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DEPARTMENT OF ELECTRONIC AND ELECTRICAL ENGINEERING

THIN FILM ENCAPSULANTS FOR GALLIUM ARSENIDE

by

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This thesis is dedicated to my mother and the memory of my aunt.
Abstract

The problems associated with the use of ion implantation during the preparation of compound semiconductors have been examined. In particular, the use of an encapsulant as protection during annealing was considered and the properties and ease of preparation of the ideal encapsulant were studied.

Among the experimental techniques used to study the surface of thin film coatings on the semiconductors materials, reflection high energy electron diffraction (RHEED) was extremely useful in allowing the study of thin layers. Other techniques used in the work included scanning electron microscopy (SEM), Rutherford backscattering (RBS), rapid thermal annealing using a graphite strip heater and thin film deposition by evaporation and sputtering. Among the encapsulants studied were aluminium nitride and the zirconium nitride the former being the most important.

A study was also made of the chemical reactivity of aluminium nitride to oxidation and hydration. It was found that AlN was resistant to oxidation in air up to about 1000°C and in an inert atmosphere up to at least 1400°C. It was shown that aluminium nitride reacts readily with water to form AlOOH.

The reproducibility of a good quality evaporated AlN film as an encapsulant was found to be difficult to control, but a combination of AlN and Si₃N₄ in a "sandwich" proved to be more successful. Zirconium nitride was found to be useful as a passivation layer up to 700°C.

Sputtered AlN coatings seemed to offer the best hope of success but further work is needed to improve the sputtering techniques so that free Al, or Al₂O₃ is not present in the AlN layers.
Abstract

Contents

<table>
<thead>
<tr>
<th>Chapter 1</th>
<th>Background</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Introduction</td>
</tr>
<tr>
<td>1.2</td>
<td>Annealing techniques</td>
</tr>
<tr>
<td>1.3</td>
<td>Encapsulation</td>
</tr>
<tr>
<td>1.4</td>
<td>Scope of the thesis</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 2</th>
<th>Literature Survey</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Introduction</td>
</tr>
<tr>
<td>2.2</td>
<td>Ion Implantation</td>
</tr>
<tr>
<td>2.3</td>
<td>Properties of an ideal encapsulant</td>
</tr>
<tr>
<td>2.4</td>
<td>Properties of real encapsulants</td>
</tr>
<tr>
<td>2.4.1</td>
<td>Silicon dioxide</td>
</tr>
<tr>
<td>2.4.2</td>
<td>Doped silicate glass</td>
</tr>
<tr>
<td>2.4.3</td>
<td>Aluminium</td>
</tr>
<tr>
<td>2.4.4</td>
<td>Silicon nitride</td>
</tr>
<tr>
<td>2.4.5</td>
<td>Aluminium nitride</td>
</tr>
<tr>
<td>2.4.6</td>
<td>Zirconium nitride</td>
</tr>
<tr>
<td>2.4.7</td>
<td>Multilayer cap</td>
</tr>
<tr>
<td>2.5</td>
<td>Capless annealing</td>
</tr>
<tr>
<td>2.6</td>
<td>Conclusions</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 3</th>
<th>Experimental Techniques</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Introduction</td>
</tr>
<tr>
<td>3.2</td>
<td>Reflection high energy electron diffraction (RHEED)</td>
</tr>
<tr>
<td>3.2.1</td>
<td>RHEED application</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Electron diffraction</td>
</tr>
<tr>
<td>3.2.3</td>
<td>Application of the electron diffraction method</td>
</tr>
<tr>
<td>3.2.4</td>
<td>Reflection diffraction patterns</td>
</tr>
<tr>
<td>3.2.5</td>
<td>RHEED apparatus</td>
</tr>
<tr>
<td>Page No</td>
<td>Section</td>
</tr>
<tr>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>21</td>
<td>3.2.6</td>
</tr>
<tr>
<td>21</td>
<td>3.2.7</td>
</tr>
<tr>
<td>24</td>
<td>3.2.8</td>
</tr>
<tr>
<td>25</td>
<td>3.3</td>
</tr>
<tr>
<td>25</td>
<td>3.3.1</td>
</tr>
<tr>
<td>25</td>
<td>3.3.2</td>
</tr>
<tr>
<td>31</td>
<td>3.3.3</td>
</tr>
<tr>
<td>31</td>
<td>3.4</td>
</tr>
<tr>
<td>32</td>
<td>3.5</td>
</tr>
<tr>
<td>33</td>
<td>3.6</td>
</tr>
<tr>
<td>36</td>
<td>3.7</td>
</tr>
<tr>
<td>37</td>
<td>3.7.1</td>
</tr>
<tr>
<td>39</td>
<td>3.7.2</td>
</tr>
<tr>
<td>39</td>
<td>3.8</td>
</tr>
<tr>
<td>40</td>
<td>3.8.1</td>
</tr>
<tr>
<td>41</td>
<td>3.8.2</td>
</tr>
<tr>
<td>42</td>
<td>3.8.3</td>
</tr>
<tr>
<td>42</td>
<td>3.8.4</td>
</tr>
<tr>
<td>44</td>
<td>4.1</td>
</tr>
<tr>
<td>44</td>
<td>4.2</td>
</tr>
<tr>
<td>44</td>
<td>4.2.1</td>
</tr>
<tr>
<td>45</td>
<td>4.2.2</td>
</tr>
<tr>
<td>45</td>
<td>4.2.3</td>
</tr>
<tr>
<td>46</td>
<td>4.2.4</td>
</tr>
<tr>
<td>47</td>
<td>4.2.5</td>
</tr>
<tr>
<td>47</td>
<td>4.2.6</td>
</tr>
</tbody>
</table>
4.3 Sputtered aluminium nitride films 54
   4.3.1 RHEED results 54
   4.3.2 X-ray diffraction results 54
   4.3.3 Rutherford backscattering analysis 55
   4.3.4 Scanning electron microscopy and X-ray elemental analysis

4.4 AIN powder 62
   4.4.1 Oxidation resistance of AIN powder 62
   4.4.2 Thermal stability of AIN powder 62
   4.4.3 Reaction of AIN powder with boiling water 63

Chapter 5 Results for ZrN 67
5.1 Introduction 67
5.2 RHEED results 67
   5.2.1 Results from as-deposited and annealed samples 67
   5.2.2 Etching characteristics 68
5.3 Scanning electron microscopy 68
   5.3.1 As deposited and annealed samples 68
   5.3.2 Acid treatment of annealed films 71
5.4 X-ray elemental analysis 71
   5.4.1 As deposited and annealed films 71
   5.4.2 Acid treated films after annealing 72
5.5 Rutherford backscattering analysis 76

Chapter 6 Discussion 80
6.1 Introduction 80
6.2 RHEED 80
6.3 General review of encapsulation 81
   6.3.1 Encapsulation of GaAs and III-V compounds 81
   6.3.2 Deposition technique and problems 82
   6.3.3 The annealing temperature and the required material 83
   6.3.4 New thin films candidates 85
Chapter 1

Background

1.1 Introduction

GaAs is becoming the preferred material for use in the fabrication of high speed integrated circuits based on the Schottky barrier field effect transistor (MESFET). In this technology ion-implantation is the main method used to fabricate the electronic devices. In the fabrication of such devices ion implantation has the advantage of allowing the use of the dopant species which would be difficult to introduce by diffusion[1,2]. Yet there are a variety of problems associated with implantation in compound semiconductors which have impeded the development of the technology. Many of these are well documented in several reviews[3-6].

In general, the most persistent problem in III-V ion implantation work is the need for an effective and reliable method of protecting the surface of the semiconductors from thermal decomposition during annealing. This high temperature annealing process is necessary to remove the damage produced in the target crystal by the implantation process. As implanted ions penetrate a solid they lose their energy by several mechanisms including the displacement of target atoms from their lattice sites. The extent of the damage created by these collisions depends on ion mass, dose, energy and target temperature. The removal of the damage is important since it tends to mask the required electrical effects of the implanted ions by compensation.

