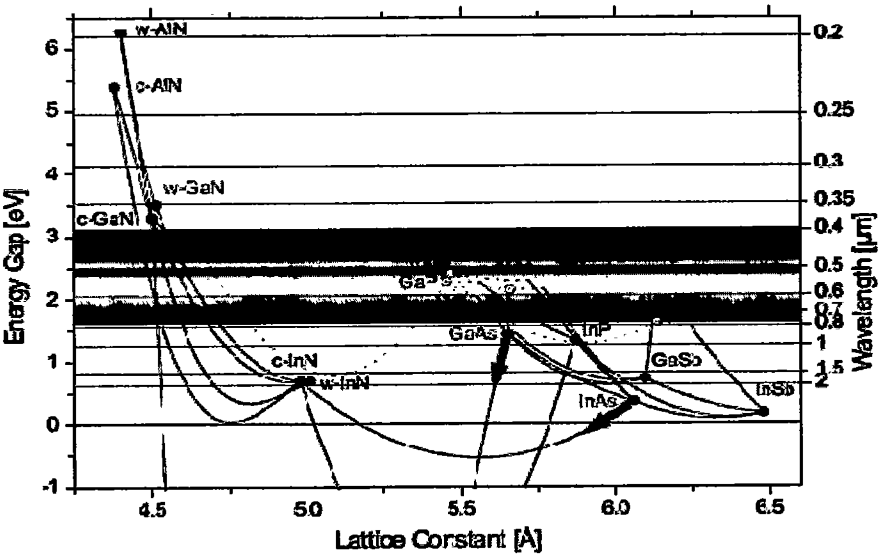


Figure 1.3 Band gap energy as a function of lattice constant [5]

II-Vegard law:

The lattice constant of ternary alloy are usually described by Vegrad law. It states that lattice constant of ternary alloy can be expressed as a lattice constant of combination of 2 binary compounds. The lattice constant changes linearly as composition changes. This linear behaviour is called Vegard law. Usually the band gap energy varies nonlinearly. The expression shows the band gap is calculated at any value of composition.

$E_g(AB_xC_{1-x}) = x.E_g(AB) + (1-x).E_g.(AB) + b.x(1-x)$ 1.1

And $AB_xC_{1-x} = GaAs_{1-x}N_x$..1.2

Where AB is GaN and AC is GaAs.The b is bowing coefficient which is composition dependent and has value is less than 1 eV. The above equation describes that band gap energy changes with composition in dilute regime. The solid lines Figure 1.3 represent the direct band gap and dotted line represents the indirect band gap. Colour band gap represents the visible range .GaAs and GaN are given in red region which are shown by red arrows.

III- Energy band gap and bowing coefficient of III-V semiconductors

In equation 1.1 b is called bowing coefficient. The bowing coefficient accounts the deviation from linearity of lattice parameter. The $GaAs_{1-x}N_x$ has been studied for more potential application because of giant bowing coefficient. The bowing coefficient changes the band gap of semiconductors .The variation of bowing and energy is given in the table.

Table 1.2 Energy band gap and bowing coefficient of III-V semiconductors

Alloys names	b(eV)	E_B-E_c(eV)	Alloys names	b (eV)	E_B-E_c (eV)
AlPAs	0.22	0.1	InPSb	1.9	0.3
GaPAs	0.19	0.1	GaPSb	2.7	0.3
InPAs	0.1	0.1	GaAsN	120.4-100x	1
AlAsSb	0.8	0.2	InAsN	4.22	1
GaAsSb	0.43	0.2	InPN	15	0.9
InAsSb	0.67	0.2	GaPN	0.9	3.9

IV-Effect of defects

It is well known facts that defects play an important role in optical and electrical properties. They can reduce the life time of charge carriers. They can acts as a relative recombination centres and

ABSTRACT

GaAs is a group III-V compound semiconductors in which Gallium belong to 3rd group and Arsenic belong to 5th group. It is used in high speed, high frequency and low resistive and low power electronic devices. It has low noise and maximum electron mobility. The main motivation for using GaAs compound semiconductors for device applications is found due to the optical properties. The band gap of GaAs can be change from 1.1 to 1.42 eV for low dose or dilute nitrogen and 1.42 to 3.4 eV for high dose of nitrogen. When dose is high then Arsenic is totally replaced by nitrogen. The band gap varies from 3.2 to 3.5 eV. The nitrogen is implanted by plasma nitriding technique. The samples were treated for 30 min,, 45 min 60 min,90 min and 130 min. The value of current was 0.8 Amp. The samples were annealed to remove the defects. The annealing temperature was 650°C and time was 30 min. After implantation the followings characterizations were performed. XRD was studied to investigate the crystal structure. Rutherford back scattering (RBS) was used to find out the nitrogen composition as compared to Ga and As. Film thickness and depth was also calculated by RBS. Diffused reflectance spectroscopy was used to calculate the band gap. By Tauck plot and Munk function, the band gap was calculated

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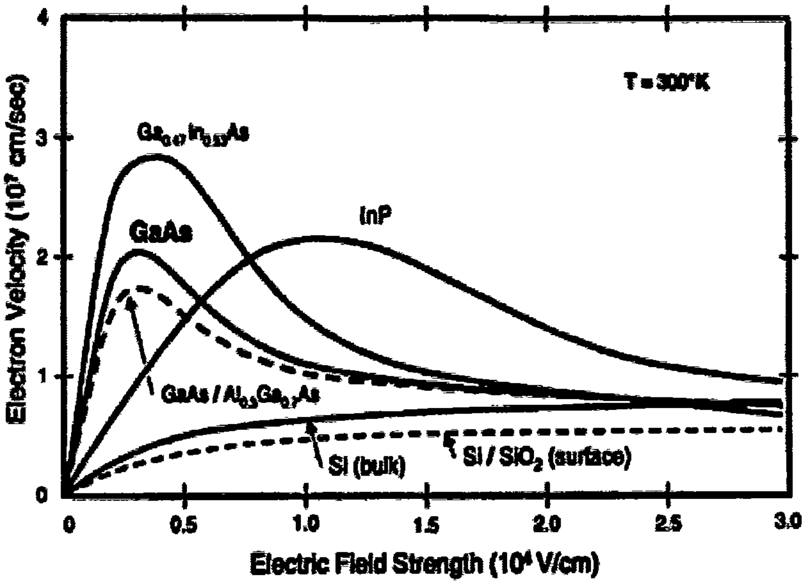

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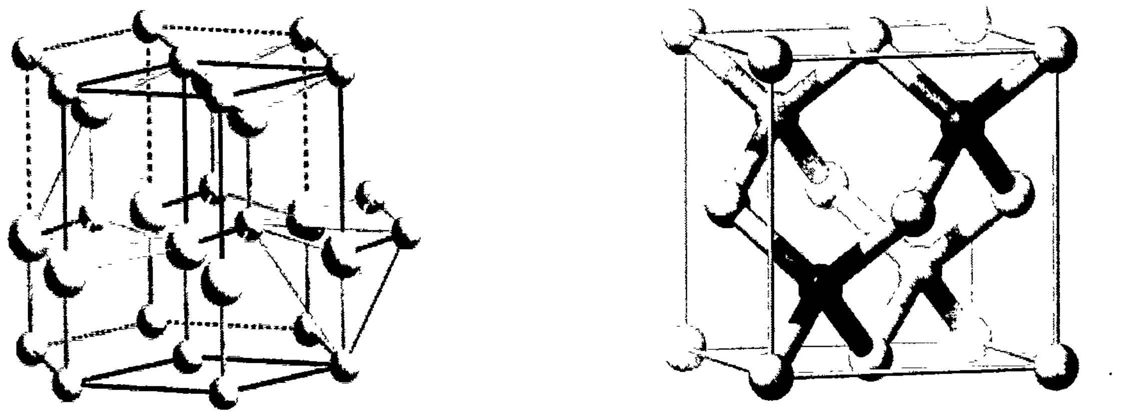

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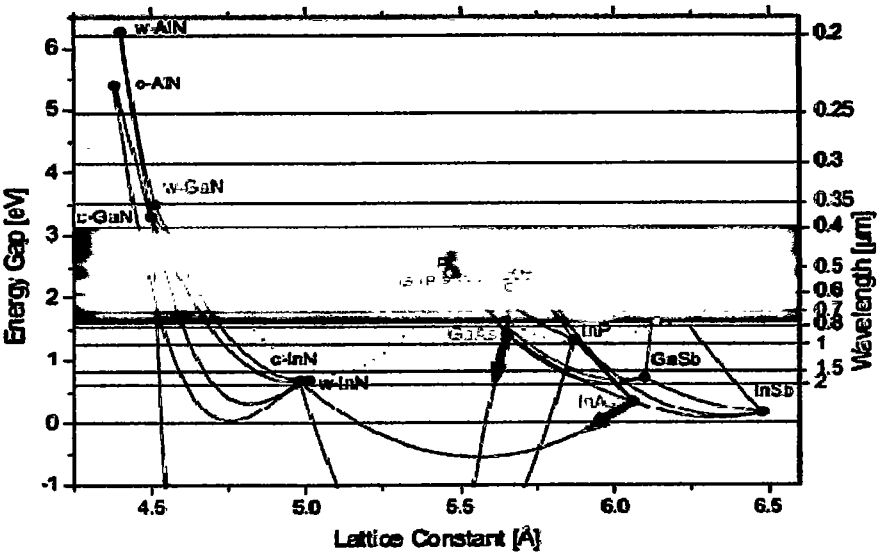

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$E_g(AB_xC_{1-x}) = x.\,E_g(AB) + (1-x).\,E_g(AB) + b.x(1-x)$ ……………………………………………1.1

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Where AB is GaN and AC is GaAs.The b is bowing coefficient which is composition dependent and has value is less than 1 eV. The above equation describes that band gap energy changes with composition in dilute regime. The solid lines Figure 1.3 represent the direct band gap and dotted line represents the indirect band gap. Colour band gap represents the visible range .GaAs and GaN are given in red region which are shown by red arrows.

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InPAs	0.1	0.1	GaAsN	120.4-100x	1
AlAsSb	0.8	0.2	InAsN	4.22	1
GaAsSb	0.43	0.2	InPN	15	0.9
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IV-Effect of defects

It is well known facts that defects play an important role in optical and electrical properties. They can reduce the life time of charge carriers. They can acts as a relative recombination centres and degrade the optical property of laser and optoelectronics devices. Thus the inclusion of defects in the crystal can play a vital role in the in the properties of interest.

V-Physical aspects of groups V elements and optical properties

The table shows the properties of Group V elements, including atomic mass, electro negativity difference, electronic configuration and covalent radii. These physical aspects have significant effects on optical properties of GaAs. The electro-negativity and the covalent radii play a vital role in the formation of defects in a structure. From the table 1.3 it is clear that the electro negativity difference between As and N is much larger than other elements of V elements.

Table 1.3 Physical aspects of groups V elements

Element	Electronic Structure	Atomic Mass (g/mol)	Covalent Radius (nm)	Electro negativity
N	(He) $2s^2p^3$	14.007	0.07	3.04
P	(Ne) $3s^23p^3$	30.79	0.106	2.19
As	(Ar) $3d^{10}\,4s^2\,4p^3$	74.92	0.118	2.18
Sb	(Kr) $4d^{10}\,5s^2\,5p^3$	121.75	0.136	2.05
Bi	(Xe) $4f^{14}5d^{10}6s^2\,6p^3$	208.95	0.145	2.02

1.7 Statement of problem

GaAs is III-V compound semiconductors used in high speed electronic devices. We can tune its band gap from 1.42 to 3.4 eV. The band can be decreased or increased as it depends upon the concentration of nitrogen. At low concentration the band gap decreases but for high concentration the band gap increases. When band gap increases then light of shorter wavelength emits which means blue shift. When concentration is low then band gap decreases and we moves towards red shift. The nitrogen was implanted by plasma discharge method by using screen cage due to its lesser energy consumption and cost as compare to commercially available solutions. This technique provides a lot of opportunities to study the effects of various parameters on GaAs like temperature, pressure, and flow rate of gases mixture of gases. We have studied the effects of implantation timing on optical properties of GaAs in the environment of 1:1 of argon and Nitrogen at a flow rate of 50sccm.

1.8 Thesis layout

This thesis consist of five chapters. First chapter deals with the introduction of the problem at hand, regarding GaAs and nitriding. The second chapter is related to literature review about plasma nitriding and GaAs. In third chapter the experimental setup is discussed. Chapter four is a brief introduction of chractrization techniques utilized in the research. Chapter five is about experimental results and discussion where XRD, diffused reflectance spectroscopy, Rutherdford back scattring and FTIR results are discussed. In this chapter we also discussed absorption coefficient, reflectance and transmittance as well as the band gap by using the Munk function.

Chapter 2

Literature Review

2.1 Historical based research on GaAs

Gallium arsenide (GaAs) is a III-V compound semiconductor having great importance on technical and fundamental applications. Many techniques were used to tune its optical and electrical properties for the desired results. These techniques may include the inclusion of various elements like, Bismuth, Nitrogen Indium and silicone etc, however our motivation is to focus on the nitrogen based techniques like plasma nitriding. When we use different techniques for nitrogen treatment then we have to adopt different environment and different parameters. These parameters are temperature, mixture of gases, high and low dose etc. These parameters cause enormous changes in GaAs substrate in various directions. These changes may be defects, Band gap, surface hardness, crystal structure, reflectance, transmittance etc. The knowledge about these parameters and techniques is necessary.

Role of hydrogen for surface passivation

A remote N_2-H_2 (mixture of 97% N_2-3% H_2) was used by G.Capozzi et al [19] to form a thin GaN layer which is valuable technique for chemical and electronic passivation of GaAs (100) surface. Nitrogen was treated on semi insulating GaAs (100) substrate that was ultrasonically cleaned by dichloromethane and ethanol. Dilute HCl was used to remove the native oxide and surface contamination. The radio frequency was 13.56 MHz with RF power 200 Watt. It was observed that GaAs passivation induced by N_2-H_2 (97% N_2-3% H_2) is more effective than conventional GaAs hydrogenation. This is because hydrogen atoms play a vital role for removal of Arsenic, while pure nitrogen does not provide GaAs passivation. A strong increase in PL intensity was observed in this case and Fermi level shifted near the valance band. Longer the nitridation time, higher the yields was. This leads to increase in surface thickness and rise in the mobility of charge carrier. X-ray photoelectron spectroscopic measurement was performed to analyze the chemical bonding of atoms at the surface. SE measurements were performed to analyse the information on structure, chemistry and thickness of layers.

Structural changes induced by fast nitrogen ions in GaAs .

The influence [20] of implantation with fast nitrogen ions on GaAs single crystal structure was studied by D.Zymierska et al.

The energy of nitrogen was 2.85 MeV and dose 5×1014 cm^{-2}. The scanning electron microscope revealed that burried layer of defects was created at 20 μm depths. Swift heavy ions cause the damages inside the GaAs. The investigation of structural changes induced by implantation in such model semiconductor is important for diffraction effect. They have practical application in production of special structures in semiconductors.

Investigation of GaN layers on GaAs by MOVPE.

In 1998, V.V.Lundin et al [21] investigated the GaN layers doped with Arsenic atoms. The Arsenic atoms were injected into GaN by metal organic vapour phase epitaxial technique. At high temperature, the over growth of thin GaAs layer on GaN causes the Arsenic atoms to diffuse into GaAsN and produces a thick homogenously doped GaN:As regions. When Arsenic atoms diffuse into GaN then bright band gap produces in the photoluminescence spectrum at 2.5 eV. They have investigated the conditions for ejection of Arsenic atoms into GaN layers during MOVPE growth. They have shown that deposition of GaAs on GaN surface reduces the stress and give partial relaxation to GaN surface layer. At high temperature, the subsequent overgrowth of GaAs layer on GaN gives an emergence to a new band in PL.

Etching of GaN by MOCV deposition.

Inductively coupled plasma (ICP) [22] etch rates for GaN was reported as a function of plasma chemistry, RF power and ICP power. GaN film etched in this study were grown by metal organic chemical vapours deposition. Ions energies were provided by superimposing an RF bias 13.56 MHz on the sample. Several ICP etch conditions showed direct application to the fabrication of group-III nitrides etched rates.

Effect of Annealing on carrier concentration of GaAsN

In 2002, Ann Arbor et al [23] investigated the influence of post-growth annealing on electronic properties of gallium arsenide nitride alloy film. GaAsN film, with Nitrogen concentration was grown by plasma-assisted molecular beam epitaxy, using Ga, As_2 and N_2 flow. It was found that free carrier concentration and electron mobility increases with increasing the temperature. Post growth annealing was performed from 650 to 800° C for 60s in nitrogen flow. Free carrier concentration increases exponentially with temperature up to room temperature which is related to the removal of N-induced deep level trapping centre.

Ion implantation into GaN by MOCVD.

In 2000, C.Ronning et al [24] used the metal organic chemical vapour deposition (MOCVD) technique for ion implantation on GaN. Ions were implanted at different temperature and different dose. The range of temperature is 298- 300 K at different doses. X-ray diffraction (XRD), transmission electron microscopy (TME), secondary ion mass spectroscopy (SIM), Rutherford scattering (RBS) and photoluminescence were used for measurements on GaN. It was observed that microstructure changes in host substrate which occurs during ion implantation due to loss of kinetic energy. The electronic and nuclear interaction appears between incoming ions and host material so the loss of kinetic energy takes place. The damages created in host material were removed by annealing process. The melting temperature of GaN is 2791°C and therefore annealing temperature is 1500°C.

Treatment of Nitrogen on GaAs(100) and Ga/GaAs systems studied by XPS.

In 2003, Y.Oluld-Metidji et al [25] performed the nitridation of GaAs using RF cell. The influence of pressure and temperature was studied. During nitridation, X-ray photoelectron spectroscopy is used to monitor the surface changes. But in this process, we cannot obtain the pure GaN layer s on the surface due to presence of As atoms in the nitride layer. To stop the migration of arsenic in nitride layer, we improved the nitridation method with an additional technique that consists of deposition of metallic gallium in well controlled quantity. To get rid of the oxides on this nitride layer the ionic pump was used.