Therefore the damage needs to be eliminated or at least reduced significantly by treatment at a high temperature. This process serves the additional purpose of electrically activating the implanted impurities by providing energy for them to move into substitutional sites.
1.2 Annealing techniques

The important variables are the same in the various methods of annealing and consist of the temperature and the time of anneal, the rate of change of substrate temperature, the nature of the environment at the surface of the sample and the means by which the sample is heated. The various methods applied to anneal GaAs are mainly the following:

a) Annealing in a furnace

b) Transient annealing by means of one of the following:

1. Graphite strip heater[7]
2. Electron beam[8]
3. Laser beam[9]
4. Incoherent light[10]

Standard furnace annealing can give good electrical activities but this has not prevented investigations into other methods such as transient annealing. Pulsed laser beams and electron beam annealing produce good recrystallisation from the melt, and high carrier concentrations in excess of $1 \times 10^{19}$ cm$^{-3}$ have been achieved for high dose implants. However, defects are introduced which can affect the intended doping levels. Furthermore, mobilities are reported to be lower than expected and low doses do not become electrically active.

For transient annealing using the graphite strip heater, good electrical activities were reported for a variety of dopants in GaAs[11-15]. However, the maximum electron concentration reported was only about $4-5 \times 10^{18}$ cm$^{-3}$ whereas it is in fact desirable to achieve a maximum carrier concentration of the order $1 \times 10^{19}$ cm$^{-3}$. The latter condition is required for the fabrication of non-alloyed ohmic contacts.
1.3 Encapsulation

The annealing temperatures used are above those for which III-V compounds exhibit preferential evaporation of the group V constituents from unprotected surfaces. Unprotected GaAs and InP surfaces maintained at temperatures above the maximum congruent evaporation point exhibit gross degradation in surface morphology [16-19]. Such morphological changes result when, after evaporation of the group V elements, the lower group III metal agglomerates into liquid droplets which thermally "etch" the underlying substrate. Before visible morphological surface damage occurs, the electrical and optical characteristics of the GaAs surface can be seriously degraded[20-22]. Generally, the vapour pressure of the group V elements over the compounds increases with decreasing periodic table row number[23]. With the range of standard annealing temperatures, the vapour pressure of phosphorus over InP is approximately three orders of magnitude higher than that of arsenic over GaAs, making thermal degradation problems much more severe for InP [24].

In the light of these observations, it is necessary to protect the surface with a stable dielectric film deposited at a low temperature. The most successful caps reported for GaAs are SiO₂, Al, AlN, Si₃N₄ and combinations of SiO₂/Si₃N₄ and Si₃N₄/AlN[12,25].

1.4 Scope of the Thesis

In the present work one of the most important problems associated with III-V semiconductors - encapsulation - is studied. In Chapter 2 a brief survey is given of the reported effectiveness of (a) various thin films used on GaAs and InP as encapsulants and (b) some alternative techniques which do not employ thin films, that is capless annealing methods are also discussed. Some general conclusions from this review are listed. The major technique used in this work is reflection high energy electron
diffraction (RHEED), but X-ray diffraction (XRD) has also been used extensively, and the two methods provide useful information about the crystallographic structure of the surface and the bulk structure of these films respectively. Rutherford backscattering (RBS) was used to study both composition of the layers and also the amount of the damage produced during the annealing process.

Surface morphology was studied using scanning electron microscopy and the elements present in the thin films and substrates were analysed by the attached electron probe microanalyser.

An advanced method of annealing i.e., rapid thermal annealing was used employing a graphite strip heater. Thin films of AlN and ZrN deposited on GaAs substrates were annealed for short times at various temperatures prior to analysis. Thus the various methods used to deposit the AlN and ZrN film are discussed together with the annealing method. These are included in Chapter 3.

The fourth and fifth chapters include the results obtained from the various films on GaAs. The effects of the rapid thermal annealing cycle on the AlN and ZrN layers were investigated to evaluate the effectiveness of the layers as encapsulants for GaAs. A wide range of temperatures (500–1150°C) was used in this study. The coating was removed by etching and the revealed surfaces were also examined. Also in this chapter some work carried out on AlN powders is described. The thermal stability and chemical reactivity were investigated and the results compared with those of deposited films on GaAs.

In Chapter 6 a discussion of the results is presented in detail. Conclusions drawn from this work are detailed in Chapter 7 which also includes suggestions for future work.
Chapter 2

Literature Survey

2.1 Introduction

This chapter contains a survey of the published work concerning encapsulants used to protect GaAs and III-V semiconductors during annealing after ion implantation. The properties necessary for a successful encapsulant are discussed.

2.2 Ion implantation

The use of ion implantation to dope III-V semiconductors, and in particular GaAs has become important because of the application to the manufacture of field effect transistors for analogue and digital integrated circuits. The main problem associated with ion implantation is the damage produced in the target material. This damage takes place when energetic ions are injected into the target material, and undergo violent collisions with the atoms of the target, thereby displacing others, the net result being the production of vacancies and interstitial atoms. Thus a highly disordered region is produced around the path of the ion. The penetration of the ions depends on their energy, the masses and the atomic numbers of both ions and target atoms. The damage produced by the implanted ions is proportional to the dose and the distribution of the ions in the target. The electrical properties of the implanted semiconductors are affected by the damage and it is therefore necessary to anneal in order to remove the damage. Since gallium arsenide and III-V semiconductors tend to dissociate on heat treatment, it was found impossible to anneal bare without surface degradation. Thus, the protection of the surface with an encapsulant is necessary, and plays a key role in the success or failure of ion implantation doping in GaAs[5]. Developing an effective and
reliable encapsulant has been one of the main research topics for many laboratories throughout the world. The properties of various encapsulants will be discussed in the following sections.

2.3 Properties of an ideal encapsulant

The required properties of an encapsulating thin film layer are summarised in the following points:

1. It should prevent the host and implanted atoms from leaving the substrate at the annealing temperature.
2. It should not react chemically with the substrate or diffuse into the substrate material.
3. It should not stress the substrate at room temperature as a result of intrinsic stress in the film[26].
4. It should not stress the substrate at elevated temperatures because of differences in thermal expansion coefficients of the film and substrate.
5. It should exhibit good adherence to the substrate and be resistant to cracking, blistering and peeling.
6. It should be homogeneous in composition and free from structural defects such as pinholes.
7. It should be capable of deposition at temperatures below the decomposition temperature of the substrate.
8. It should be resistant to oxidation during the annealing process.
9. It should be easily removed (by chemical etchant) without affecting the substrate.

Such stringent and often conflicting properties seem to be difficult to attain in thin film encapsulants. However, many thin films have been used as encapsulants in the past few years but none of them proved to be perfect[1].
2.4 Properties of real encapsulants

We shall discuss briefly the encapsulants which have been reported so far and the current state of the art of encapsulation will be summarised in the next few sections.

2.4.1 Silicon dioxide

This encapsulant was the first reported material used on GaAs. The SiO₂ is mainly prepared by the pyrolytic oxidation of silane at low temperature (250–400°C) using nitrogen as the carrier gas[13,27–30]. Phosphine and arsenic may be added to the silane to improve the plasticity and the expansion match with the GaAs. Recently SiO₂ layers were prepared using r.f. plasma sputtering from a SiO₂ target. Aside from a tendency to crack, other problems may limit the application of SiO₂ as an annealing cap for GaAs. Numerous studies have demonstrated that the SiO₂ encapsulant permits gallium to diffuse during annealing at temperatures above 750°C[1,13,27]. In another study arsenic was found dissolved in SiO₂ layers on GaAs, also it was found, using transmission electron microscopy, that β-Ga₂O₃, was formed after annealing above 500°C[30].

2.4.2 Doped silicate glasses

A variety of doped silicate glasses such as phosphosilicate glass (PSG), arsenic silicate glass (ASG) and borosilicate glass (BSG) have been examined for use as encapsulants for III–V semiconductors. Films of ASG and BSG have not been as widely used as have films of PSG. In the case of ASG, this may be due to a reluctance to deal with arsenic based gasses or due to the pronounced gallium out-diffusion through SiO₂ caps on GaAs. ASG is predominantly used in multilayer encapsulants together with Si₃N₄[1,31].
2.4.3 Aluminium

An aluminium coating was first reported as encapsulant for GaAs at Surrey University. GaAs was coated with about 300-800 nm of aluminium which was deposited from a heated tungsten filament at a pressure of $2-3 \times 10^{-6}$ torr. Good electrical activity was achieved using this encapsulant up to 700°C. However, at higher temperatures it was difficult to remove the aluminium layer due to chemical reaction with the substrate[32].

2.4.4 Silicon nitride

Silicon nitride has become the most common thin film encapsulant for annealing GaAs. These caps have been deposited in several ways:-

a) Chemical vapour deposition (CVD)[33,34].

b) r.f. Plasma sputtering of a $\text{Si}_3\text{N}_4$ target[2,35].

c) Plasma enhanced chemical vapour deposition (PECVD) [36-38].

d) Reactive sputtering of a silicon target in pure nitrogen gas[39].

The chemical vapour deposition is achieved by the reaction between silane and ammonia on the hot substrate at 650-750°C, while in the case of PECVD technique a plasma of silane and nitrogen is reacted at about 340°C. Sputtered silicon nitride may be deposited from a silicon nitride target with a relatively higher oxygen content $\approx 18\%$, than that of reactively sputtered layers, 2-3\% of the nitrogen content[2,35]. Conflicting reports have been published about the effect of oxygen in the nitride layer when applied to Si implanted GaAs. It is believed that the presence of oxygen may be responsible for the out diffusion of arsenic and gallium from the GaAs substrate during the annealing process (1,2,5,25,31). In other reports Si $O_x$ $N_y$ films were deposited by the pyrolytic reaction of $\text{SiH}_4-\text{NH}_3-\text{O}_2$ system at 700°C with $N_2$ as carrier gas[40]. Many reports have agreed that silicon nitride may work efficiently up to 950°C for
GaAs. One major problem of this encapsulant is the stress due to mismatch of the thermal expansion coefficient with that of GaAs. Blistering and the formation of pits have also been reported to occur at temperatures above 900°C[31]. Recently reported results from zinc implanted GaAs annealed with an e-beam proved that CVD Si₃N₄ may withstand temperatures of up to about 1200°C for very short annealing times (35s) in vacuum[34].

2.4.5 Aluminium nitride

In the past few years considerable effort has been devoted to developing new and better encapsulants for ion implanted III-V compound semiconductors. A superior cap to Si₃N₄ was required especially when annealing at temperatures of 1000°C or above. This is necessary for removal of damage from high dose, heavy mass implants such as Se, Te and Sn. Si₃N₄ would seem to be impossible to use successfully at such high temperatures, so a more attractive cap was studied. Thus a refractory material, AlN, was found attractive to many researchers since it has a high melting point (2200°C) and a thermal expansion coefficient close to that of GaAs (6.3 x 10⁻⁶°C⁻¹) which minimises the effect of the interfacial stress[41], and AlN is soluble in several solutions which do not react with the substrate material.

The main reported methods to prepare AlN films for encapsulation purposes are:-

a) r.f. Sputtering of an aluminium target using pure N₂ or a mixture of Ar-N₂ gasses[41,42,45,46].
b) r.f. Sputtering of AlN target[43].
c) Vacuum evaporation of aluminium in N₂-NH₃ atmosphere [25,44].

Work has been published concerning an oxygen free AlN layer which was deposited by r.f. sputtering of aluminium in a nitrogen atmosphere. When using these films on GaAs, GaAlAs and GaAsP, no degradation of the semiconductors occurred when heated up to 900°C. Rutherford backscattering spectra
indicated that the oxygen atomic concentration was less than 1%[46]. In other published work a reactively sputtered AlN layer of more than 1.2µm thick was used on GaAs with an oxygen content below the detection limit of RBS. This layer was used for annealing temperature up to 1000°C[41,44]. The published results have demonstrated that AlN is the most promising encapsulant which minimises the effect of interfacial stress produced during annealing. Reactively evaporated AlN was used to anneal Se and Sn implanted GaAs up to 1000°C by pulse thermal annealing using a graphite strip heater[44]. Details of this encapsulant will be discussed in the following chapters. Aluminium oxynitride films prepared by r.f. sputtering of an aluminium target were also used as an encapsulant for Se implanted GaAs. The oxygen content of these films was 82% of the nitrogen content when examined by the RBS technique[43]. The reported electrical results using this cap proved superior to those obtained using Si₃N₄ at annealing temperatures between 800-1000°C[42,43,47].

2.4.6 Zirconium nitride

ZrN has been considered as one of the most stable refractory mononitrides. The chemical and physical properties[48-50] of this compound made it an attractive candidate as a new encapsulant for GaAs during the annealing which is carried out to remove ion implantation damage.

The thermal expansion coefficient of ZrN is very close to that of GaAs (7.24 x 10⁻⁶°C⁻¹). ZrN is also easily removed by concentrated hydrofluoric acid whilst leaving the GaAs unaffected. Recently ZrN was shown to be an excellent barrier against aluminium and silicon diffusion during an annealing process up to 550°C in helium[51]. The kinetics of oxidation of reactively sputtered ZrN films in dry oxygen were studied[52], to assess the feasibility of using ZrN in metal oxide semiconductor (MOS) integrated circuits. It was found that ZrN transforms into ZrO₂ when annealed in oxygen in the temperature range of 475-650°C. These temperatures
are lower than standard processing temperatures of Si-device fabrication and therefore passivation would be required. ZrN was used in wear resistance coatings, thin layers of which can significantly affect the tribological response of mechanical parts. The presence of a ZrN layer prevents uneven wear and improves their surface properties[53-55]. Few workers have investigated the use of ZrN as a diffusion barrier and none have studied the encapsulation effectiveness of ZrN thin films on GaAs. In particular there is a lack of knowledge concerning rapid thermal annealing.

2.4.7 **Multilayer cap**

To overcome the problems associated with Si$_3$N$_4$ at temperatures above 900-950°C, such as blistering and thermal pits, work has been done using 100 nm plasma deposited Si$_3$N$_4$ layer over coated with 300 nm CVD SiO$_2$ layers, doped with arsenic. This encapsulant is reported to withstand annealing temperatures up to 1100°C when used to anneal Se-implanted GaAs[47]. In this study scanning electron microscope results show no sign of mechanical failure. The same group has studied the optimisation of the double layer encapsulant. They found that the ratio of As-doped silicon oxide to silicon nitride of over 4:1 produced a defect free surface following annealing at 1050°C and that the best layer thickness combination was 50 nm Si$_3$N$_4$ and 200 nm of As-doped SiO$_2$. This combination produced the least amount of interface strain due to thermal expansion mismatch[31].

2.5 **Capless annealing**

In the past few years a number of capless annealing techniques have been developed in an attempt to bypass the problems associated with thin film encapsulants. The majority of these techniques rely on providing a controlled vapour pressure of a group V element during the anneal. A variety of sources have been used to supply the necessary
vapour such as powder of similar chemical composition[56], close contact with another appropriate semiconductor wafer[57-59], melt-controlled ambients[60] or directly applied gases[19,61-63]. The methods utilising gaseous sources appear to be favorable since they permit a large degree of control over the excess vapour pressure. Aside from eliminating the processing step of encapsulant deposition, capless anneals offer the advantage of avoiding possible surface strain effects due to the encapsulant. A drawback of this technique is possible incorporation of unintended impurities into the bare surface of material from the annealing furnace itself[1]. Even more recent than the development of capless furnace anneals are transient annealing methods, which perform anneals within nano-seconds to seconds instead of minutes. These transient techniques employ laser beams[64-67], electron beams[68-70], graphite strip heaters or alternative high intensity radiative sources[71-72]. Although these methods in principle do not require samples to be encapsulated, in practice, most studies have involved the use of a cap. In a recent publication capless annealing using a pill box made of a graphite was reported. In this method the samples were placed face down in close contact with a sheet of graphite in a stationary inert gas atmosphere and provided with a sufficiently high partial pressure of arsenic by arsenic out-diffusion from the back of the sample or by placing metallic arsenic in the box. Excellent surface quality for anneals up to 1100°C were reported[73].

2.6 Conclusions

A review of the properties of encapsulants used to anneal ion implanted GaAs has been carried out. From this review it is possible to draw the following conclusions:

1. $\text{Si}_3\text{N}_4$ is superior to $\text{SiO}_2$ and Al. It is the most widely used cap and it may work well up to 900-950°C when contamination due to oxygen is at a low level. At
higher temperatures Si₃N₄ fails as an encapsulant unless the annealing time is very short and of the order of seconds.

2. AlN films proved superior to those of Si₃N₄ especially the oxygen free films or those whose oxygen content was below the detection limit of RBS. AlN may withstand temperatures to about 1000°C. This encapsulant needs further development before it is accepted as a replacement for Si₃N₄.