Concentration of GaN as function of temperature and time.

The ion induced nitridation of GaAs(100) has been investigated by Y.G.LI et al [26] in 2001. The ions were implanted by home-built twin chamber ultrahigh vacuum (UHV) system equipped with growth chamber. Argon was used to remove the oxygen and carbon contamination. It was observed that concentration of GaN increases with time. The degree of nitridation increases below 450° C and decreases when temperature is greater than 450° C.

Effect of low energy low energy ions on GaAs .

In 2007, Vitoldas et al [27] studied the effect of low energy ions on GaAs. The samples were treated by drift ion technique. Surface nitridation by such low energy ion method has some advantages over plasma nitridation source. There are more possibilities to control the parameters of technological process such as current density and ions energy. They treated the samples at 293K with angle 70°, $N2_{+}H_2$ (97:3) gas mixture, pressure 4.10^{-2}-10^{0} Pascal and energy domain 65 eV-320eV. It was concluded that thickness of the layer has direct relation with ions beam energy and ions current density but the relation of increasing angle was contrary to it.

Synthesis of GaN by implantation of N ions into GaAs

Nitrogen ions [28] with dose of 3×10^{17} cm^{-2} and energy of 100 keV were implanted on GaAs substrate. The sample was annealed in a furnace at 750°C for 30 min. Implantation of nitrogen ions into GaAs substrate was done by furnanance. The synthesis of wurzite GaN was registered by cathodoluminescence, Raman spectroscopy and infrared reflection spectroscopy. The SIMS measurement revealed that only a small amount of ions take part in nitrogen synthesis at wafer surface.

XRD of epitaxial zinc-blende GaN on GaAs (001) by HVPE

In 1998, Chien-Cheng Yang et al [29] used the hydride vapour-phase epitaxial reactor to grow a cubic GaN epitaxial film on GaAs (001) at low temperature. X-ray diffraction spectra indicate that epitaxial film contains zinc-blended GaN as well as wurtzite GaN. Wurtzite peaks appear at (002) and (101). Zinc-blended peaks appear at (002) and (004) with angles 39.8° and 86.6° They also calculated the crystalline size D of zinc-blended structure by using Sherrer formula $D=0.94\lambda/\beta cos\theta$. Where β denotes the breadth of 2θ detector. Hydride vapor phase epitaxy is an alternate and faster technique than MOCVD technique. The samples were deposited by HVPE with GaCl and NH_3 as a Ga and N source at atmospheric pressure. The temperature range is 545 to 750°C

2.2 Optical properties

In optical properties we study the interaction of light with matter i.e. absorption, reflection refractive index, band gap and transmission of light through matter. We focus our attention on band gap as a function of treatment time of nitrogen.

(1) Tauc Plot and Diffused Reflectance Spectroscopy

The band gap was calculated for material by J. Tauc, R. Grigorovici. [30]. They used the Tauc plot method and Kubelka Munk function for direct band gap and indirect band gap. First of all spectrums by DRS was characterised .They draw the graphs between energy and Tauck function. By drawing the tangent at curve we can observe the value at x-axis. The following relations proposed by Tauck are used

$$(hv\alpha)^n = A(hv - E_g) \qquad 2.1$$

For direct band and indirect band we have different values. The curve that plots the value of $(hv - (h\alpha(F(R))^2$ and tangent gives values of energy

Reduction of band gap and metallic character of GaAsN

The band gap can also be calculated by A.F Tsatsul et al [31]. By using photoluminescence the wavelength is plotted along x-axis and intensity is plotted along y-axis. By using E=hc/λ we can calculate the band gap.

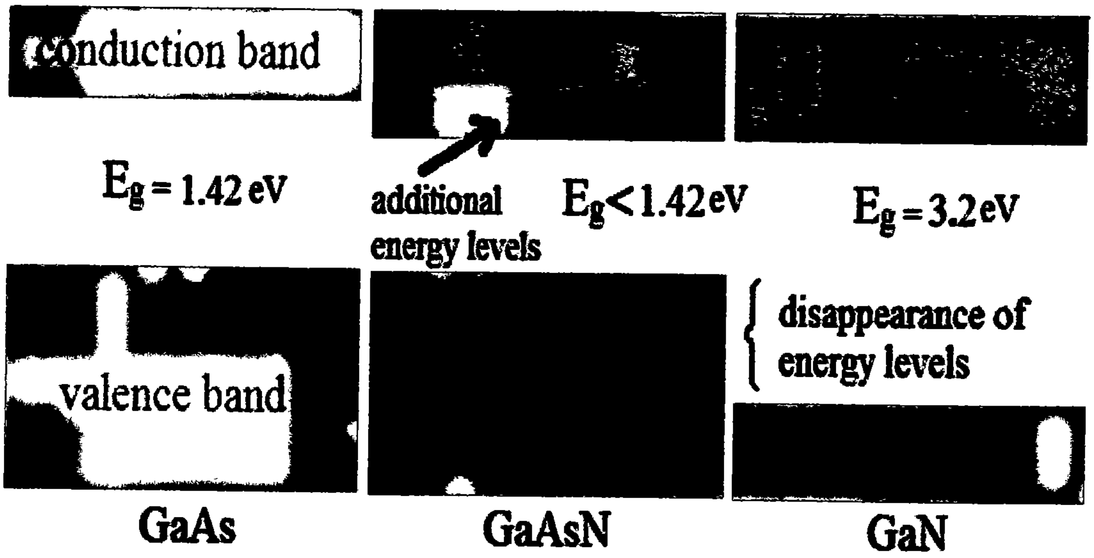


Figure 2.1 Band gap comparisons of GaAs and Nitrogen base compounds

To shift the emission towards longer wave length, we use the GaAs-GaN

(2) Photoluminescence

The optical properties have been investigated by PL shows in Figure 2.1.The YL emission (Yellow emission) near the band-edge is attributed to defects in GaN region. There is also a GL (green emission) at 2.45 eV. In these spectra we have distinguished three ranges, important for the discussion. In range 1, the obtained peak is due to the GaN compound present in the GaAs wafer. The range 2 shows the peaks, appeared due to the oxide formation or arsenic impurity in GaN. The arsenic impurity causes the reduction in the band gap of GaN . The third region shows the peaks confirming the presence of $GaAs_{1-x}N_x$. A small addition of nitrogen into GaAs causes reduction in the band gap of GaAs . The starting point of peak at 930 nm corresponds to the band gap of 1.333 eV. In other words this absorption peak is due to a dilute addition of nitrogen; showing the reduction of band gap of GaAs which was 1.44 eV For addition of dilute nitrogen, the energy states in deep valence bands do not contribute in reduction of band gap, that's why the theory of the $GaAs_{1-x}N_x$ alloy focus on the conduction band. But higher addition of nitrogen causes the disappearance of energy states from the maxima of valence band of GaAs and responsible that band gap increase

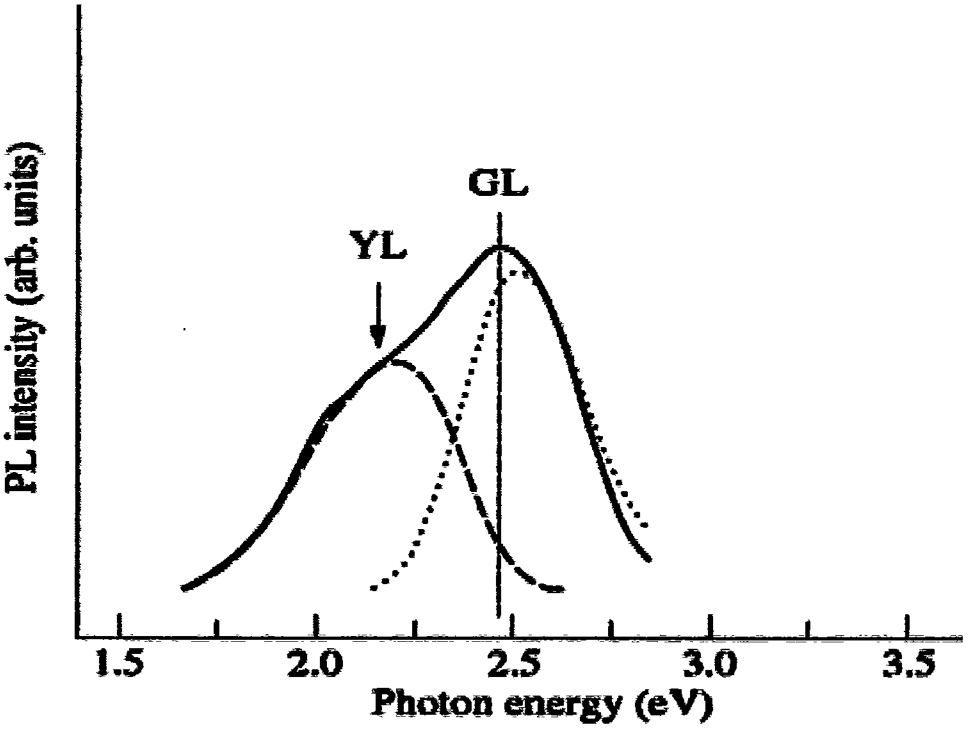


Figure 2.2 (a) Graph between Energy and intensity [31]

When band gap increases then we obtain the blue shift the reason is that high energy photon emotion take place. When band gap decreases then we get red shift because photon has low energy. The band gap may increase or decrease. When nitrogen is completely replaced then we get GaN .The band gap of GaN is 3.4 eV. If nitrogen is not completely replaced then GaAsN is obtained. The band gap of GaAsN is less than 1.42 eV. The graphs 2.2 (a) and (b) show that band gap fluctuates as a function of nitrogen concentration .Similarly yellow shift may be obtained. The yellow shirt, blue shifts and red shift has great application in LEDs and traffic signals

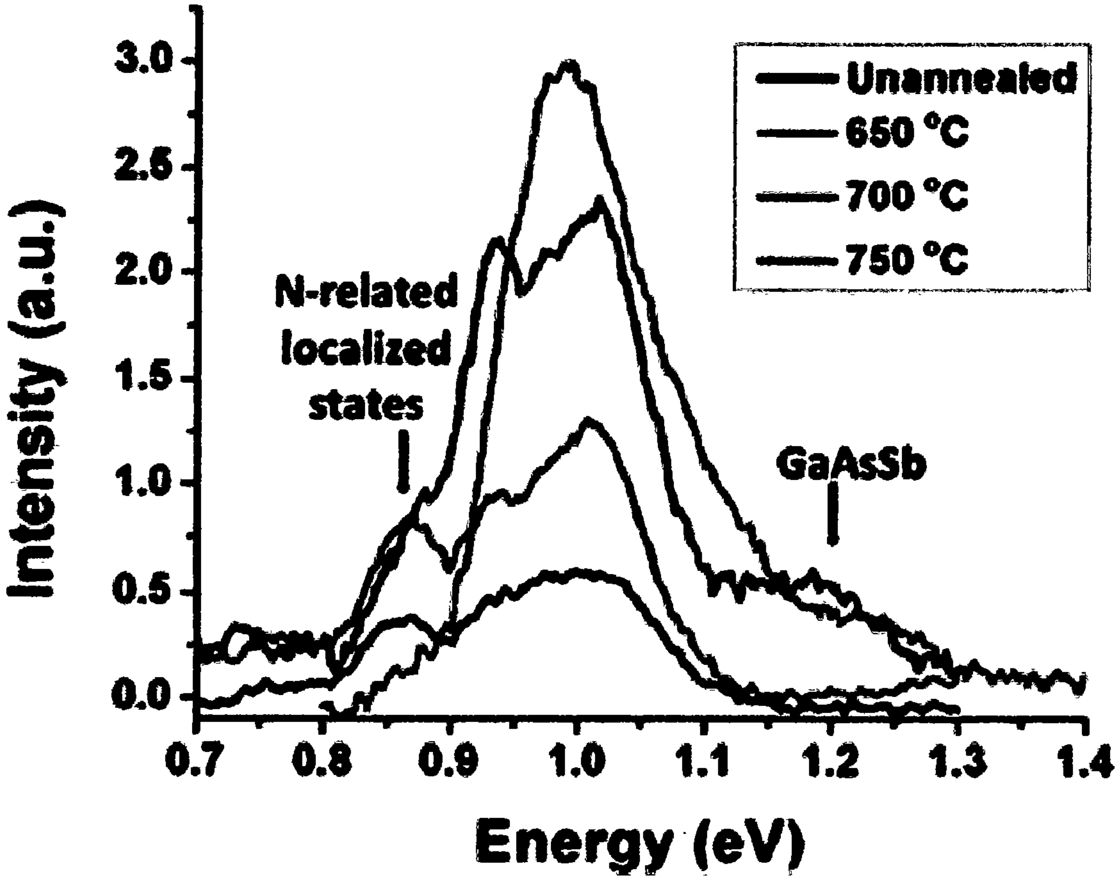


Figure 2.3 Band Gap by Photoluminescence [33]

Dilute GaAsN has received high attention with a nitrogen concentration upto 5 % for both technical and fundamental reasons [33]. The GaAsN formed from GaAs and GaN, both having direct band gap that is 1.42 eV and 3.4 eV respectively.

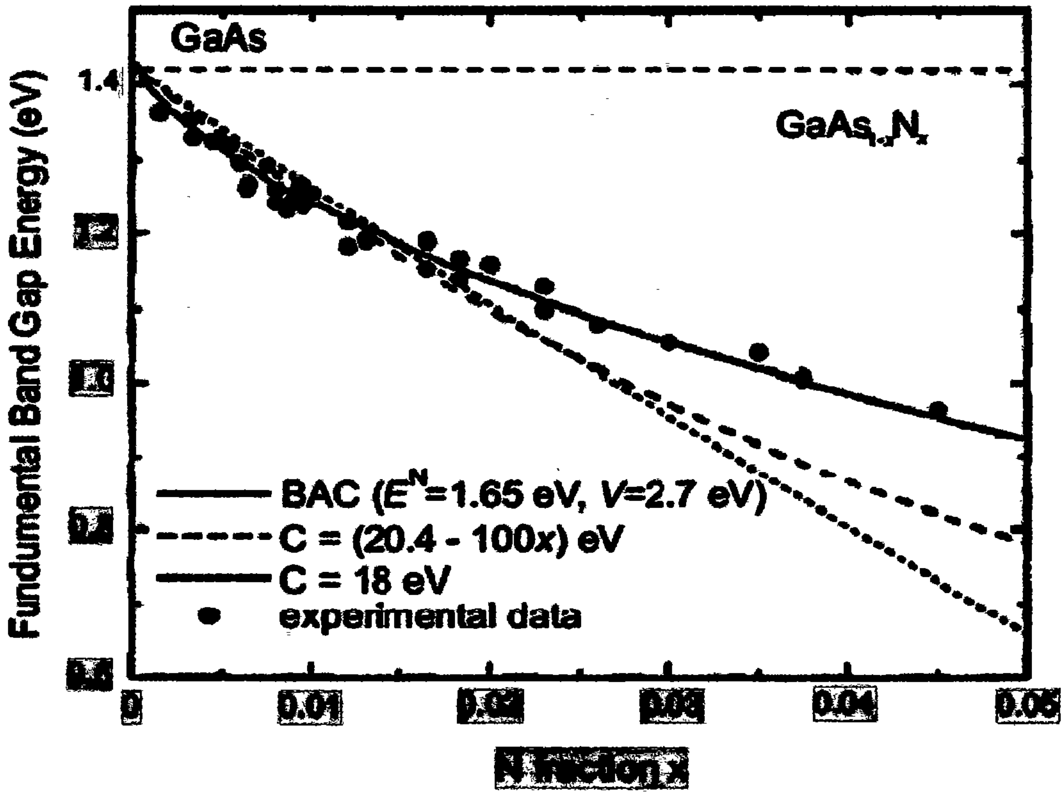


Figure 2.4 Metallic Character of GaAsN increases with increasing nitrogen [34].

One can expect dilute GaAsN to cover the visible and ultraviolet nitrogen. The band gap of GaAsN decreases approximately 180 meV per 1% nitrogen concentration increases.

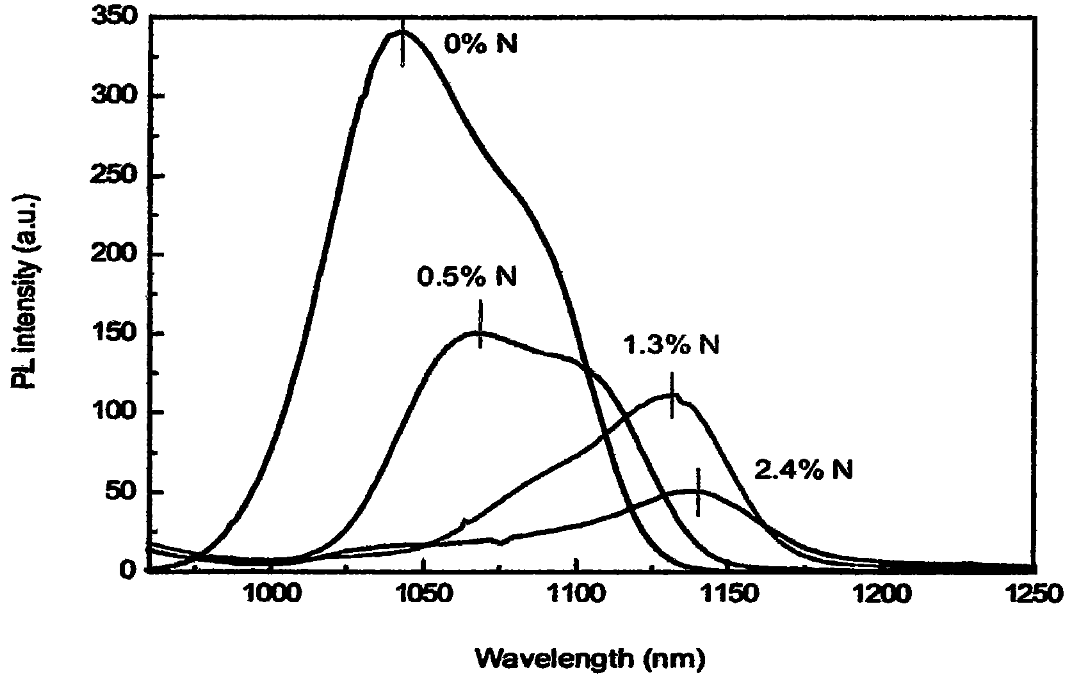


Figure 2.5 wavelengths as a function of % composition [34]

The increase in concentration of nitrogen leads the band gap towards metallic character because of reduction of band gap . In metals the size of atoms increases and due to increase of size the grip of nucleus on outer most electrons become weak. The electrons become free due to decrease in the coulomb interaction between nucleus and outermost electrons. The atoms are bonded due to free electrons and this bond is called metallic bond.

Reflectance, Transmittances and Absorbance

We can study the effect of nitrogen doping on transmittance, reflectance and on absorption coefficient as shown in Figure 2.3. From these graph we can observe that increase of film thickness increase the transmittance and shift towards higher wave length and attain its perfects shape at 500 nm. The increase in the transmittance was observed due to increase in the crystalline size.

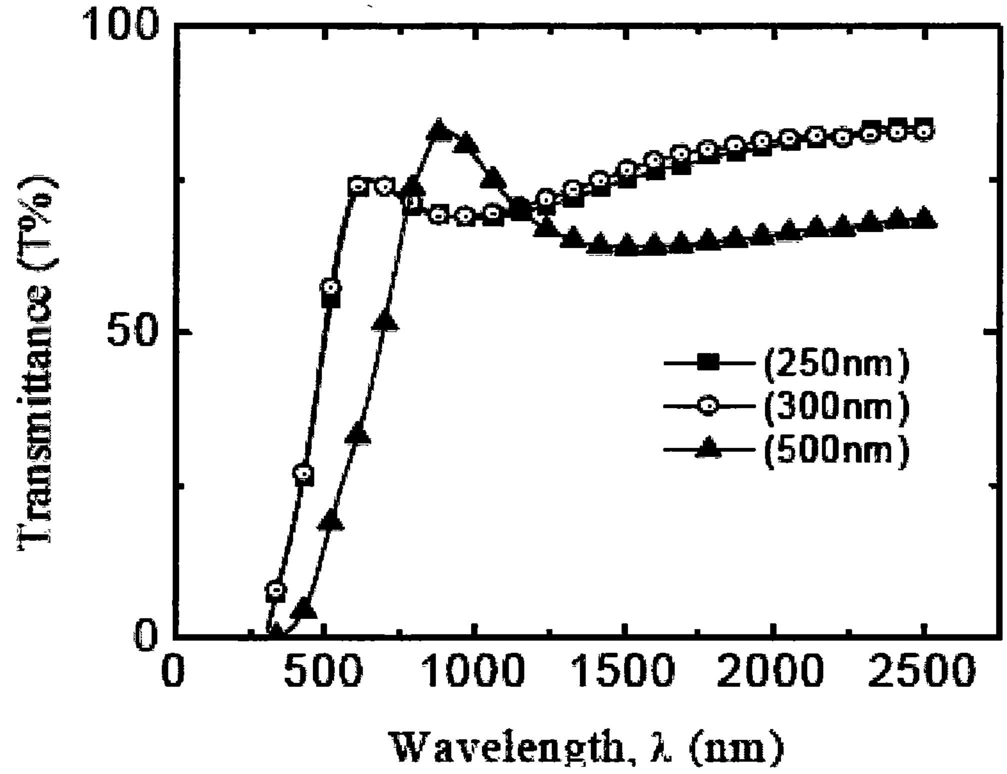


Figure 2.6 Graph between transmittance and wavelength [34]

Peak shifting due to Nitrogen and Zn

The shape and position of PL peak changed for the undoped and doped GaAs. The undoped GaAs peak was at 1.41eV. The Zn-doped p-GaAs film had a peak at 1.35eV and the Se-doped n-GaAs layer at 1.32eV. The red-shift effect of doping was attributed to band gap reduction and to residual strain from dopant incorporation. The widths of the peaks films at (0.125eV for n-GaAs and 0.085eV for p-GaAs) were also broader than for the undoped GaAs (0.061eV). Broader lines suggest higher densities of defects. [35,36]

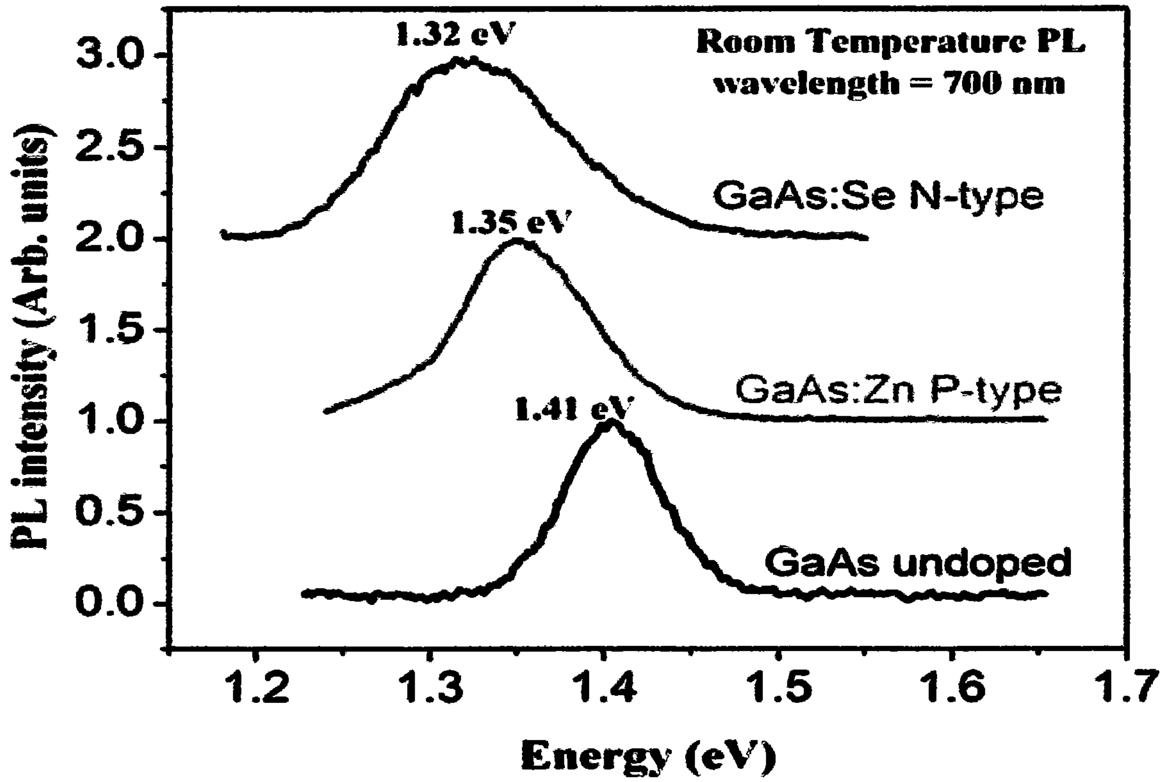


Figure 2.7 Room-temperature PL spectra of GaAs, doped with Zn- and Se [37]

2.3 Technique used to tune the band gap of GaAs

The process of nitriding was introduced in early of 20^{th} century [38, 39]. In those days NH_3 gas was used for nitriding, and the method is called ammonia or gas nitriding. At higher temperature NH_3 gas decomposes into hydrogen and nitrogen. The 2^{nd} type introduced in 1930, is called salt bath nitriding as the source of nitriding is in Salt form. The 3^{rd} technique introduced in 1932, is known as plasma discharge or plasma nitriding. In 1974, Edenhofer and Keller [40, 41] showed that plasma nitriding or plasma discharge nitriding is the batter than other type of nitriding. This type of nitriding has large advantages on gas and salt bath nitriding. The reason is that in plasma nitriding

- Small amount of energy is needed.
- No environmental effect.
- Short treatment time is required.
- The microstructure can be controlled.

2.4 Types of nitriding

Gas Nitriding.

The gas nitriding was developed in 20th century [42]. This is called gas nitriding because NH_3 gas is used as a donor. In order to avoid the damage, to keep the temperature of chamber at fixed level and to control the internal environment, a circulating fan is used. The material nature is such that it does not show any type of reaction with NH_3. To control the flow of gas, we used the flow meter. The temperature of internal part and sample was raised in range of 500 to 700°C. During the collision gas is heated and ammonia (NH_3) convert into hydrogen and nitrogen as indicated by reaction equation.

$$NH_3 \leftrightarrow N+3H \tag{2.2}$$

The nitrogen becomes source or donor for thin film deposition. [43,44].The rate of decomposition can be expressed as

$$\frac{\textit{Amount of decomposition}}{\textit{Total amount}} \times 100 \tag{2.3}$$

Advantages and disadvantages of gas nitriding

There are following advantages of this techniques

- Gas can be bombarded from all sides.
- It is a low cost method to provide hardness.
- This process can be control by computer application.
- The disadvantages are that samples cannot be treated from specific direction.
- We have to start the surface activation before treatment and experiment.
- It is dangerous because in the case of leakage of ammonia, the corrosive mixture is harmful.
- Also Ammonia gas is dangerous for environment.
- Due to oily or contaminated surface, the results will not well.
- The process takes a large time.

Salt Bath Nitriding.

In order to get uniform nitriding, another technique was developed in 1930 called salth bath nitriding. These methods removed the defects which were faced by gas nitriding. In this process the salt consisting cyanide salt etc, is used as a source of nitrogen. The salt percentage varies from 60% -70% for sodium salts and 30- 40% for potassium. Nitriding time is fixed from 3 to 48 hours at temperature 556°C. By adding Sulphur or by applies pressure, the salt bath process can be enhanced [45]. When salt is heated then it gives the nitrogen which deposit on the surface of samples. Safety precautions and ventilation (air flow) are necessary for your protection.

Advantages and disadvantages of salt bath nitriding.

- In this process, treatment time is very small as compared to other nitriding methods.
- To attain temperature, the sample and salt both are heated together.
- The salt is changed after 3 to 4 months because it gives the corrosion.
- Serious health hazards can take place because of leakage of cyanides.
- It has larger size and It is very difficult to operate .

Plasma based nitriding

Plasma nitriding which is also known as glow discharge nitriding is an industrial technique is used to make the metal surface hard. It provides the batter hardness and stability as compared to salt bath and gas nitriding. Plasma can be generated in vacuum chamber with the help of electrons cyclotron source, capacitive couple source, inductively couple source, radio frequency source and DC discharge sources. To nitride a gas on the surface of samples, first of all a gas is changed into plasma ions by intense electric field around the sample. The heater is used to heat the sample. The ions are accelerated towards the sample by applying the voltage. The striking nitrogen ions may diffuse inside the sample and thin film is formed. The parameters of treatment like time, pressure, voltage and temperature are important factors. Due to collision, the temperature of surface is raised. An external heater is used to increase the internal temperature. Argon gas is used for sputtering. The temperature range is 400 to 500°C. Generally the pressure variation is from 1 to 5 torr in the nitriding process. The mechanism of nitriding was not well known till 1965. S.M.Mohamed et al studied the RF discharge for nitriding in 2011 [46]. George and his co-worker introduced the Active screen cage plasma nitriding [47]. This technique has solved the problems of uniformity, corner effect and arching. This technique improves the surface hardness. It has no hollow cathodic effect. The voltage is applied at screen instead of direct application of load. Plasma strikes on the cage, which surround the base plate and sample. Sample may be biased or placed on floating potential. The screen heats the samples in small time by radiations.

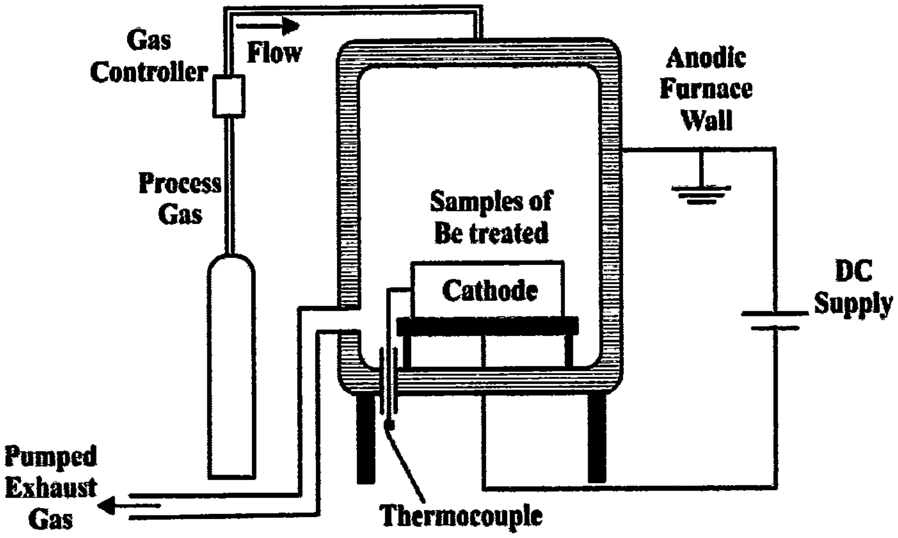


Figure 2.8 Active screen cage plasma nitriding systems

Advantages and disadvantages of plasma nitriding

- It controls the microstructure for the samples.
- Operate easily to increases the corrosion resistances, when nitrogen is diffused into the surface of sample.
- After plasma nitriding of metals, machines enhance their lifetime.
- Small treatment time
- Apparatus is very expensive and availability is rare.
- There is a limited temperature control in this process. Hollow cathodic effect is appear
- Without screen cage uniform nitriding is not possible.
- There is an arcing problem can be faced in plasma nitriding.

2.5 Plasma discharge and its mechanism

A dc glow discharge can be obtained by connecting the high DC voltage with electrodes at low pressure. Some electrons and ions are present due to weak ionization caused by cosmic back radiations. When DC voltage is applied across the electrodes then electrons and holes are moved towards anodes and cathode. These electrons collide with atoms of gas and due to elastic and inelastic collision the atoms of gas excite. When these atoms de-excite they emit electromagnetic radiations which is responsible for luminosity of plasma. Due to luminosity of plasma, it is called glow discharge. If we use the alternating voltage then the electrons oscillate between electrodes.

Important regions of plasma discharge

- **Aston dark region**

This region has very strong electric field. The electrons are in the process of gaining of energy. Due to small energy the electrons are not able to produce the ionization. This region has very small width and it is just in front of cathode.

- **Cathode glow**

This region is visible region because the electrons and positive ions combine and emit the radiation. In this region the electrons have not sufficient energy that they excite the atoms but due to recombination the region is visible. It depends upon the pressure and nature of gas and this region merged into Aston dark space

- **Cathode dark space**

In this region the density of electrons is very high. In this region the electrons are in the process of gaining the energy. They do not have sufficient for excitation or ionization

- **Negative glow**

The region next to the dark space is negative glow. In this region the electrons are accelerated and having sufficient energy that they can ionize and excite the atoms of gas.

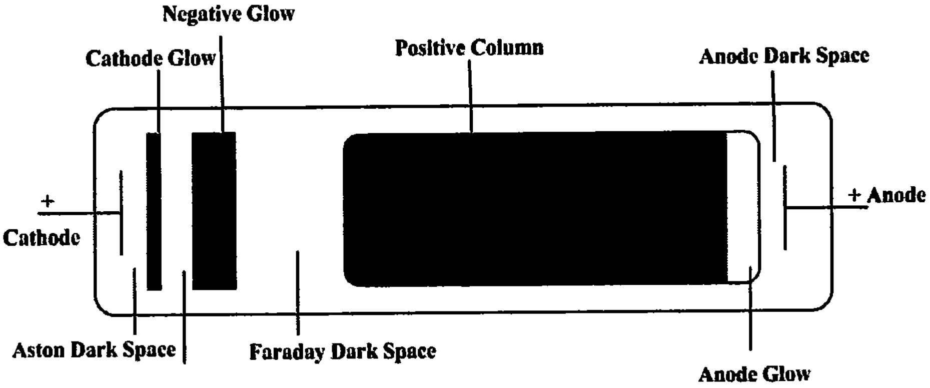


Figure 2.9 Region of Glow Discharge

- **Faraday dark space**

The region on right side of negative glow. The electrons have not enough kinetic energy to excite or ionize the atoms or molecules. Here the electrons are in the process of gaining the energy with small density.

- **Positive column**

In this region the plasma is in quasi neutral form along with electric field. The lengths of positive column increase as length between electrodes increases. Some electrons are capable of producing the ionization by gaining energy.

- **Anode glow**

This region is brighter than positive column. It is right side of positive column. In this region the electrons recombine with ions.