3. A few reports on multilayer caps have shown the advantages of SiO₂/Si₃N₄ and Si₃N₄/AlN layers which may withstand temperatures up to about 1100°C.

4. Capless annealing did not result in good electrical activity in some studies while in others it proved successful and annealing temperatures of 1100°C can be used with excellent surface quality[73]. This is exceptional and needs further confirmation.

5. In order to determine the effectiveness of the cap both the thin film encapsulant and the substrate must be critically examined before and after annealing.

In view of the above comments it should be clear that no single method for protecting compound semiconductor surfaces during annealing has proved perfect, especially when temperatures in excess of 1000°C are needed to achieve good crystallinity and electrical activities after implantation. Detailed studies of the composition of deposited films for the most promising encapsulants are necessary to identify the causes of any deficiency. In addition it seems important to continue to search for a new and better encapsulant.
## Summary

**Encapsulants for GaAs**

<table>
<thead>
<tr>
<th>Material</th>
<th>Methods of Deposition</th>
<th>Sign of Failure</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>Silox (CVD) Sputtered</td>
<td>As or Ga out-diffusion at 750°C or above</td>
<td>13, 27-30</td>
</tr>
<tr>
<td>Doped Silicate Glass</td>
<td>Silox (CVD)</td>
<td>As above, plastic</td>
<td>1, 2, 31</td>
</tr>
<tr>
<td>Aℓ</td>
<td>Vacuum evaporation</td>
<td>Above 700°C, Al₂O₃ stable</td>
<td>32</td>
</tr>
<tr>
<td>Si₃N₄</td>
<td>PECVD, Sputtered, reactively sputtered, reactive pyrolytic CVD</td>
<td>Pin holes, blister, pits above 900°C strain</td>
<td>1, 2, 33-39</td>
</tr>
<tr>
<td>AℓN</td>
<td>Sputtered, evaporated, reactively sputtered</td>
<td>Stronger ≈1000°C</td>
<td>25, 41-47</td>
</tr>
<tr>
<td>SiO₂/Si₃N₄</td>
<td>CVD, sputtered</td>
<td>Better ≈1100°C</td>
<td>1, 31, 47</td>
</tr>
<tr>
<td>Si₃N₄/AℓN</td>
<td>CVD, evaporated</td>
<td>Good up to 1140°C</td>
<td>25</td>
</tr>
</tbody>
</table>
Chapter 3

Experimental Techniques

3.1 Introduction

This chapter describes the experimental techniques used in this study. The major part of this chapter includes the description, calibration and improvement of the reflection high energy electron diffraction camera (RHEED) followed by other sections which give details of the other techniques used for analysis, methods of preparation of the encapsulants and the annealing techniques.

3.2 Reflection high energy electron diffraction (RHEED)

3.2.1 RHEED application

RHEED is a useful method for the study of surfaces because electrons are scattered very strongly by other electrons. For example electrons are scattered $10^6$-$10^7$ more strongly than the X-rays used in X-ray diffraction[74]. As a result of this, it is possible to determine a crystal structure using less than $10^{-5}$ g of material. Electron diffraction can be used for studying the crystal structure of specimens obtainable in the form of a film of a few nm thick. Such films prepared by vacuum deposition or otherwise are now of great technical importance, and their study is one of the main applications of electron diffraction. In the reflection mode of electron diffraction, glancing angles of about 1° are used, when the beam penetration is a few nanometers, and the scattering is very intense by the surface layers.

Recently there has been an increased interest in reflection high energy electron diffraction (RHEED) and the technique is now important in several branches of surface science.[75] Some current applications of RHEED include:-
1. The study of the surface during molecular beam epitaxy MBE[76,77].

2. The study of reconstructed semiconductor surfaces [78,79] and surface imaging by reflection electron microscopy[80,81].

3. The study of the growth of various thin film layers on semiconductor surfaces by sputtering, evaporation chemical vapour deposition (CVD) and metallo-organic chemical vapour deposition (MOCVD).

It therefore seems that RHEED will be a very suitable method for the study of layers of aluminium nitride and zirconium nitride used as encapsulants for gallium arsenide crystals and other semiconductors. It was therefore decided to construct a RHEED apparatus for this purpose. Unlike electron microscopy, it is not possible readily to purchase standard RHEED apparatus. Furthermore, as the number of research centres using RHEED is very small, the technique is not widely known and is therefore difficult to acquire. The University of Surrey has been accumulating experience with RHEED for about fifteen years and can thus claim to be exceptionally experienced in this field.

3.2.2 Electron diffraction

Normally Electron diffraction patterns are usually obtained from crystalline material using very thin samples in the electron microscope. Single crystals give a characteristic "spot" pattern, whilst polycrystalline material gives a series of rings. The "d" spacings (the distance between the layers of atoms in the crystal) can be calculated from the distances of the spots or rings from the undeviated beam, after the experimental set-up has been calibrated with a standard material. The orientation of single crystals can also be deduced from the spots present and the angles between their beams.
When the samples to be examined are in the form of thick specimens it is often more convenient to use reflection electron diffraction from the surface of the material than transmission electron diffraction.

3.2.3 Application of the electron diffraction method

If a small amount of material is available, electron diffraction is the most sensitive of the three diffraction methods (X-ray, Neutron, Electron diffraction) commonly used in crystal structure analysis[82]. The following points can be regarded as some of the advantages of the electron diffraction method:

1. the extremely small amount of material required for study (as little as 1/100000 gram),
2. the comparative rapidity and simplicity of preparation of specimens,
3. the possibility of observing a diffraction pattern on a fluorescent screen before it is photographed,
4. short exposure time.

The interpretation of electron diffraction patterns is usually more difficult than that of X-ray diffraction patterns, since extra lines and spots may appear. The intensities are also more difficult to relate to structure. In structural studies, transmission recording is mostly used, in association with electron microscopy. However, results may be obtained by recording the reflection from the surface of massive specimens. The reflection method overcomes the problem of removing the surface layer undamaged or etching a large thickness down to suitably thin films.

3.2.4 Reflection diffraction patterns

Patterns of this type are obtained when the electron beam is reflected from the specimen surface in a special electron diffraction apparatus. The scope of the electron diffraction
technique was greatly extended by the discovery of Nishikawa and Kikuchi in 1928[83], that diffraction patterns could be obtained using electrons reflected from the smooth surface of a specimen inclined at a few degrees to the incident electron beam. The technique was later called reflection high energy electron diffraction, RHEED. Only half the pattern seen in a transmission electron diffraction photograph is obtained as the other half of the pattern is covered by the shadow from the specimen. The depth normal to the surface which the electrons penetrate is very small owing to the small glancing angle involved. The minimum thickness to give a detectable pattern with 30kV electrons is of the order of 1—1.2 nanometer (Thomason)[84]. For 30—60kV the penetration is of the order 2—4 nanometer respectively (Pinsker)[85]. The depth of penetration of the beam depends very much on the smoothness or roughness of the surface (Thomason)[84].

3.2.5 RHEED apparatus

The RHEED apparatus used in these studies was built in order to study ion implanted materials (along the lines recommended by Kehoe)[86]. In previous studies using this apparatus the best conditions for work were found to be 35kV. In the present work 40kV has been found to be the best energy to operate the RHEED apparatus (as shown in the figures 3.1 and 3.2).

The RHEED apparatus consists of:

a) electron source  
b) deflection coil  
c) condenser lens  
d) specimen holder  
e) detectors  
f) pumping system
a) **Electron source:**
A tungsten wire of 0.005" diameter is bent into a hairpin shape. This filament is heated by passing a current of a few amperes through it. The electrons are accelerated by a potential of 40kV. The accelerating voltage is obtained from a Brandenburg voltage multiplier which gives a dc output from 0 to 100kV at a current of 1mA.

b) **Deflection coils:**
These coils help in aligning the beam by adjusting the current passing through them.

c) **Condenser lens:**
A large coil of 1000 amp-turns strength is connected to a stabilized dc power supply of 0-350V and current of 0-150mA. Suitable working values for a 40kV accelerating voltage of the electron beam are 200V at 45mA current.

d) **Specimen holder:**
The specimen holder consists of a brass screw clamp mounted on a rack and pinion assembly to provide translational and rotational motion.

e) **Detection:**
The fluorescent screen on which the diffraction pattern can be observed lies perpendicular to the beam. The screen can be moved out of the way so that the patterns can be recorded on a photographic film.

f) **Pumping system:**
A rotary pump and oil diffusion pump are employed. The vacuum in the camera is typically $10^{-4}$ to $10^{-5}$ torr.
RHEED apparatus

P.C. = Filament chamber  D.C. = Deflection coil
C.L. = Condenser lens  S.C. = Specimen chamber
S.M. = Specimen manipulator  V.P. = Viewing port
H.T. = High tension unit

Figure 3.1
3.2.6 Improvements to existing RHEED apparatus

Initial work on surface studies of ion-implanted material using the Chemical Physics RHEED apparatus was first carried out by T. Tunkasiri[87], who demonstrated the application of this technique to thin surface layers of semiconductor crystals. In this work the method of Tunkasiri was developed in the following way:

1) A better vacuum was obtained with improved seals etc.
2) A smaller aperture was used to reduce the beam size.
3) Filament life was increased from a period of 4 weeks to a period of 12 months as a result of the improvement in the vacuum and the adoption of a suitable cooling down time.
4) The operating voltage range was increased. In Tuckasiri's work the maximum voltage used was 35kV. In this work a pattern of gold rings has been obtained at 60kV and 50kV. The optimum value for the best working conditions has been found to be 40kV.
5) The amount of detail which could be recorded on the photographic film has been improved. This was achieved by moving the upper part of the apparatus relative to the recording film. This preliminary work occupied about 18 months.
6) An exhaustive investigation of the accuracy obtainable using the apparatus was carried out in the determination of the camera constant. This is described in Section 3.3.

3.2.7 Determination of the interplanar spacing "d"

The electron beam is diffracted by a crystal in a similar manner to an X-ray beam. The wavelength of the electron beam depends on the accelerating voltage, which can be calculated using the approximate formula;

\[ \lambda = \gamma / 150/V \]  

where \( \lambda \) = wavelength of the electron beam in nm 
\( V \) = accelerating voltage in volts
In Fig. 3.3, the electron beam is incident and reflected at an angle "θ" to the planes of atoms with interplanar spacing "d". Strong reflection occurs if Bragg's equation,

$$2d \sin \theta = \lambda \quad 3.2$$

is satisfied. If the specimen is a polycrystalline material, the diffracted beam which is at an angle 2θ from the incident direction will form a cone of semi-angle 2θ, and fall on a photographic plate in a circle of radius R

$$\frac{R}{L} = \tan 2\theta \quad 3.3$$

where L = specimen to plate distance.

The angle 2θ in electron diffraction is so small that 

$$\tan 2\theta \approx 2\theta, \quad \sin \theta \approx \theta. \quad \text{By eliminating } \theta \text{ in (1) and (2),} \quad \frac{R}{L} = \frac{d}{\lambda} \quad 3.4$$

If \( \lambda L \) (camera constant) is known and R measured directly from the photographic film, "d" can be calculated. If the specimen is a single crystal the diffracted beam forms either a streak or spots, depending on the roughness of the surface.
Fig. 3.2. Sectional diagram of RHEED apparatus.

Fig. 3.3. Diagram for derivation of Basic Equation of electron diffraction.
Table 3.1 briefly describes features of electron diffraction patterns which are commonly encountered[82,84,85,88 - 91]

Table 3.1

<table>
<thead>
<tr>
<th>Pattern Type</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kikuchi lines</td>
<td>perfect single crystal, from a specimen of $10^{-5}$cm $^2$ thickness of single crystal (kinematic and dynamic theory) characteristic of dynamic scattering. May be used to determine crystal orientation.</td>
</tr>
<tr>
<td>Cross grating spot pattern</td>
<td>obtained from single crystals or group of single crystals (mosaic) with an angular scatter of the order 2-3° small changes in specimen orientation may alter intensity of spots. A thin crystal gives streaky spots.</td>
</tr>
<tr>
<td>Ring pattern</td>
<td>obtained from aggregates of randomly distributed crystals.</td>
</tr>
<tr>
<td>Arc pattern</td>
<td>preferred orientation in the sample of polycrystalline material.</td>
</tr>
<tr>
<td>Twin spots</td>
<td>twinning a phenomenon commonly observed and explained as 180° rotation about twin plane normal (twin axis) or due to plastic deformation and recrystallization.</td>
</tr>
<tr>
<td>Diffuse halo</td>
<td>amorphous surface, non-crystalline material (common with polished surfaces).</td>
</tr>
<tr>
<td>Streak pattern</td>
<td>origin unknown, stacking fault in any structure can lead to streaking in diffraction pattern, or because of the thermal vibration of the atoms in the plane.</td>
</tr>
<tr>
<td>Texture patterns (Rings and Arcs)</td>
<td>texture pattern obtained from crystals uniformly orientated on the specimen support and having one degree of freedom (one face being parallel to specimen support but random azimuthal distribution crystals).</td>
</tr>
</tbody>
</table>
3.3 RHEED Calibration - Camera Constant

3.3.1 Standard materials

The electron diffraction patterns obtained from GaAs specimens can be analysed if the camera constant of the apparatus is known and for this purpose four substances have been used as standards[74,88,91];

1) Thallium chloride evaporated from a tungsten boat onto single crystal GaAs surface.
2) Very thin gold leaf.
3) Pure aluminium wire evaporated onto a glass slide.
4) GaAs specimen which has been carefully abraded using a fine grade emery paper. The resulting surface powder was removed by washing the specimen in hot methanol for a few minutes. The specimen was then dried and prepared for RHEED examination.

3.3.2 Electron diffraction patterns obtained from standard materials

When the standards were examined using the RHEED camera a transmission pattern was obtained for the gold leaf whereas reflection patterns were obtained for the thallium chloride, aluminium and GaAs samples.

Measuring the radii of the rings, and using the basic equation, the camera constant was found from the data for each standard material. The results are listed in Tables 3.2, 3.3, 3.4 and 3.5 and shown in Fig. 3.4a, b, c, d.
Table 3.2
Camera Constant (λL) Calculated from Thallium Chloride Pattern. (Measured from Figure 3.4.a)

<table>
<thead>
<tr>
<th>hkl</th>
<th>d(nm)ASTM</th>
<th>R(mm)</th>
<th>λL(nm x mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.3839</td>
<td>6.25</td>
<td>2.399</td>
</tr>
<tr>
<td>110</td>
<td>0.2717</td>
<td>8.65</td>
<td>2.350</td>
</tr>
<tr>
<td>111</td>
<td>0.2218</td>
<td>10.60</td>
<td>2.351</td>
</tr>
<tr>
<td>200</td>
<td>0.1921</td>
<td>12.20</td>
<td>2.344</td>
</tr>
<tr>
<td>210</td>
<td>0.1718</td>
<td>13.60</td>
<td>2.336</td>
</tr>
<tr>
<td>211</td>
<td>0.1568</td>
<td>14.90</td>
<td>2.336</td>
</tr>
<tr>
<td>220</td>
<td>0.1358</td>
<td>17.30</td>
<td>2.349</td>
</tr>
<tr>
<td>300</td>
<td>0.1281</td>
<td>18.25</td>
<td>2.337</td>
</tr>
<tr>
<td>311</td>
<td>0.11583</td>
<td>20.30</td>
<td>2.350</td>
</tr>
<tr>
<td>222</td>
<td>0.11091</td>
<td>21.10</td>
<td>2.340</td>
</tr>
</tbody>
</table>

mean λL value = 2.348 (nm x mm)

Footnote

hkl = Miller indices of set of interplanar spacings.
d(nm) = Interplanar spacings.
R(mm) = Radius of the rings on the diffraction pattern.
λL(nm x mm) = Calculated camera constant.
### Table 3.3

Camera Constant Calculated from Aluminium Pattern
(Measured from Figure 3.4.b)

<table>
<thead>
<tr>
<th>hkl</th>
<th>d(nm)ASTM</th>
<th>R(mm)</th>
<th>AL(nm x mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>0.2338</td>
<td>9.95</td>
<td>2.326</td>
</tr>
<tr>
<td>002</td>
<td>0.2025</td>
<td>11.25</td>
<td>2.318</td>
</tr>
<tr>
<td>022</td>
<td>0.1432</td>
<td>16.25</td>
<td>2.327</td>
</tr>
<tr>
<td>113</td>
<td>0.1221</td>
<td>19.10</td>
<td>2.332</td>
</tr>
<tr>
<td>222</td>
<td>0.1169</td>
<td>19.95</td>
<td>2.332</td>
</tr>
<tr>
<td>133</td>
<td>0.0929</td>
<td>25.10</td>
<td>2.331</td>
</tr>
<tr>
<td>224</td>
<td>0.0827</td>
<td>28.30</td>
<td>2.340</td>
</tr>
<tr>
<td>331,115</td>
<td>0.0779</td>
<td>29.85</td>
<td>2.325</td>
</tr>
<tr>
<td>244,006</td>
<td>0.0675</td>
<td>34.55</td>
<td>2.332</td>
</tr>
</tbody>
</table>

**Footnote**

- hkl = Miller indices of set of interplanar spacings.
- d(nm) = Interplanar spacings.
- R(mm) = Radius of the rings on the diffraction pattern.
- AL(nm x mm) = Calculated camera constant.