2.6 I-V characteristic curve of plasma glow discharge

When we apply the cathode and anode of gas filled tube then glow discharge take place as shown in the figure 1.5

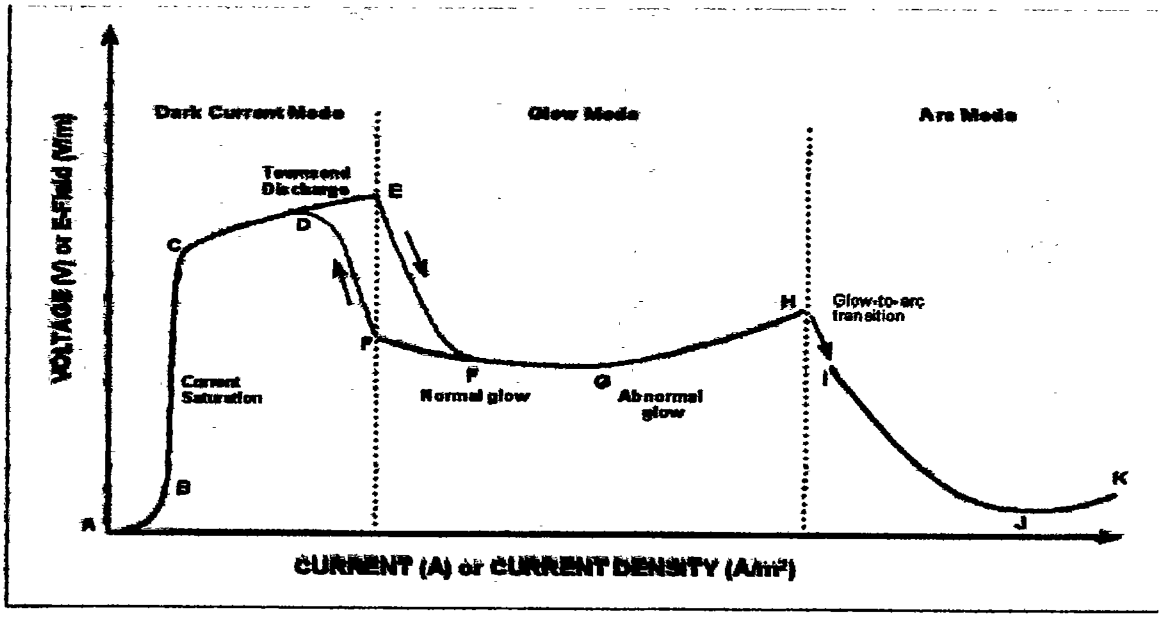


Figure 2.10 Plasma discharge curve

The current in through discharge depends upon the applied voltage. The voltage drop across electrodes varies with current. The change inside the discharge can be explained according by I-V curve. This curve has three main regions

- **Dark discharge**
- Glow discharge
- **Arc discharge**

- **Dark discharge**

The curve A-B shows the current due to back ground radiation. With increasing the voltage, current remains constant. It is shown by B-C portion. This region is called Townsend region. On further increasing the voltage the current increases the exponentially is represented by B-E.

- **Glow Discharge**

The glow discharge can divided into two parts. First part is represented by E-F which gives the information about drop of voltage. Beyond F, voltage becomes constant and called normal glow discharge. It is represented by E-G. The abnormal glow started after G point

Arc Discharge

In this region the breakdown of gas takes place. It is represented by H-J. Continuous bombardment of ions causes the emission of electrons and glow discharge jump into arc discharge.

RF discharge

RF can also be used for plasma discharge. The range of frequency in RF discharge is of range 1-100 MHz At high RF power from generator, causes noise in radio receiver. In order to solve this problem, a frequency range is 13.56 MHz

2.7 Active screen cage as a capacitive couple plasma source (CCP)

The active screen cage acts as a capacitively couple source to generate the plasma. The wall of the chamber acts as a anode and cage acts as a cathode. It is called capacitive plasma source because its geometrical shape is similar to the capacitor. Capacitor has two plates; one is negative and other positive.

Role of pulse DC method

In plasma nitriding, plasma discharge was produced by DC voltage. Due to continuous bombardment of ions on cathode, the temperature rises and apparatus can be destroyed. To avoid the heating problem, pulse option is preferred in plasma discharge.

Hollow cathodic effect and ASPN

In 2014, Mr.D.Cleugh and his coworker [48] showed that active screen cage plasma nitriding is more effective as compared to the DC plasma nitriding. They placed the active screen cage at floating potential. They observed that there are more molecules available for nitriding. Active screen cage is used as it has no pollution, small energy consumption; it has uniformity and no corner effect. In pulse discharge, due to distortion of field, the thin film thickness and surface hardness is non uniform. This problem was solved by using the active screen cage.

R. R. M. de Sousa et al[49] performed the experiment by using the active screen cage in 2002. They studied the shape of active screen cage like holes of cage, distance between samples and cathode, its material composition as well as composition of the nitriding for different gases. By DC plasma nitriding, hollow cathodic effect, non-uniform nitriding and arcing effects were observed. Li CX, Bell T et al [50] used the active screen cage technology to improve the durability of the life.

Role of Hydrogen in nitriding

Bejar *et al* [51] used the electro sparking process for coating of sample of aluminium. They used the composition of nitrogen and hydrogen. It was found that by mixing the hydrogen, the surface hardness can be improved.

Effect of distance between cage and samples and sputtering role

Zhao et al in 2006 showed that sputtering particles play vital role in the nitrogen deposition process. The sputtering absorbs the nitrogen atoms in non-uniform ways [52]. Nishimoto *et al* studied the ASPN [53]. The distance between sample and cage was changed from 10 mm to 50 mm. They showed that the hardness and distance has inverse relation. In 2010, effect of distance between screen and sample on active screen cage was studied by Akio et al. They showed that plasma nitriding has clean environment, has no pollution, has high nitrogen concentration, and parameter can be controlled by this method.

Parameters of Active screen cage

In 2007, Sh.Ahangrani and his coworker studied [54] the active screen cage technique in detail along its dimensional parameters. These parameters are time, temperature, types of mesh, holes size, distance between samples and anode. The treatment of nitrogen at at 550-580 °C was studied. The hardness and resistance was increasing by increasing the pressure, temperature, hole size and treatment time.

CHAPTER 3

EXPERIMENTAL SETUP

In this chapter the experimental setup for the plasma nitriding of the gallium arsenide (GaAs) samples is discussed. Plasma discharge, chamber setup and factors affecting the process of nitriding are discussed.

3.1 Plasma Nitriding

Plasma, a quasi neutral combination of charged and neutral particles exhibiting collective behaviour, can be produced by the application of energy to the gas molecules. It can be classified into two main regimes i.e. cold and hot plasmas based on the energies of the plasma constituents. Cold plasma can be generated in a variety of ways like DC discharges, RF generated, ICP, CCP and barrier discharges etc. In this experiment the nitrogen plasma required for the plasma nitriding is generated by the means of pulsed DC glow discharges coupled with active screen cage. The glow discharges produce energetic nitrogen ions, accelerated by the potential difference, which strike the surface of the sample with high energy making them capable of penetrating into the bulk. This in turn may fill the voids in the structure of the sample creating a hardened surface as well as may substitute some atom of the sample and may change various properties of the material. In this work efforts are carried out to produce and study the effect of the nitrogen plasma produced by active screen cage on the GaAs samples.

3.2 Plasma chamber

For this experimental work we use a cylindrical stainless steel chamber of 62.5 x 60.5 cm cross-sectional area as indicated in the schematics diagram presented in Figure 3.1. The chamber has 8 operational ports. One of the ports is used for pressure gauge while another one is connected with the vacuum system. One port is used to control the internal pressure by controlling the flow of gas while remaining ports are closed. There are eight windows in the chamber. One window is used to observe the plasma during experiment while two vertical windows are used for the biasing voltage and the sample as well as the screen cage placement. The bottom window is connected to the base plate which also serves as the housing of thermocouple and heater as well as the sample placement. Instead of placing the sample directly on the base plate it is insulted from it by placing the sample on a ceramic plate. The top window dwells a feed through for the cathodic biasing voltage of the active screen cage. The wall of chamber serves as anode.

Vacuum system

Plasma operation strongly depends upon the pressure as well as on the electrode spacing. Normally, in the laboratory plasma with the electrode spacing in centimetres the pressure of the operating gas has to be reduced from the standard room pressure. Along with this to avoid the impurities in the experiment the operational chamber has to be evacuated. To serve this purpose a vacuum system comprising of vacuum pump and the measuring gauges was required. A rotary vane pump is used to create the low pressure up to 10^{-2} mbar. To rough measurement of the gas pressure in the chamber a capsule type gauge having the pressure range of 0-25 mbar is used. For better measurement a pirani gauge is used. The vacuum pump as well as the gauges is given in Figure 3.2

Cooling system

As the experiment progresses the interaction of plasma species with the walls as well as the heat radiated from the plasma along with the elevation of sample temperature by means of a heater raises the temperature of the chamber. This raise in temperature may cause a problem for the vacuum as well as the plasma operation. To avoid this, chamber is wrapped with copper pipes having circulating chilled water. This keeps the temperature of the chamber at the required temperature thus helps in avoiding any temperature related anomalies that may happen during the experiment.

Valve

There are two types of valves connected to the chamber. In our experiment one of them is gas valve used to control the flow rate during experiment while other one is connected with chamber to control the pressure of chamber. This is connected with chamber and vacuum pump.

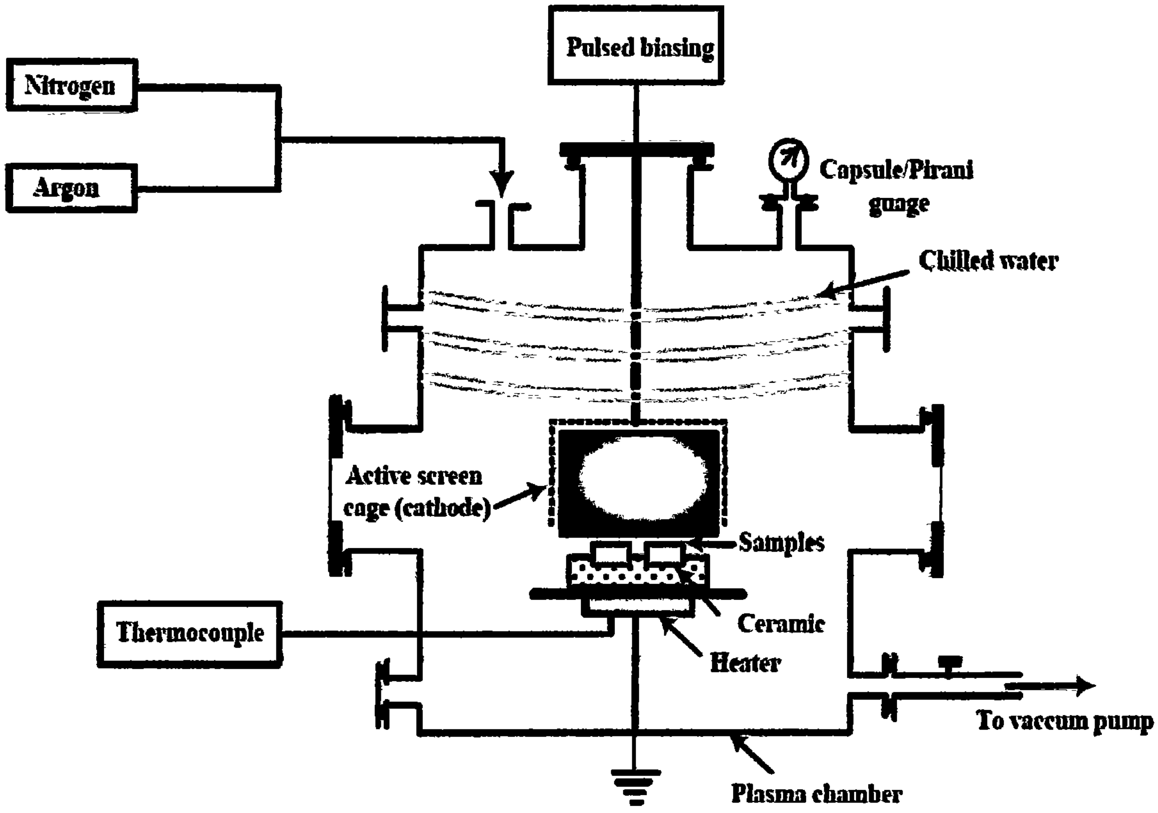


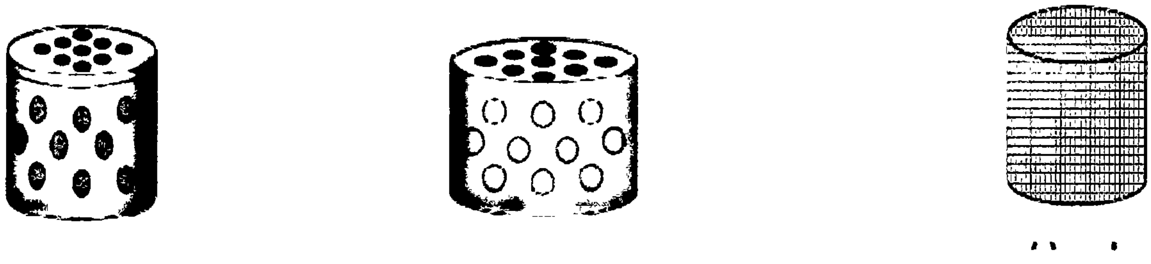
Figure 3.1 Label diagram of plasma chamber

Gas flow system

In our system argon and nitrogen are used for sputtering and nitriding respectively. But a better performance requires a proper control on the flow of gas into the system. This gas flow system has two parts; flow meter and transducer. The flow meter controls the transducer to provide the required mass flow of the gas to system. The gas flow system measures the flow in standard cubic centimetre (sccm) that is standard cubic centimetre.

Screen cage

Before screen cage technique, the components were subjected to the high cathodic potential to produce the plasma directly on the surface of sample, but that introduces non-uniformity in the thickness, microstructure and hardness of nitriding layers. Recently there has been considerable interest in active screen cage. The edging effect was completely removed because plasma is not produced directly on the surface of sample. Active screen cage of hollow cylindrical geometry with holes of 8mm diameter and with cage height of 18 cm while having cage diameter of 17 cm is used.The distance between sample and cage is kept at 5.5 cm.



(a) Pipe (b) Foil (c) Mesh

Figure 3.2 Diagram of Screen Cage of different types

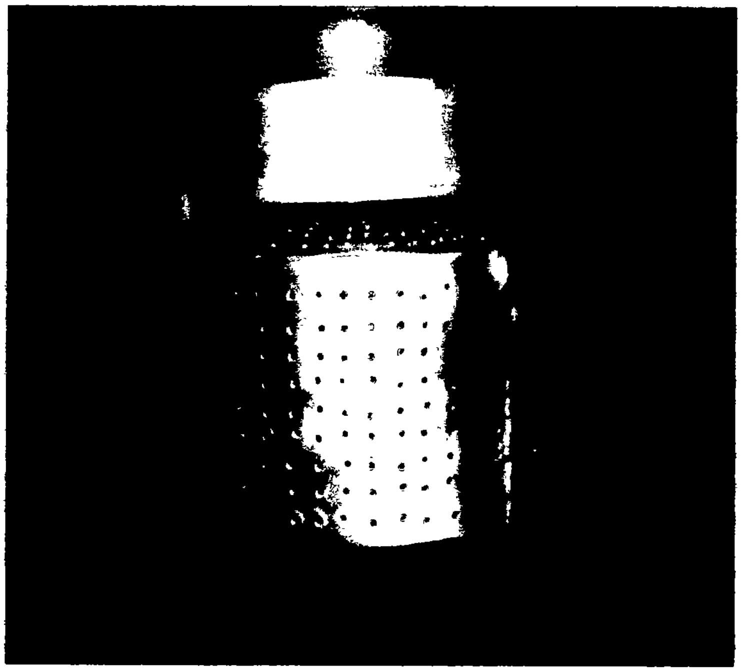


Figure 3.3 Screen Cage used for experiment

Power supply

To generate the plasma for experiment the pulsed AC source is used. The voltage is set at 950 V with the current of 0.8 A.

Process parameters

Various plasma nitriding parameters that effect the operation are:

(1) Treatment time.

(2) Gas flow system

(3) Temperature rise rate and cool down rate

(4) Chamber pressure.

(5) Biasing mode DC or pulsed DC.

(6) Type of cage, its holes size and its spacing with sample.

These parameters have already been studied for the production of active species in the plasma and have been optimized for the system.

3.3 Experiment

(i) Sample preparation

The wafer of GaAs is brittle and cannot be cut by ordinary methods therefore laser cutting was used to cut the wafer to the samples of the required size of 1 x 1 cm. Usually for the material processing the samples are further treated with various cleaning solution to remove the oxide layer and to bring the native pristine layer for the procedure. But the plasma nitriding process has a major advantage that no such cleaning mechanism is required for the procedure. The etching can be carried out in the evacuated chamber by the help of inert gases. This reduces the chances of impurity insertion which is otherwise present with the samples.

Figure 3.4 Plasma nitriding reactor at Quaid e Azam University

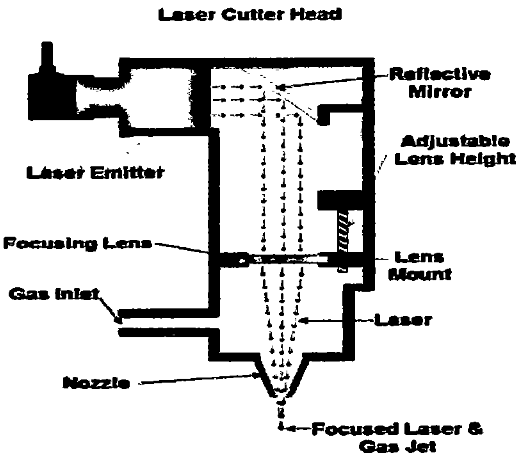


Figure 3.5 Diagram of laser cutter

(ii) Vacuum creation

After placing the sample at ceramic plate the vacuum is created inside the chamber upto 10^{-2} mbar which is necessary to remove the air inside the chamber.

(iii) Sputtering

The laser cut samples of GaAs have an inherited oxide layer on the top surface but for plasma nitriding pristine layer of GaAs on the samples is required. Therefore to remove the oxide layer argon plasma is used. The energetic species of argon plasma sputter the oxide layer from the sample upon impact. However to avoid the deep penetration of the species and to prevent the sample damage the power of the plasma source is kept a low level. The current was set at 0.8 ampere and voltage was kept at 250V. However during the etching process the samples are kept at steady 300°C to assist the de oxidation process. The time for the sputtering is about 30 minute.