**Footnote**

mean AL value = 2.329 (nm x mm)
Table 3.4

Camera Constant Calculated from Gold Pattern (Transmission)
(Measured from Figure 3.4.c)

<table>
<thead>
<tr>
<th>hkl</th>
<th>d(nm)</th>
<th>ASTM</th>
<th>R(mm)</th>
<th>λL (nm x mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>0.2355</td>
<td></td>
<td>10.10</td>
<td>2.378</td>
</tr>
<tr>
<td>200</td>
<td>0.2039</td>
<td></td>
<td>11.60</td>
<td>2.367</td>
</tr>
<tr>
<td>220</td>
<td>0.1440</td>
<td></td>
<td>16.36</td>
<td>2.359</td>
</tr>
<tr>
<td>311</td>
<td>0.1230</td>
<td></td>
<td>19.14</td>
<td>2.354</td>
</tr>
<tr>
<td>331</td>
<td>0.09358</td>
<td></td>
<td>25.17</td>
<td>2.356</td>
</tr>
<tr>
<td>420</td>
<td>0.09120</td>
<td></td>
<td>25.77</td>
<td>2.351</td>
</tr>
</tbody>
</table>

mean λL value = 2.360 (nm x mm)

Footnote

hkl = Miller indices of set of interplanar spacings.
d(nm) = Interplanar spacings.
R(mm) = Radius of the rings on the diffraction pattern.
λL(nm x mm) = Calculated camera constant.
Table 3.5

Camera Constant Calculated from GaAs Pattern
(Measured from Figure 3.4.d)

<table>
<thead>
<tr>
<th>hkl</th>
<th>d (nm ASTM)</th>
<th>R (mm)</th>
<th>( \lambda L ) (nm x mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>0.3260</td>
<td>7.20</td>
<td>2.347</td>
</tr>
<tr>
<td>220</td>
<td>0.1999</td>
<td>11.70</td>
<td>2.339</td>
</tr>
<tr>
<td>311</td>
<td>0.1704</td>
<td>13.70</td>
<td>2.334</td>
</tr>
<tr>
<td>400</td>
<td>0.1413</td>
<td>16.65</td>
<td>2.352</td>
</tr>
<tr>
<td>331</td>
<td>0.1297</td>
<td>18.10</td>
<td>2.347</td>
</tr>
<tr>
<td>422</td>
<td>0.1154</td>
<td>20.35</td>
<td>2.348</td>
</tr>
<tr>
<td>333</td>
<td>0.1088</td>
<td>21.50</td>
<td>2.339</td>
</tr>
<tr>
<td>440</td>
<td>0.09993</td>
<td>23.45</td>
<td>2.345</td>
</tr>
<tr>
<td>620</td>
<td>0.08939</td>
<td>26.35</td>
<td>2.355</td>
</tr>
<tr>
<td>533</td>
<td>0.08622</td>
<td>27.15</td>
<td>2.340</td>
</tr>
<tr>
<td>711,551</td>
<td>0.07916</td>
<td>29.65</td>
<td>2.347</td>
</tr>
</tbody>
</table>

mean \( \lambda L \) value = 2.346 (nm x mm)

Footnote

- **hkl** = Miller indices of set of interplanar spacings.
- **d(nm)** = Interplanar spacings.
- **R(mm)** = Radius of the rings on the diffraction pattern.
- **\( \lambda L \)(nm x mm)** = Calculated camera constant.
a: Thallium chloride on 100 GaAs

\[ \begin{align*}
  a &= 100 \\
  c &= 111 \\
  e &= 210 \\
  g &= 220 \\
  i &= 311
\end{align*} \]

b: Aluminium thin film on glass

\[ \begin{align*}
  a &= 110 \\
  b &= 002 \\
  d &= 200 \\
  e &= 022 \\
  f &= 211
\end{align*} \]

c: Transmission pattern from gold leaf

\[ \begin{align*}
  a &= 111 \\
  c &= 220 \\
  e &= 331
\end{align*} \]

d: Polycrystalline ring pattern of GaAs obtained from mechanically damaged sample

\[ \begin{align*}
  a &= 111 \\
  b &= 200 \\
  d &= 311 \\
  e &= 222 \\
  f &= 420
\end{align*} \]

Figure 3.4 Patterns obtained from standard materials
3.3.3 Results of camera constant calculations

The mean values for the camera constants were found to be 2.348, 2.329, 2.360 and 2.346 from Tables 3.2, 3.3, 3.4 and 3.5 respectively. The overall mean value was therefore taken as $2.35 \pm 0.02$. This value was considered to be sufficiently accurate for the present work since it was to be used to index patterns from known materials. It is well known that the reflection diffraction method is not as accurate as the transmission method since penetration of the sample at such a small angle causes the value for camera length to be uncertain[89,90,92].

The position of the irradiated area on the specimen is also less certain as the area irradiated is much larger than in the transmission method.

3.4 X-ray diffraction (XRD)

The X-ray data was collected using a Philips PW1050 goniometer fitted with a graphite single crystal monochromator. Copper radiation was used at 45kV, 36mA, the scan speed was $2^\circ$ of $20$ min. and a full scale deflection of $1 \times 10^3$ CPS was typical. The angle range of scan was from $90^\circ$ 2θ to $20^\circ$ 2θ the angle marker indicating every half degree.

To overcome the problem of differing thickness of substrate and thin film from sample to sample, a special sample holder was made. This consisted of a platform onto which the sample was stuck, the platform height being adjustable by means of a screw thread. This enabled the surface of the samples to be accurately positioned in the focus plane of the goniometer.

Sputtered AIN thin films of about $1 \mu m$ thick gave diffraction peaks when examined, whereas evaporated AIN (0.1-0.2μm thick) and ZrN (~12μm thick) did not.
The Scanning Electron Microscopy (SEM) and the Electron Probe micro-analyser

The Scanning Electron Microscope (SEM) was used to study the surface topography of coated layers before and after heat treatment and after acid treatment. The surface study was carried out in the Structural Studies unit of the University. A modern combined scanning microscope and probe analyser the JSM35CP linked with an energy dispersing X-ray detector was used for examining the ZrN and the A1N samples before and after heating and acid treatment. SEM micrographs provide information concerning the state of the surface after thermal treatment in the range of 500° to 1000°C for the ZrN samples. Some of the A1N samples prepared by evaporation or sputtering were also examined to obtain information about the composition of the deposited layers. After acid treatment the (SEM) was used to reveal information concerning any remaining layer or surface degradation or contamination which the GaAs substrate may have undergone. The electron probe microanalyser supplied compositional information on the elements present in the films and the substrate and had a light element detector designed to detect elements such as oxygen, nitrogen as well as heavy elements such as Zr, Hf, etc. Standard Al2O3 and BN samples were used to calibrate the machine and to prove that light elements could be detected. Details of the technique can be found in Reference[90].

An accelerating voltage of 10keV was used to excite the X-rays from the largest specimens. These X-rays can be dispersed using both energy and wave length spectrometers. Elements present in the sample under investigation were recorded using special chart labelled with the elements of the periodic table. Useful information was obtained from the ZrN and the A1N samples and results are presented in Chapter 4.
3.6 Rutherford Backscattering (RBS)

The Rutherford backscattering technique is a powerful method for the analysis of surface and near surface composition of solid materials. The technique involves the measurement of the energy distribution of high energy ions which have been caused to undergo large angle elastic scattering due to collision with target nuclei. In this study the RBS technique was used to analyse the composition of the aluminium nitride and the zirconium nitride films.