(iv)Treatment with nitrogen and cool down

After sputtering process the argon source is switched off and nitrogen is allowed to enter in the system. The treatment time is varied at 30 min, 60 min, 90 min, and 130 min for different samples. After the treatment the system is allowed to naturally cool down to room temperature.

(v) Annealing in nitrogen atmosphere

During the treatment by nitrogen plasma, the plasma species strike the surface of wafer and penetrate deep into it. When positive ions interact with host atoms, due to electro-negativity difference and atomic size, the defects are generated which creates the zones of disorder. As the implanted ions increases, the amorphous layers start to appear due to destruction of the periodicity. After implantation, very high temperature is necessary to remove the lattice damage and for activation of doping ions. Therefore, the samples are annealed in furnace at 650^0C in nitrogen environment. Of course the complete damage recovery is not possible but the annealing process reduces the damages produce during implantation as well as activates the implanted ions.

Chapter 4

Characterization techniques

4.1 X-ray Diffraction

X-ray scattering technique is a common technique which gives information about crystal structure. It can also help in estimating the chemical compositions as well as to visualize the stresses generated in the system during the experimental procedure

This technique depends upon the observation of scattered intensity as a function of scattered angle, polarization and wave length.

Braggs Law

English Physicist Sir W.H.Bragg and his son Sir W.L.Bragg developed a relation given as,

$$2dsin\theta = n\lambda \tag{4.1}$$

where d is the distance between atomic layers in crystal θ is the angle of the scattered beam. λ is the wavelength. m is the diffraction order m=0, 1, 2, 3, 4...

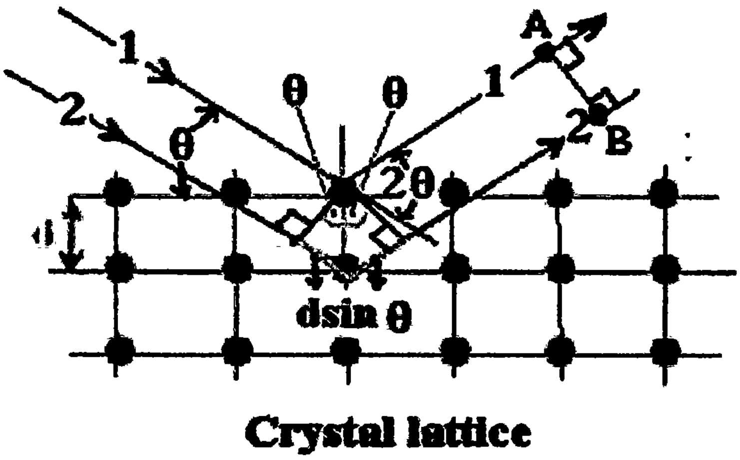


Figure 4.1 Two dimensional crystal lattice

Working of XRD

An XRD consist of an X-ray tube. X-ray detector and sample which is under investigation. The mono-chromatic radiation is obtained from K-radiation of pure metal target. These radiation passes through typical radiation filter has absorption edge between K_α and K_β .The K_β component is filtered without changing the intensity of K_α. When beam strike on the sample with angle θ and beam is diffracted such that the angle between the incident and diffracted beam is 2θ.The detector is attached to a computer. The range 10 -80° is enough to cover the useful part of spectrum. If the system scans with speed of 2° per minute, a trace can be obtained in approximately 30 minutes. Figure 4.1 represents a typical XRD spectrum indicating the miller indices. Cyrstallite size can also be measured from the peaks of the XRD pattern by using scherrer formula given as

$$\tau = \frac{K\lambda}{\beta\cos\theta}$$

Where K is constant K is a dimensionless shape factor, with a value close to unity, λ is the wavelength

And β is the line broadening at half the of full width half maximum (FWHM).

4.2 Diffused Reflectance Spectroscopy

Diffused reflectance spectroscopy (DRS) is a method that measures the reflectance spectrum when light passes through a medium. The mechanism is absorbance and scattering which change with wavelength and produce the reflectance. This spectrum gives information about reflectance, absorbance and transmittance in visible, infrared and ultraviolet region which helps in calculating the various optical coefficient of material. By Kubelka Munk function and by Tauc plot we can calculate the band gap of semiconductors.

Reflectance, transmittance and absorbance

Reflectance is the amount of flux that reflected by the surface normalized by the amount of flux incident upon it. Transmittance is the amount of flux transmitted by the surface normalized by the amount of flux incident upon it. Any flux that is not reflected or transmitted is absorbed. By conservation required that,

$R + T + A = 1$

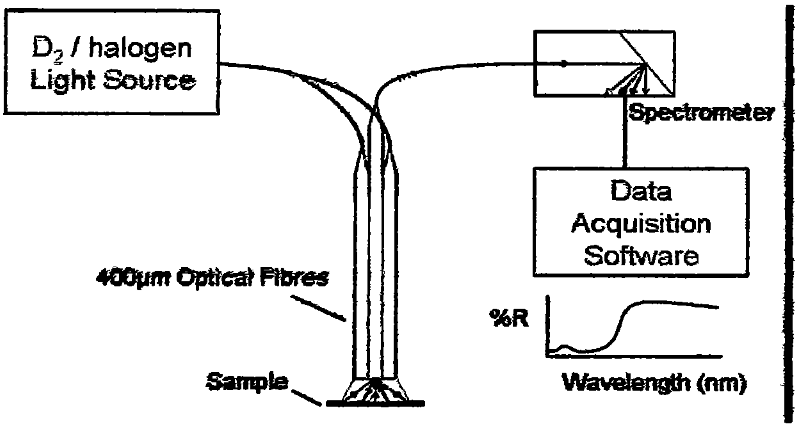


Figure 4.2 Diffused reflectance spectroscopy

Visible, Infrared and ultraviolet

Infrared region is a type of electro-magnetic waves covers the range of wavelength from 1mm to 750 nm. This can be detected into three parts, Far infra-red, mid infra-red and near infrared region. Though there are different types of radiations. Gamma rays, x-rays, ultraviolet, visible radiations, visible radiations, infrared red, microwaves and radio waves.

4.3 Rutherford Back Scattering

Rutherford backscattering (RBS) spectroscopy is the ion beam analyses which are used to find the information about composition of target material and depth profile.

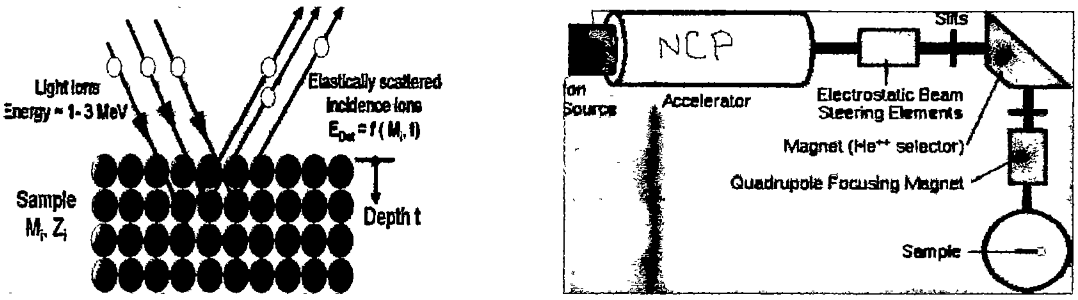
Instrumentation

Rutherford instrumentation consists of the following parts.

- Ions source known as alpha source or protons.
- Linear particle accelerator which accelerate the particles to high energy.
- A detector which measure the energy of scattered particles

Basic Principles:

Rutherford back scattering is an elastic collision between incident particles and stationary particles as given in Figure 4.4 .The detector converts the detection into current signals. This energy is directly proportional to current signals. In this collision no energy is loss or gained



Rutherford back scattering **Rutherford back scattering experiment**

Figure 4.3 RBS

Kinetic Factor

For an incident beam with energy E_0 and scattered beam with energy E_1, the ratio of these energies is called Kinematic factor.

$$K = \frac{E1}{Eo} = \left[\frac{(M12 - M12\sin\theta^2)1/2 \ +M1\cos\theta}{M1+M2}\right]^2 \qquad 4.2$$

Where M_1= mass of projected ions.

M_2 = mass of target material.

and θ is the back scattering angle.If E_0, E_1, M_1 and θ and known then we can find the mass of investigated materials. The Energy of back scattered ions from the surface of the materials is greater than the energy of ions scattered inside of the materials. The ions may lose the energy before the detector. First during penetration into material, second in coming out from material after collision with atoms.

$$\Delta Es = (1-k)Ex \qquad \text{Kinematic loss}$$

$$\Delta Ein = \left(\frac{dE}{dx}\right).\Delta x \qquad \text{Loss during penetration}$$

$$\Delta E_{out} = \left(\frac{dE}{dx}\right)_{out}.\ \frac{\Delta x}{\cos\theta} \qquad \text{Loss during coming}$$

The detected energy is

$$\cong \quad K.E_o - [\left(\frac{dE}{dx}\right) - K + \left(\frac{dE}{dx}\right) out.\frac{1}{\cos\theta}$$

Advantages

- R.B.S is used to find the compositional analysis of the samples without destruction .It is used to measure the impurity distribution.
- It is used to measure the thickness of thin film.
- It is also used to study the nature and composition of interfaces.

4.4 FOURIER TRANSFORM INFRARED SPECTROSCOPY

This technique is used to get the infrared spectrum for emission, reflection and transmit ion of light through a material at a specific wavelength. This technique is called FTIR to honor J.B.J Fourier. He had applied this technique by using the Fourier transformation .According to this technique the raw data is converted into spectroscopic form by using Fourier transformation. The goal of these techniques is that how a material reflects, absorb and transmit the light at a particular wavelength region. The apparatus is shown in Figure 4.4

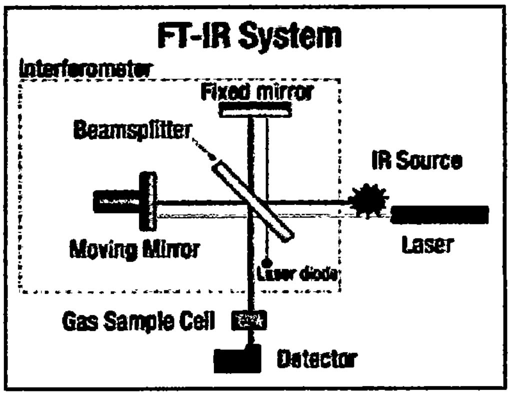


Figure 4.4 FTIR apparatus

First of all a signal called interferogram is generated by spectrometer. This interferogram is a record of signal or intensity which is a function of path difference. This signal is subjected to transformation that give the spectrum .This spectrum depends upon the frequency.

$$\int_{-\infty}^{\infty} I(x)e^{i2vx\pi}dx \quad = F^{-1}i(x) \quad = S(v) \qquad 4.3$$

Where $$I(x) = \int_{-\infty}^{\infty} S(v)e^{-2ixv\pi}dv = F[S(v)] \qquad 4.4$$

Chapter 5

Results and discussion

5.1 X-ray Diffraction

The structural information of untreated and treated samples is shown in the 5.1 and 5.2 The XRD data was obtained from NCP. The XRD parameters have been used as given

Source:	CuK_α and Ni filter
Wavelength:	1.54 Å
2θ range:	30° to 70°

Table 5. 1 samples with increasing the treatment times

Sr.No	**Sample Name**	**Treatment time (minutes) Before annealing**	**Treatment timing (minutes) After annealing**
1	Sample A	untreated	No
2	Sample B	30 minutes	30 minutes
3	Sample C	60 minutes	60 minutes
4	Sample D	90 minutes	90 minutes
5	Sample E	130 minutes	130 minutes

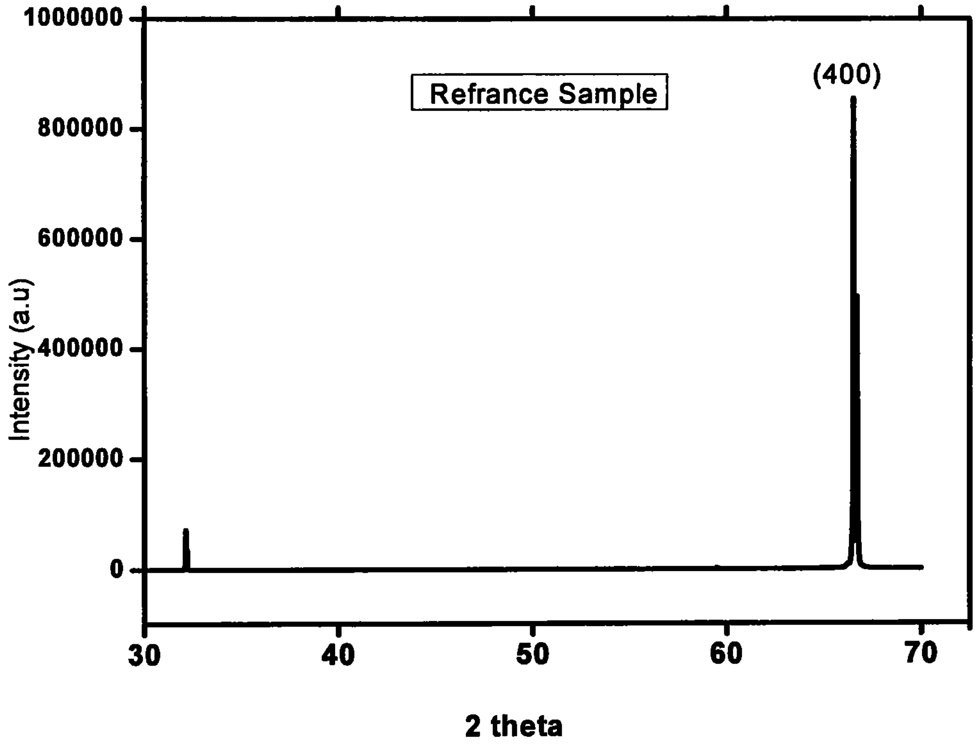


Figure 5.1 XRD pattern for Sample A

The XRD graphs gives information about grain size and crystal structure. The peak at 66.36 are corresponds to the GaAs. The corresponding miller indices are (400). The samples nitrogen-treated for E shows that the broadness of peaks increases. The broadening of peaks after nitridation indicates that crystal defects have been increases. The atoms rearrange after annealing and broadness increases. In other words crystal damage caused by nitridation has been recorded. The intensity level for 130 min is decreases because of defects. XRD pattern shows that synthesized material are of cubic structure; lattice parameters for cubic structure are calculated by using the following relation

$$a = d\sqrt{l^2 + k^2 + h^2} \qquad 5.1$$

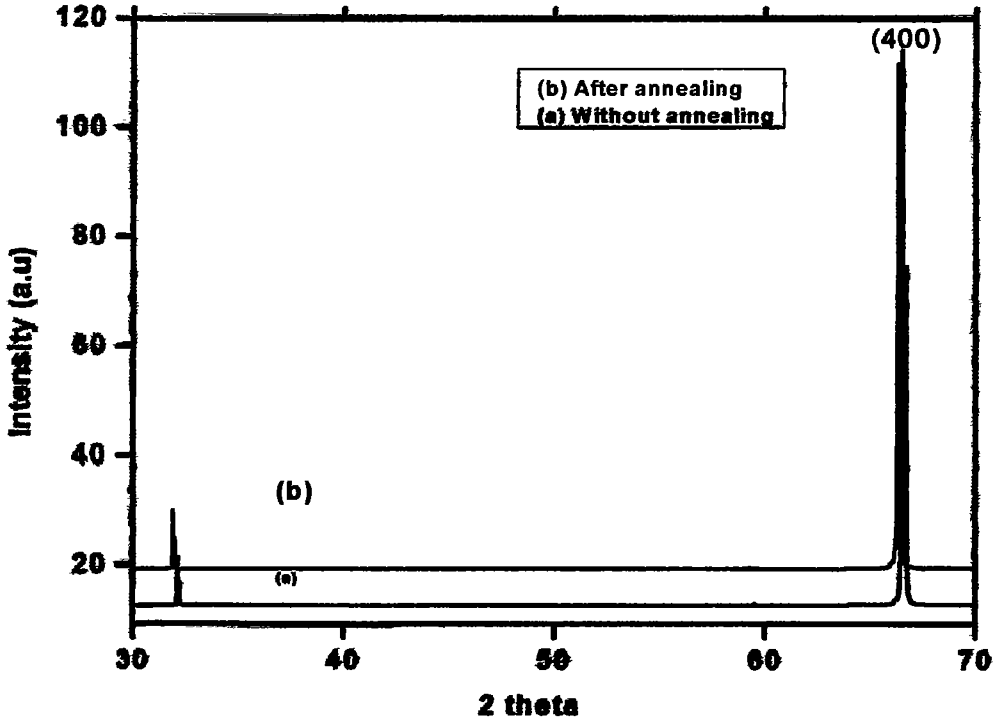


Figure 5.2 XRD pattern for Sample B

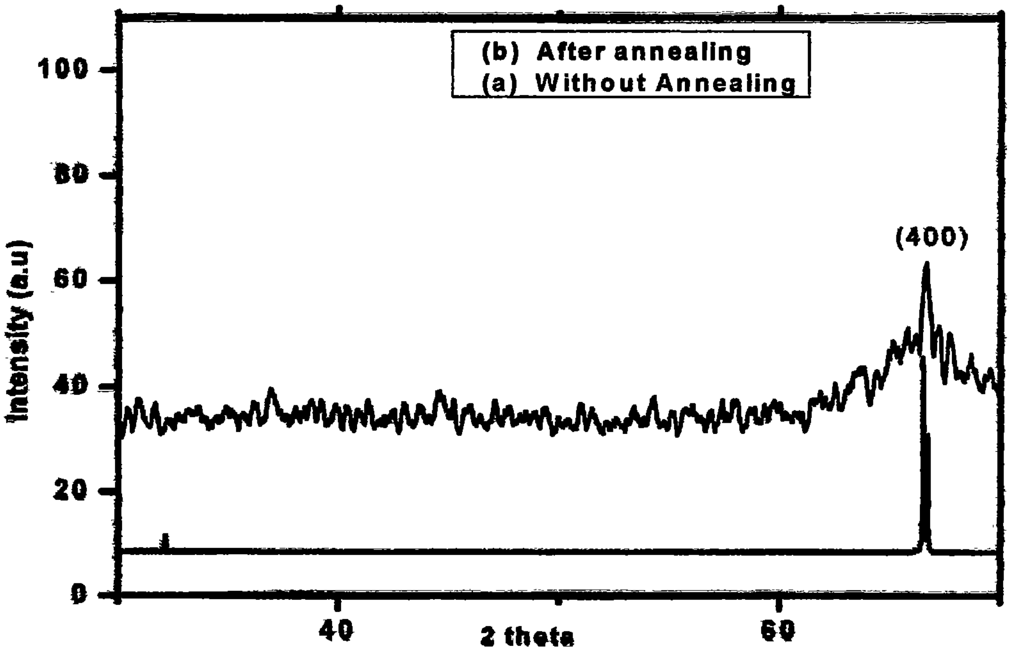


Figure 5.3 XRD pattern for Sample

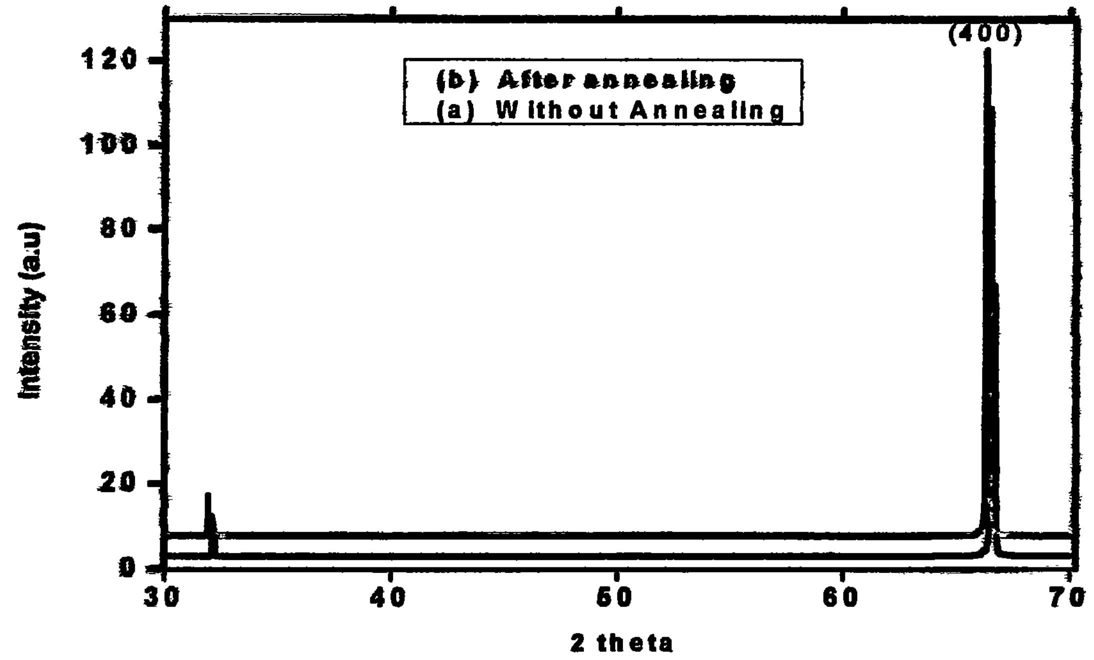


Figure 5.4 XRD pattern for Sample D

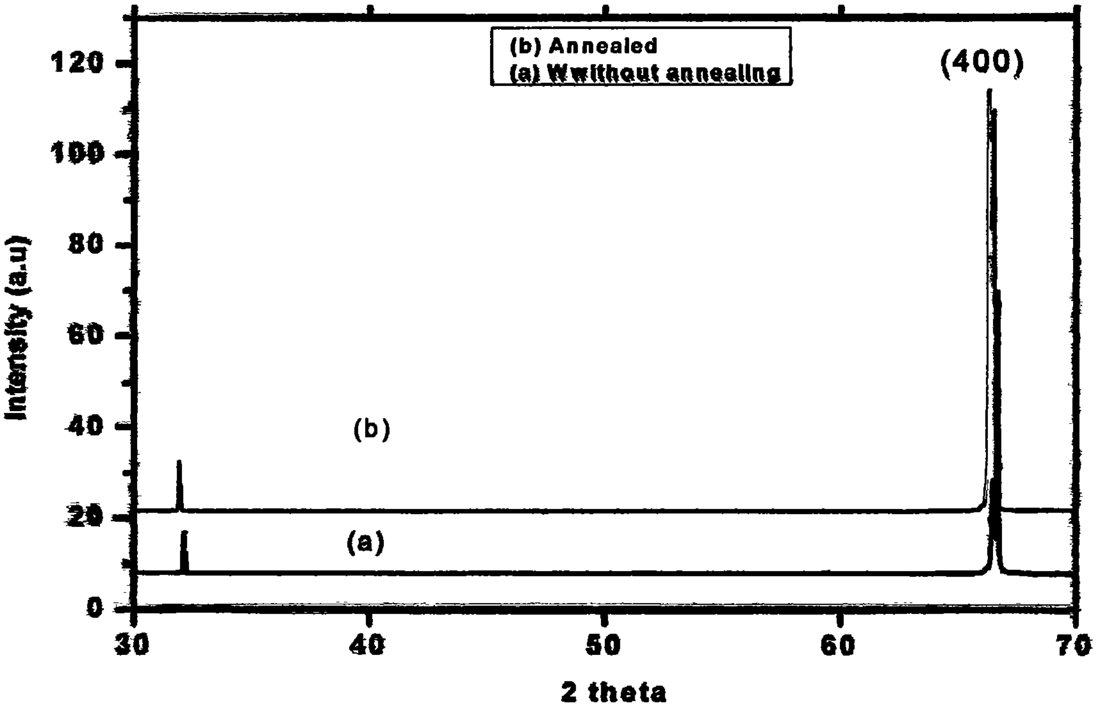


Figure 5.5 XRD pattern for Sample E

5.2 Table for XRD table before and after annealing

Sr.No	**Samples names**	**Time (min)**	**Angle (θ)**	**Miller indices (h,k,l)**	**d-spacing (Å)**	**Lattice constant (A°)**
1	A	Untreated	66.363	400	1.4069	5.627
2	B	30 (treated without annealed)	66.363	400	1.4069	5.627
3	B	30 Annealed	66.448	400	1.4069	5.627
4	C	60 (treated without annealed)	66.363	400	1.4069	5.627
5	D	90	66.420	400	1.4058	5.623
6	E	130 (treated and annealed)	66.24	400	1.4058	5.623

From XRD Table it is cleared that phase shifting take place. Phase shifting is due to decrease in lattice constant. Phase shifting has inverse relation with lattice constant. If phase increases then lattice constant decreases. It is also cleared from the the table that sample without annealing has no phase shift. Phase shifting take place after annealing.

5.2 Rutherford Backscattering Studies

Rutherford back scattering (RBS) is an excellent surface analysis technique which is used to determine the thickness of film, composition and depth profile.RBS has been performed at National Centre for Physics (NCP).The parameters used for RBS are

Ion beam	4He^{++}
Beam energy	0.3-2 MeV
Beam diameter	2 mm
Beam Current	100 nA/cm^{-2}
Detection	Silicon detector

Percentage composition and depth

The percentage composition is given in the table 5.3. The graphs are shown in Figure 5.2. The samples are treated for 30 min, 60 min, 90 min, and 130 min. From the table we can observe that nitrogen composition increases with time. The maximum nitrogen is observed for 130 min. The results confirm that nitrogen penetrate up to 89 nm .The depth changes considerably from 30 min to 130 min. Similarly nitrogen percentage is varies. From the table it is clear that As percentage decreases and nitrogen percentage increases

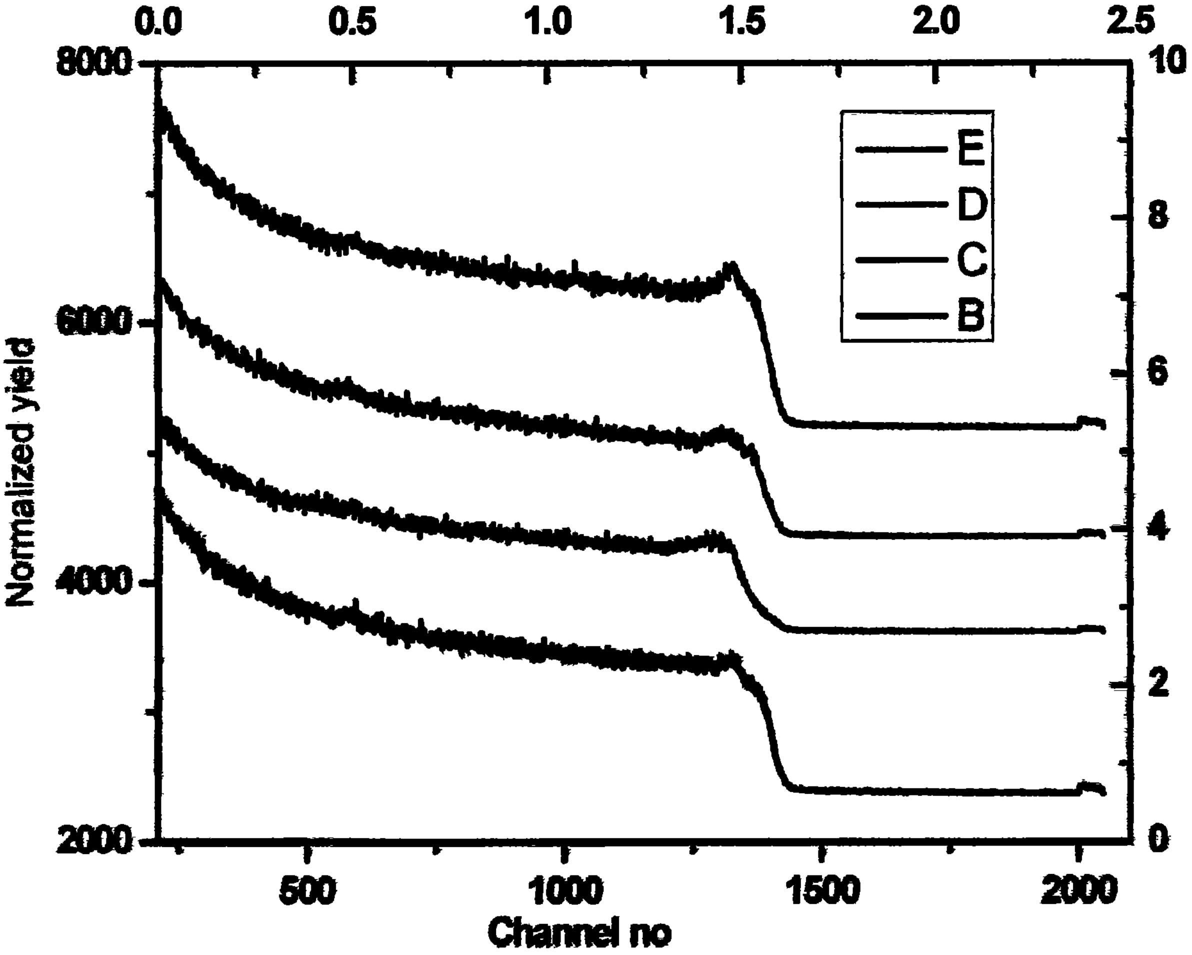


Figure 5.6 RBS pattern for all samples

Table 5.3 RBS percentage composition and depth

Sr. No	Samples Names	Treatment timing (minutes)	Depth (nm)	composition%		
				Ga	As	N
1	A	R	----	--	--	--
2	B	30	72	41	42	17
3	C	60	80	39	39	22
4	D	90	81	37	36	27
5	E	130	98	38	39	23

Surface of sample is started from the position of 1500 of channel. The width of channel is equal to the thickness of of layers of sample. The energy along x- axis shows the back scattering energy .The energy increases as atomic masses is increased. The nitrogen has low atomic mass as compared to Ga and As, therefore back scattering energy of nitrogen is low as compared to Ga and As. The implantation ions give the surface damage near the surface because the normalize yield decreases. A hump is appearing near the surface which gives the information about surface damage and peaks on right side. Yield is the back scattered alpha particles. It increases because of increase of nitrogen atoms in cubic structure.

5.3 Diffused Reflectance Spectroscopy

Diffused reflectance spectroscopy (DRS) is a technique that measure the reflectance spectrum when light passes through a medium. It is common optical phenomenon used in (NIR) near infrared, middle infrared and in visible region. It is used to get the molecular spectroscopic information. A reflection spectrum is obtained after the reflection of electromagnetic radiations from the surface of sample which is function of wavelength. In this spectrum we discuss the three important regions. By using DRS spectra we have find out the band gap of GaAs, and

GaAsN. By using Kubelka-Munk function we have find out the band gap in three regions. First regions are related to GaAs, second region is for GaN.

Calculation of Band Gap Using Tauc Plot

- Tauc plot is a method that is widely used to calculate the band gap. Shown next is the procedure for determination of band gap from DRS using Tauc plot. Following relation is used

$$(h\nu\alpha)^{1/n} = A(h\nu - E_g) \qquad 5.2$$

The value of exponent n denotes the nature of sample transition. Where h is planks constant ν is the frequency α is the absorption coefficient E_g is the band gap and A is the proportional constant. For direct allowed transition n =1/2 for indirect transition the value is n = 2

The Kubelka Munk function is

$$F(R) = \frac{(1-R)^2}{2R} \qquad 5.3$$

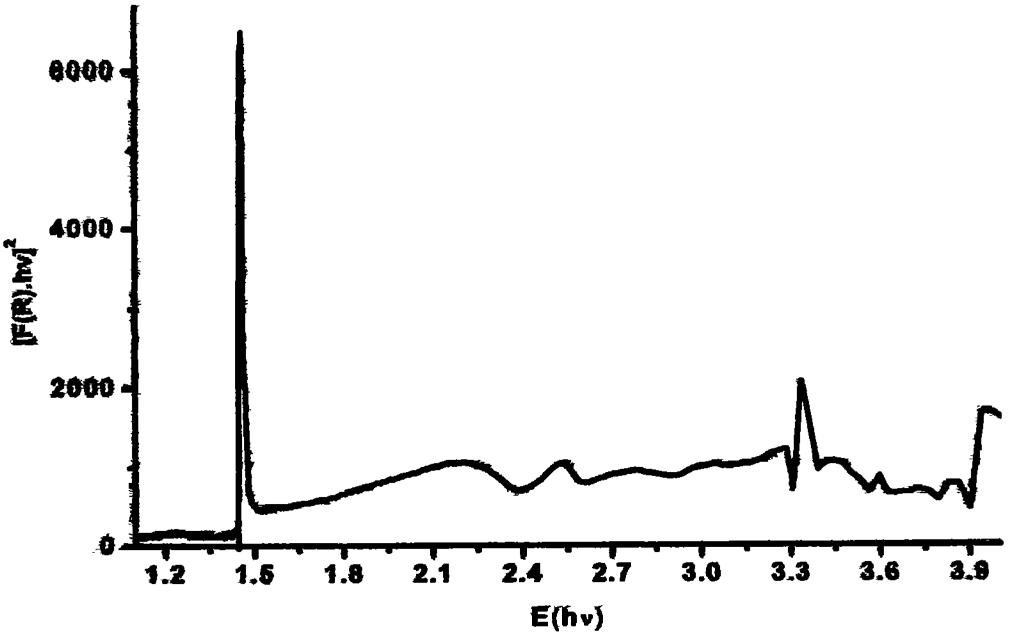


Figure 5.7 Band gap for sample A

Where R is reflectance and F(R) is called Munk function or absorption coefficient.