A schematic diagram of the experimental apparatus used is shown in Figure 3.5a. A collimated beam of helium ions with an energy of 1.5 MeV was directed at the sample under measurement. The sample was mounted on a three axis goniometer. The beam current was limited to about 5nA and the ion beam diameter was about 1mm. The energy of the backscattered ions was measured using a silicon surface barrier detector with an energy resolution of about 15keV (FWHM) which was mounted at 150° to the incident beam. The amplified signal from the detector was fed into an 800 channel analyser which recorded the backscattered energy spectrum on a CRT screen. The signal was then transferred to a hard copy on an x-y chart recorder. An on-line printer was used to print out the total number of counts in each of the analyser channels. The observed energy of backscattered particles from a depth x in the sample is given by [93]:-

\[ E_{\text{obs}} = E - \left[ \frac{x}{\cos \theta_1} \right] K - \int_0^x S(E) \, df_2 \]

where \( K \) is the Kinematic factor

\[ K = \left[ \frac{M_1 \cos \theta_2 + M_2}{M_1 + M_2} \right]^2 \]

\( S^*(E) \) and \( S(E) \) are the stopping powers of the incoming and outgoing beams.
\( \theta_1 \) and \( \theta_2 \) are the angles between the incoming and outgoing beams and the surface normal respectively. Figure 3.5b.

\[ \theta_S = \text{the total backscattering angle (150°)} \]
\[ E_{\text{obs}} = \text{energy of backscattering particle} \]
\[ E = \text{energy of the incident beam} \]
\[ M_1 = \text{mass of the incident ion} \]
\[ M_2 = \text{mass of target atom} \]

Identification of the impurities or constituents of the surface of a solid sample is most easily achieved by determining the highest energy of a peak in the backscattered spectrum corresponding to the surface, \( X=0 \), and calculating the mass of the atoms causing the peak using a known reference peak. The latter can either be an evaporated gold film or the substrate material. In this study aluminium nitride films were analysed on both GaAs and vitreous carbon which has a lower mass than the constituents of the films under study. The angular backscattering probability of the ions is given by the Rutherford backscattering formula:

\[
\frac{d\sigma}{dn} \propto \left[ \frac{Z_1 Z_2}{E} \right]^2 \left[ \frac{M_1 + M_2}{M_2} \right]^2 \frac{1}{\sin^4 \theta'/2} \text{ cm}^2 \text{ Sr}^{-1}  \tag{3.7}
\]

where

\( \theta' = \text{backscatter angle in center of mass coordinates} \)
\( Z_1 = \text{atomic number of incident ion} \)
\( Z_2 = \text{atomic number of target nuclei} \)

Thus the number of counts in the peak due to a particular atom is proportional to the square of its atomic number. The relative concentration of two constituents in a film can thus be determined using the approximation

\[
\frac{N_A}{N_B} \approx \frac{Y_A}{Y_B} \frac{Z_B^2}{Z_A^2} \tag{3.8}
\]
Fig. 3.5 Schematic Representation of the Rutherford Backscattering System

A) Diagram of Apparatus
B) Geometrical Relationship between $\theta_1$, $\theta_2$ and $\theta_s$. 
where

\[ N = \text{concentration} \]
\[ Y = \text{integrated number of counts under a peak} \]

The above approximation is valid when the atomic masses of the constituents are significantly greater than the mass of helium. Using the above approximation the relative concentration of either aluminium, zirconium, nitrogen or oxygen were determined.

The Rutherford backscattering technique can also be used as an analytical tool to measure the crystallinity of materials. If the target is a single crystal, the backscattering yield can be largely reduced when the analysing beam is directed parallel to a low index direction. The yield \( Y_1 \) obtained from such channelling can be substantially lower than the random yield, \( Y_2 \), obtained from a non-channelling direction. The ratio of the yield in a channelling and a non-channelling direction, \( Y_1/Y_2 \), can be used as a measure of the quality of single crystal specimens and is given by:

\[ X_{\text{min}} = \frac{Y_1}{Y_2} \]

A typical value of \( X_{\text{min}} \) for good quality crystal, is about 3% for silicon and larger for GaAs \( X_{\text{min}} \approx 4-5\% \).

3.7 Graphite Strip Heater for Rapid Thermal Annealing (RTA)

The graphite strip heater is the same apparatus as that used for CVD Si\(_3\)N\(_4\) deposition described in Reference[94]. It is used for both deposition of the Si\(_3\)N\(_4\) cap and annealing the GaAs samples. In the following paragraphs a description of the single and the double graphite strip heaters are presented together with the procedures adopted in controlling and measuring the sample temperature.
3.7.1 Single and double graphite strip heaters

A schematic diagram of the single and double graphite strip heater is shown in Figure 3.6 which also illustrates the positions of the various thermocouples used to characterise the system. The dimensions of each graphite strip are approximately 12 x 4 x 0.1 cm and the gap between them is in the range 1-1.5 mm. T₁, T₂ are thermocouples embedded within the graphite strips and provide the dimensions of the two strips are identical, equal temperatures are recorded. Either T₁ or T₂ was used as the sensor for the temperature controller. T₃ is a thermocouple placed in the air-space between the strips and records the same temperature within ±2°C as T₁, T₂ over an area of about 2cm x 2cm. Thermocouples were also attached to samples placed face upwards, both on top (T₅) and between (T₄) the strips so that a comparison could be made between the sample temperature and the control temperature (T₁ or T₂).

T₆ corresponds to the control temperature of the original system which employed a single graphite strip. That is, the original system corresponded to thermocouples T₅ and T₆ where T₆ was the reported temperature of the sample. We find here that T₅ is typically up to 15°C lower than T₆ depending on how good is the thermal contact between the sample and the graphite strip. Figure 3.7 summarises the results of the temperature time excursions for an annealing temperature of nominally 1000°C. T₁ and T₂ reach 1000°C with a small overshoot in four seconds. However, a sample placed on top of the graphite strip records temperature, T₅, which was found to be up to 50°C lower than the control temperature T₁ and T₂. This difference in temperature is variable due to variations in the thermal contact between samples and the strip. The temperature T₅ also has a relatively long lag time (>10s) behind the control temperature and reaches a plateau value slowly. A sample placed between the two strips also lags behind the graphite strip (T₁, T₂) but only by about two seconds. Consequently, there is no overshoot of the sample temperature. Under
Figure 3.6: Schematic diagram of the double graphite strip heater illustrating the positions of thermocouples used to characterise the temperature/time excursion of both the single and the double graphite strip heaters. The top strip represents the single graphite strip heater.

Figure 3.7: Comparison of temperature/time excursion of single ($T_1, T_2$) and double ($T_3, T_4$) graphite strips and samples ($T_5, T_6$).
these conditions the temperature reached is within $2^\circ$C of the control temperature $T_1$ and $T_2$ (see reference [95] for further details).

3.7.2 Annealing procedure

After encapsulation with either AlN or ZrN, the samples were sliced into smaller samples of approximately 4 x 4mm prior to the annealing process. The GaAs samples were placed either in the middle region of the single graphite strip or between the two graphite strips in the case of the double graphite strip heater. The chamber was then evacuated to about $10^{-4}$ Torr before being backfilled with nitrogen gas. The anneal was then performed in flowing nitrogen in order to reduce oxidation of the graphite. The power supply at the heaters was from a 100 amp transformer at 10 volts, the temperature being controlled via the feedback from a chromel-alumel thermocouple (T1) embedded in the graphite Fig. 3.6. The thermocouples were calibrated by melting small pieces of gold and silver on the graphite strip.

3.8 Materials and sample preparation

The material used in this work was mostly semi-insulating undoped GaAs grown in the (100) direction by the liquid encapsulated Czochralski method. The semi-insulating GaAs had an initial resistivity of the order $10^9\Omega$cm and was polished on one side by the manufacturer (Metals Research Limited, MR).

The encapsulation was performed on either the complete wafer or parts of the wafer. In the latter instance the wafer was sliced into a number of samples. All samples were boiled in methanol prior to the thin film deposition in order to obtain a clear surface. After annealing, samples were examined using RHEED, SEM, microprobe and the layer was then treated with HF acid to remove the cap. The samples were
then dipped in distilled water to remove the acid and finally cleaned by boiling in methanol before carrying out any test.