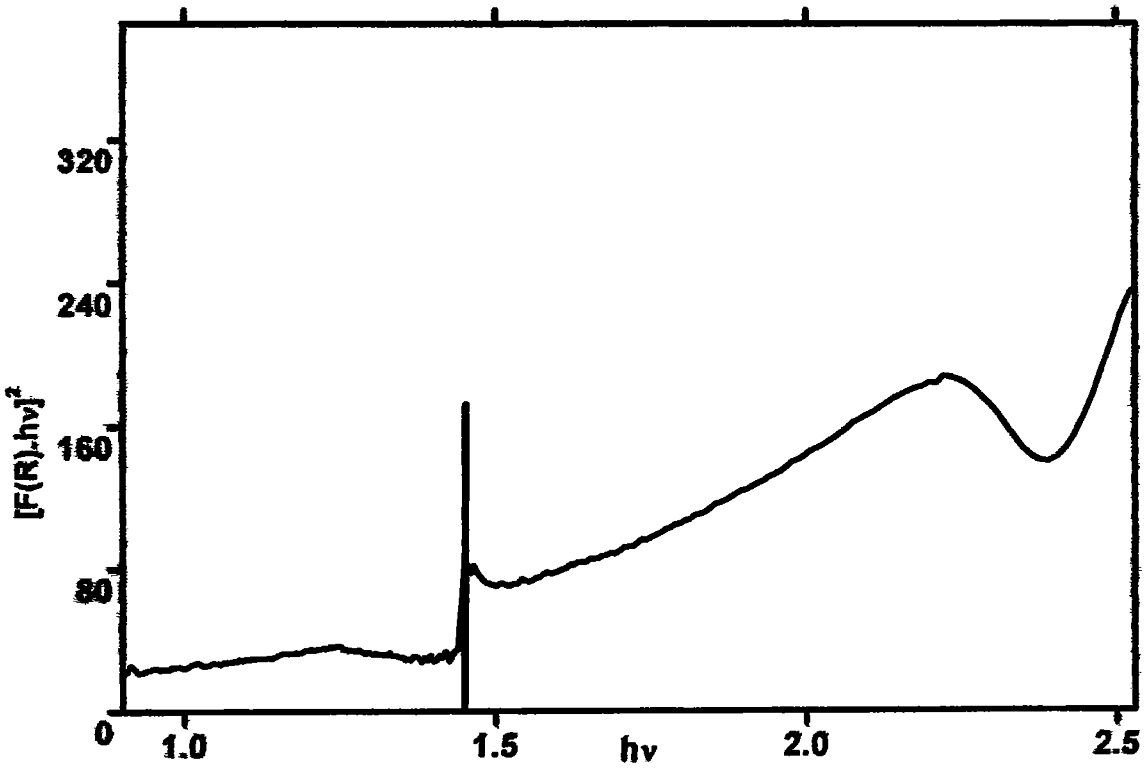


Figure (a) 5.7 Band gap for direct transition for Sample B

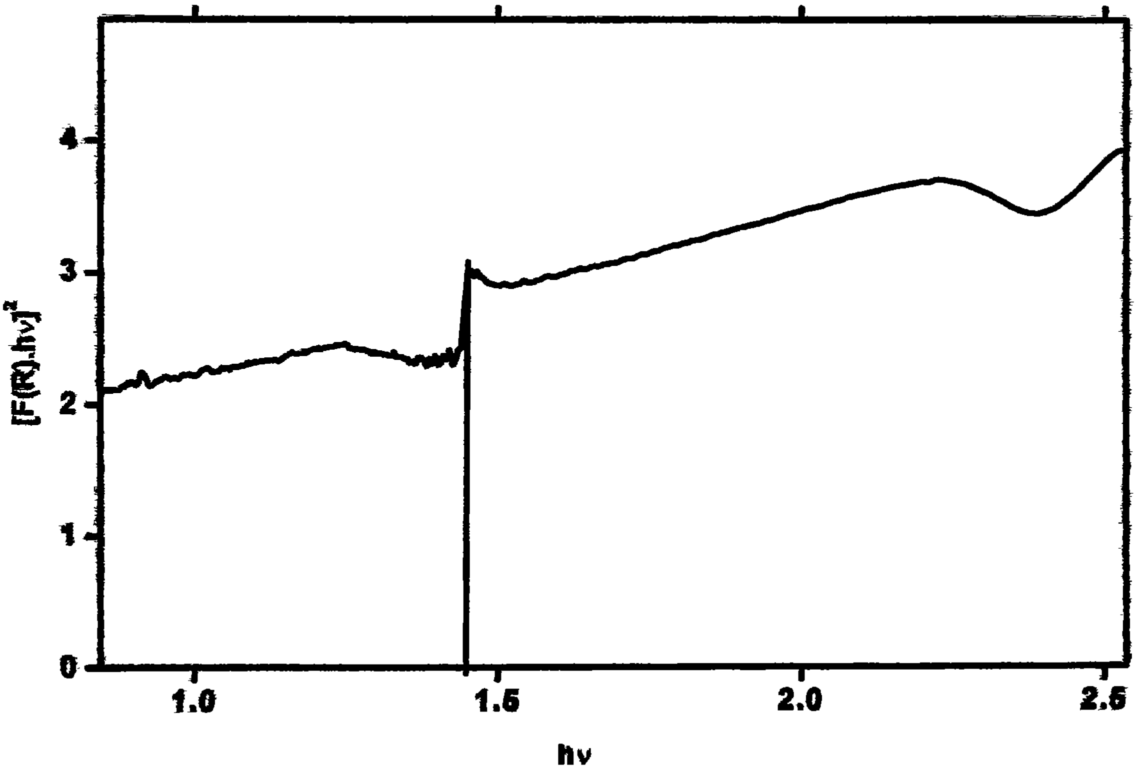


Figure 5.7 (b) Band gap for indirect transition for Sample B

- The acquired diffused reflectance spectrum is converted into Kubelka-Munk function. Thus vertical axis is converted into F(R)
- Using Kubelka Munk function [E.hν]^2 is calculated and plotted on y-axis against hν
- A line is drawn tangent to the point of inflection. (The point of inflection is the point where first derivative or slope increases or decreases). The tangent meets on x axis and gives the value of band gap

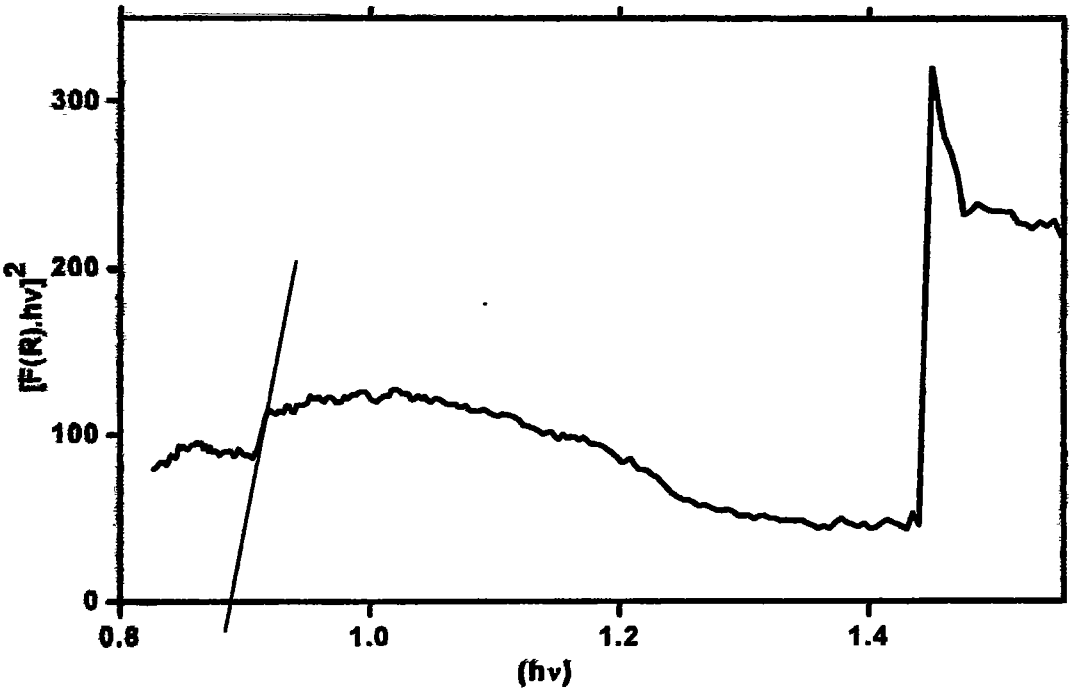


Figure 5.8 (a) Band gap for direct transition for sample C

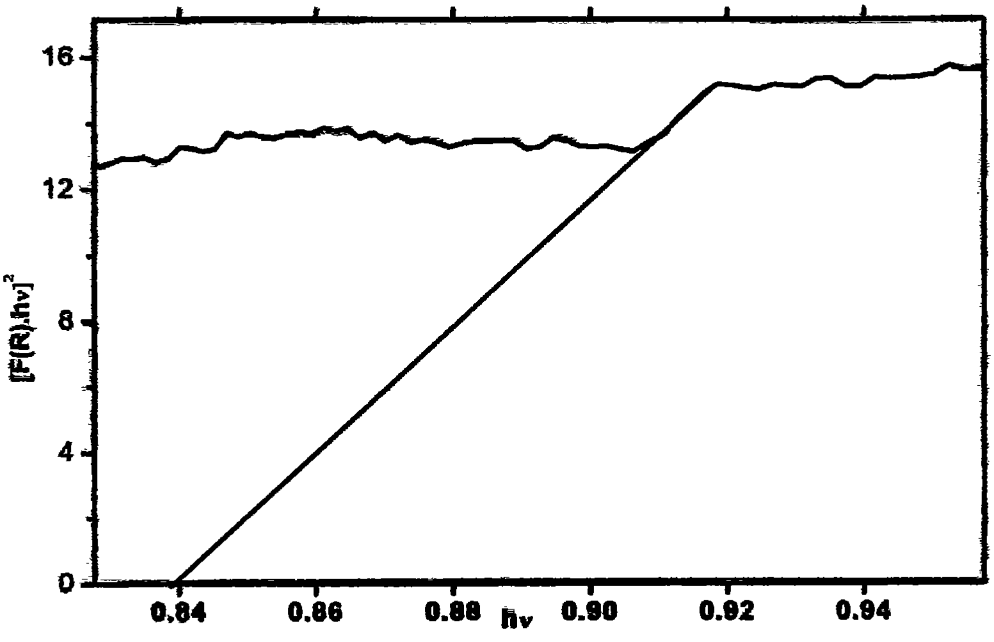


Figure 5.8 (b) Band gap for indirect transition for sample C

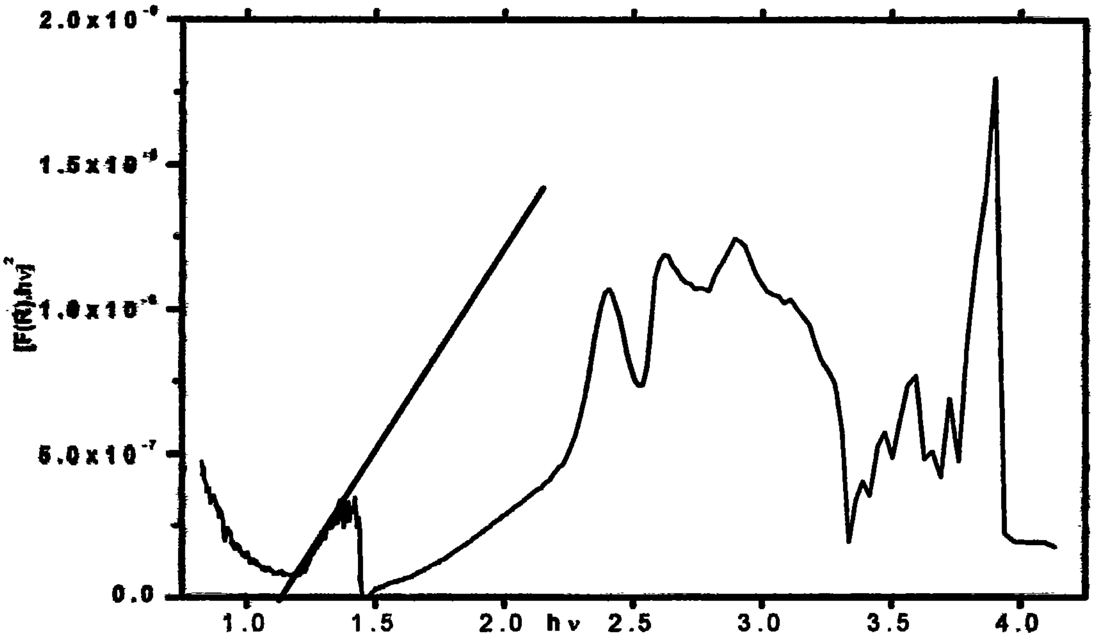


Figure 5.9 (a) Band gap for direct transition for sample D

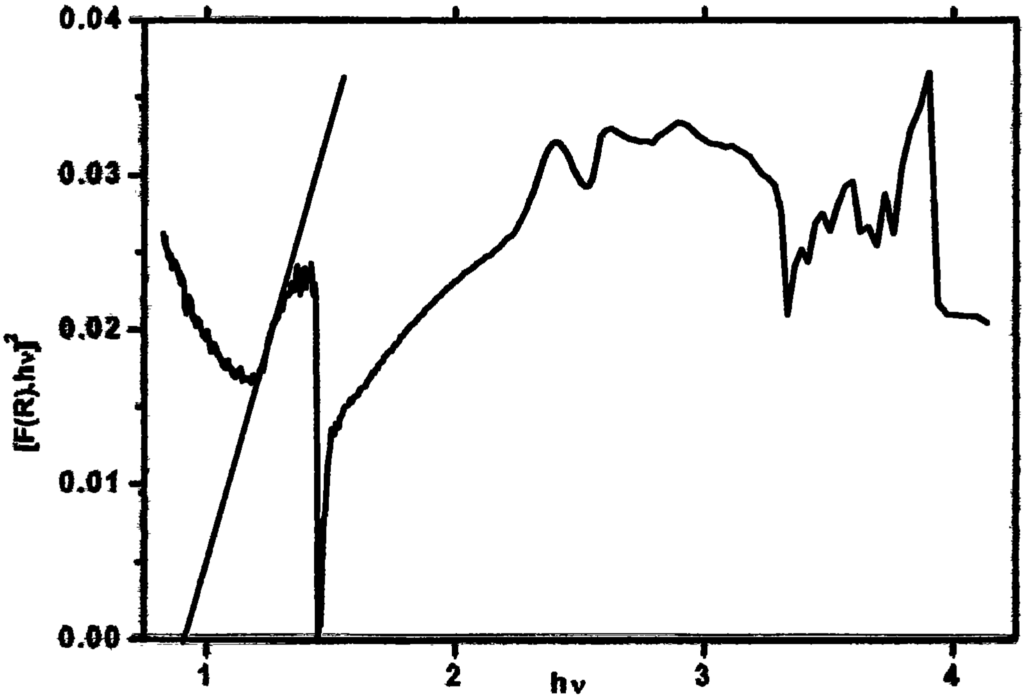


Figure 5.9 (b) Band gaps for indirect transition for sample D

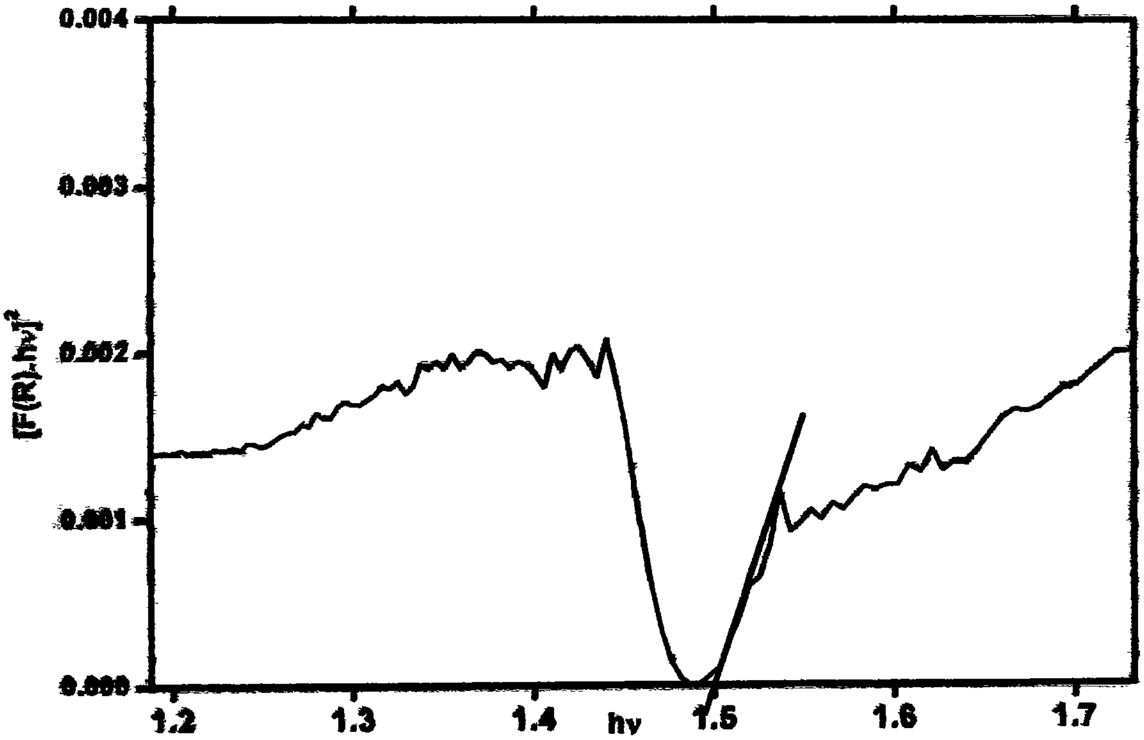


Figure 5.10 (a) Band gap for direct transition for sample E

For addition of dilute nitrogen, the energy states in deep valence bands contribute in reduction of band gap, that's why the theory of the $GaAs_{1-x}N_x$ alloy focus on the conduction band. But higher addition of nitrogen causes the disappearance of energy states from the maxima of valence band of GaAs and responsible that band gap increase. The increase in concentration of nitrogen leads the band gap towards metallic character because of reduction of band gap. The band gap of GaAsN fluctuates as a function of Nitrogen percentage. The band gap of GaAsN is less than 1.42 eV. From graphs it is cleared that band gap deduces when flow is for small time.for small time but increases when nitrogen flowed for long time.

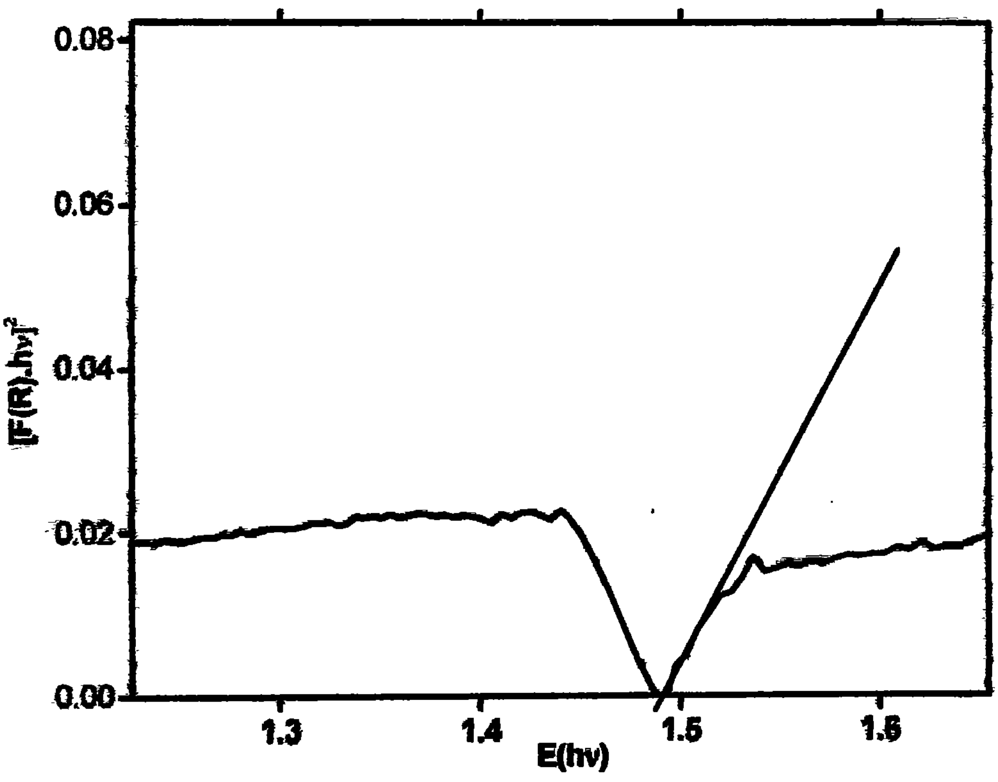


Figure 5.10 (b) Band gap for indirect transition for sample E

5.4 Fourier spectroscopy

The Fourier transformation infrared transformation measurement of nitrogen implanted GaAs have been carried out for studying the nitrogen. The nitrogen is determined by strength of vibration mode at 471 cm^{-1}.The The LVM at wave number at 529 cm^{-1} shift and overlaps. The shifting of mode is due to implantation of nitrogen. Similarly area under the band also changes. The shifting of peaks and width of band is also due to nitrogen isotopes. N^{14} increase the band whereas N^{15} decreases the band. Monitoring the LVM at 471 cm^{-1} is an efficient tool for assess the incorporation of nitrogen in GaAs. The vibration mode recorded at 668 cm^{-1} wave number is due to carbon dioxide. From graphs it is cleared that peaks shifts. The shifting of vibrational modes is due to change in bond length. The nitrogen is more electronegative as compared to Ga and As.

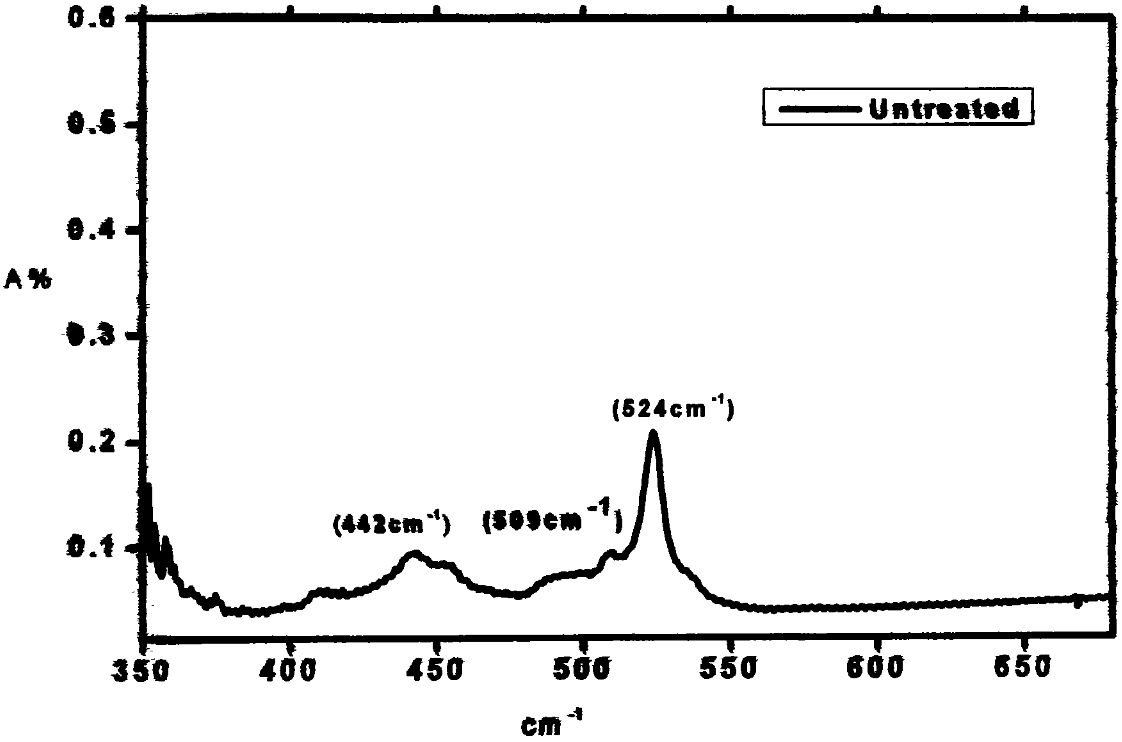


Figure 5.11 FTIR for Sample A Untreated

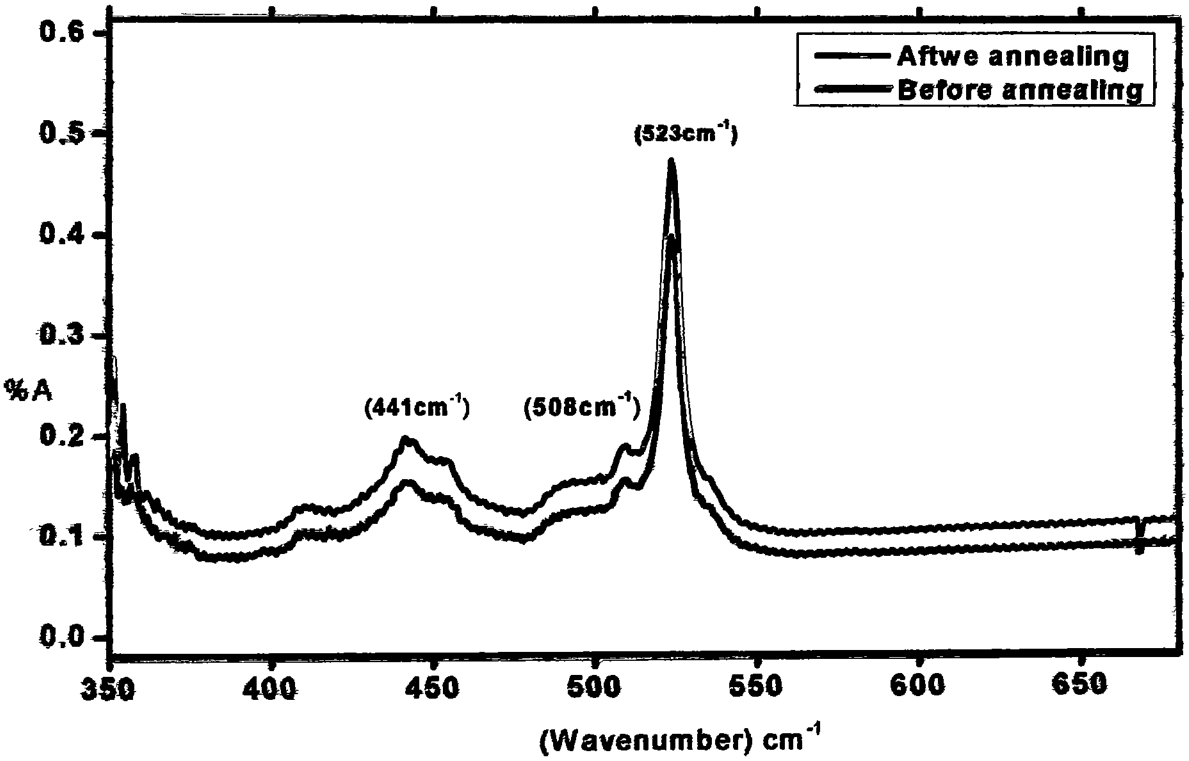


Figure 5.12 Sample B FTIR before and after annealing

Due to high electro negativity the bond length changes. The shifting of peaks also depends upon the mass. If mass of constituent is high then it has higher wave numbers and if constituent has lower mass then it has low wave numbers as given by relation

$v = \frac{1}{2\pi}\sqrt{\frac{f(m_1+m_2)}{m_1.m_2}}$, Where f is force constant and m is the mass .Similarly the nature of bond also effects the shifting of peaks. The bond between GaN is stronger than GaAs therefore stretching modes changes and shifts the peaks. The molecules vibrate , It means any change in the shape of molecule-streching of bond, bending of bond or internal rotation around the bond.Molecules absorb the IR and excite from lower level to higher level i.e. increases the amplitude. There are following types of vibration modes as shown in the Figure.

(1) Symmetric (2) Asymmetric (3) Rocking (4) Scissoring (5) Wagging (6) Twisting

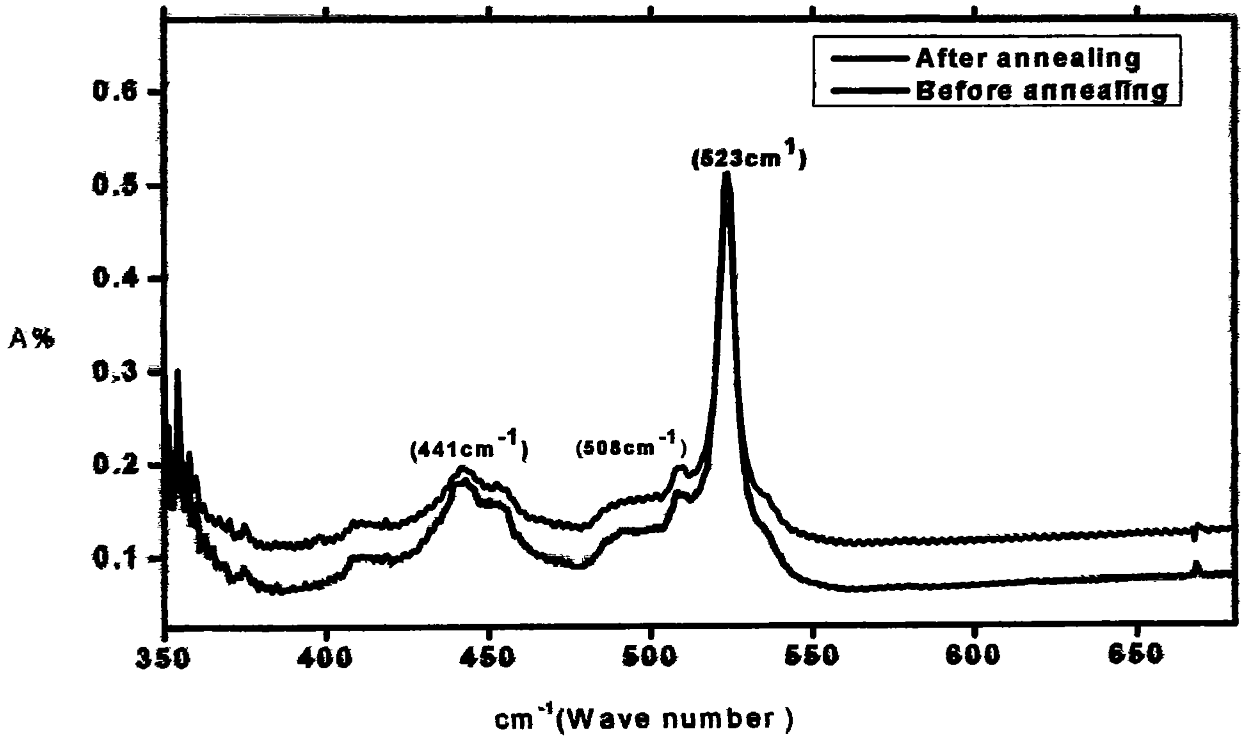


Figure 5.13 Sample C FTIR before and after annealing

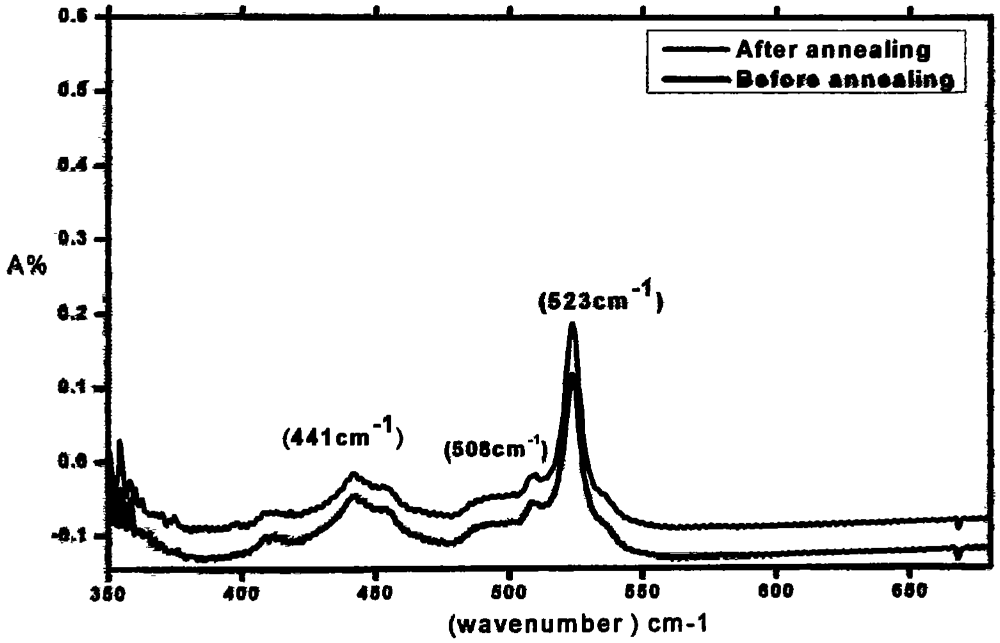


Figure 5.14 Sample D FTIR before and after annealing

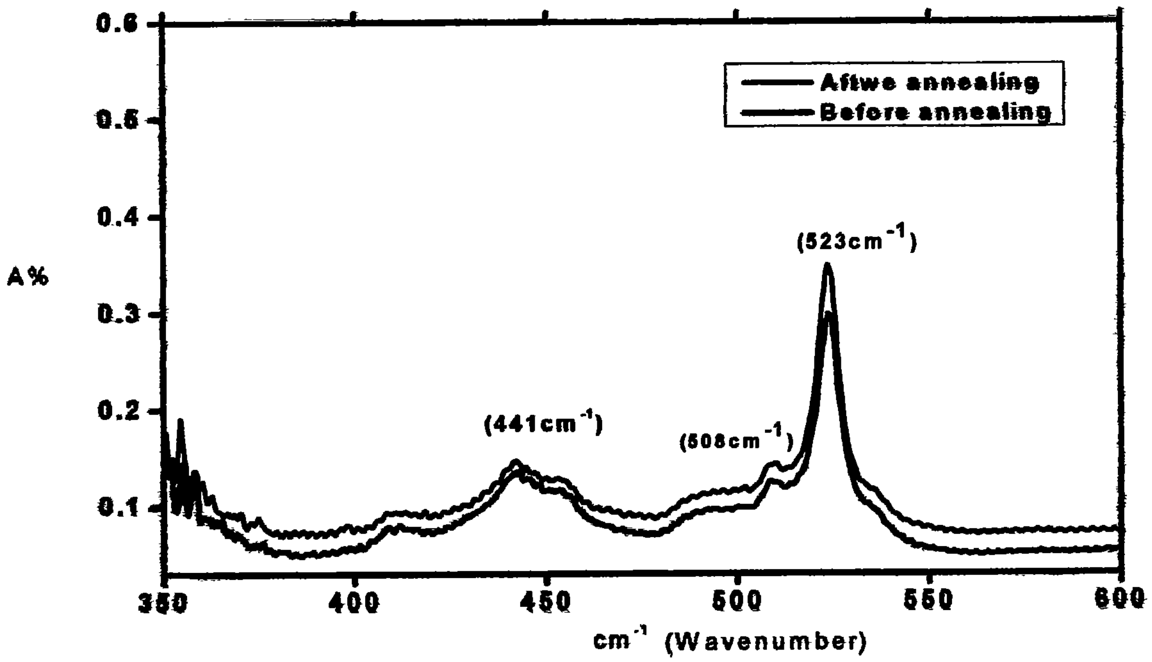


Figure 5.15 Sample E FTIR before and after annealing

Conclusion

The plasma nitriding is a low cost and small time consumption technique. This techniques has been applying for metal hardness and tear resistance. The effect of various parameters like small and long treatment time, effect of pulse DC and effect of pressure etc was studied. We can give a new direction to this technique that nitriding of GaAs. For small treatment time, XRD results do not show any change. The XRD results change for long treatment time, the lattice constant changes and intensity decreases in X-ray diffraction for two hours treatment. The disappearing of peak in 130 minutes treatment show that defects appeared and crystals structure damaged. Rutherford back scattering results shows that % composition and depth of nitrogen increases as time increases. DRS results show that band gap increases .The band may increase or decreased as it depends upon the % composition of nitrogen. For small content of nitrogen the band gap decreases but when nitrogen content increased then arsenic is completely replaced by nitrogen and band gap increases. The drawback of plasma nitriding (by active screen cage) is that arcing can affect the softness of surface and it may cause to increase the noise in our results. Therefore it is necessary to avoid the arcing affect .We only study effect of nitrogen on GaAs by mixing of hydrogen as it increases the surface hardness. Affect of high and low temperature, high and low flow of nitrogen, increasing the bising voltage etc may be studied on GaAs. The results shows that after treatment, the annealing performs a vital role on the activation of optical properties.

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