3.8.1 Evaporated AlN

The experimental apparatus used in the deposition of AlN films is a simple metal evaporator. It consists of a glass chamber housing a tungsten filament which is heated by a 10 amp power supply and a pumping system which allows a vacuum of $5 \times 10^{-5}$ Torr to be realised within the chamber. Ammonia ($\text{NH}_3$) is transported into the evaporation chamber by bubbling nitrogen through aqueous ammonia.

Some alterations to the basic evaporation system had to be made in order to produce AlN by reaction between evaporated Al and the $\text{N}_2/\text{NH}_3$ gas mixture. For instance, to improve the quality and uniformity of the AlN film it has been found useful to spray the gas mixture uniformly over the surface of the specimens.

Initially it was thought that AlN could be deposited on substrates held at room temperature simply by evaporating aluminium in a nitrogen atmosphere. However, several attempts in this direction have failed merely because the nitrogen gas needed first to be dissociated and probably also because the substrate required heating to temperatures above room temperature. Subsequently, another way of producing AlN was studied which involved the addition of NH$_3$ into the chamber and the evaporation of Al. This produced a film whose composition consisted of Al, N and O, as shown in Chapter 4. The nitrogen-ammonia pressure (hence, the mean free path of Al atoms), the rate of Al evaporation and the distance between the substrate and the tungsten filament had to be optimised in order to produce good-quality AlN. The outcome of such optimisation is discussed in length in Chapter 6 and reference [25].
A$\text{Al}_2$N powder was supplied by a) Koch Light Limited (UK) and had a particle size of 50$\mu$m and a dark grey colour and b) Alfa Products (W. Germany) which had a light grey colour and a finer particle size. XRD analysis was carried out using a Debye Scherrer camera of 11.1486mm diameter Cu K$\alpha$ radiation and glass specimen capillaries of 0.5mm diameter. The RHEED analysis was carried out using an operating voltage of 40KV at background pressure of 3-5.$\times$10$^{-5}$ Torr. The sample holder was an aluminium block (2X1X1cm) with a wide, shallow groove into which the powder was pressed. The surface was made as smooth as possible before analysis.

Samples of A$\text{Al}_2$N powder contained in porcelain boats were heated in air in a muffle furnace for 3 hours at temperatures from 600-1400°C. The samples were allowed to cool in the furnace before being analysed. Other samples of A$\text{Al}_2$N powder were placed in quartz capsules 7cm long and 2cm in diameter which were evacuated to about 10$^{-4}$ Torr and sealed. These capsules were heated in a muffle furnace for different times at temperatures from 600-1400°C, and then allowed to cool in the furnace.

In order to study the wet oxidation of A$\text{Al}_2$N and to identify any oxidation products A$\text{Al}_2$N powder was treated with 30% (wt) hydrogen peroxide. About 0.5g. of A$\text{Al}_2$N was placed in a 250ml beaker with 125ml of H$_2$O$_2$ solution, covered with a clock glass and a) heated to the boiling point for 10 minutes, or b) stirred for 5 minutes and left at room temperature for 24 hours. The suspensions were then filtered and the residues left to dry uncovered at room temperature for 24 hours. The reaction of A$\text{Al}_2$N with water was studied by placing about 0.5g. of A$\text{Al}_2$N into 125ml of water and boiling for ten minutes when ammonia gas was liberated and a white precipitate formed which was removed by filtration and then dried for 24 hours in air.
3.8.3 Sputtered AîN

The AîN films were deposited by direct sputtering from a six inch diameter AîN target in a Nordiko sputtering system. Pure argon, nitrogen and a mixture of both were used as reaction gases to deposit the AîN films on GaAs, vitreous carbon and glass slides. The sputtering chamber was pumped down to $2 \times 10^{-7}$ Torr in 3-4 hours before sputtering. The sputtering gases argon and nitrogen were bled into the system through separate needle valves so that their pressure could be controlled separately. The general sputtering conditions were as follows:-

- Target to substrate spacing 6.4cm.
- Total pressure $3-5 \times 10^{-3}$ Torr.
- d-c Bias voltage 1-1.2KV.
- r.f. Power 150, 250, 300W.

3.8.4 Sputtered ZrN Layers

The ZrN films were deposited using reactive sputtering from a high purity elemental metal target. Details of this system can be found in the literature[96]. The ZrN layers were sputtered using the Dowty Electronic Limited special sputtering system. A GaAs wafer of (100) orientation was coated with the ZrN layer. The nitride was synthesised in a pure nitrogen atmosphere and the sputtering pressure was $\approx 2 \times 10^{-6}$ Torr. The residual atmosphere of $(1-2) \times 10^{-6}$ Torr was analysed using a spectrum scientific SM 1000M miniature mass quadrupole before each sputtering experiment. The deposition rate was 10nm/min. A target temperature of approximately 1000°C was obtained and this was sufficient to allow complete nitride synthesis to occur on the surface of the target rod. After each experiment the surface nitride was removed by sputtering in pure argon to provide a clean pure metal target surface and an effective gettering surface on the large area scale to exclude unwanted contamination.
from the diffusion pumped vacuum system. The thickness of
the coated ZrN layer was about 0.1–0.15\(\mu\)m. The deposition
time was about 15 minutes at an applied power of 400 watts
r.f. and a voltage of 2KV.
Chapter 4

Results for A2N

4.1 Introduction

This chapter is divided into three sections. In Section 4.2, the results from various deposited films which have been prepared by reactive evaporation of 99% pure aluminium metal in an atmosphere of nitrogen plus ammonia are described. The effect of rapid thermal annealing on the films and the substrates are also investigated. Section 4.3 deals with the results obtained from sputtered A2N films which have been deposited from an A2N target in an atmosphere of nitrogen, argon or a mixture of argon and nitrogen. Results obtained from the analysis of these films are presented in detail in this section. In Section 4.4 the results are given for experiments carried out on the thermal stability and resistance to oxidation of A2N powder.

4.2 Reactively evaporated A2N

4.2.1 Characteristics of the deposited films

Films were deposited on GaAs, carbon and glass slides and their thickness, measured using a talystep, were found to be in the range of about 50-200 nm. The appearance of the films proved to be a good guide to their chemical composition. Thus successful evaporation to form A2N gave a transparent film on a glass slide while the unsuccessful reaction produced films with a metallic colour which contained excess aluminium. Films composed of oxide/nitride mixtures had a brown colour.
4.2.2 RHEED results from as-deposited films

The quality of the deposited films was run dependent. Films containing an excess of unreacted aluminium (e.g. Fig. 4.1a) gave RHEED patterns exhibiting texture features and the observed orientation was (002) Al/(100) GaAs. Such films were deposited when experimental conditions were badly controlled during the evaporation process. An intermediate type of film having semi-metallic features and consisting of a mixture of Al and AlN was also observed. These composite films may have resulted from a slight change either in gas mixture, partial pressure or in evaporating rates. An example of the RHEED pattern obtained from this type of film is shown in Fig. 4.1b which shows that the intensity of the (101) diffraction line of AlN is apparently increased. This is because the (111) aluminium diffraction line of d=0.234nm coincides with the (101) line of AlN at 0.237nm. The low intensity of the (002) line from aluminium at 0.2025nm could be due to the fact that there is a small amount of unreacted aluminium on top of the AlN layer. An example of the RHEED pattern from a good quality AlN film prepared by the method described in Section 3.8.1 is shown in Fig. 4.2a. The measured d-spacings were compared with a standard RHEED pattern taken from powdered AlN and proved that the film was composed of AlN. An amorphous film of possibly aluminium oxide or hydroxide (Fig. 4.2b) was also deposited by this method. RBS results from this film showed the presence of Al, O and N and the oxygen content was higher than the nitrogen in this film.

4.2.3 RHEED results from annealed films

In order to examine the encapsulant properties and the subsequent changes of these films after rapid thermal annealing, samples were heated for a short time in nitrogen and then examined by RHEED. Results of RHEED analysis are summarised as follows:
a) Aluminium rich films are converted to oxide or oxynitride when annealed at temperatures above 900°C for a short time (30 secs) in a nitrogen gas flow. (Fig. 4.3a).

b) Films of good quality AlN showed no change in the structure of AlN after annealing even when annealed up to 1100°C. However some degree of grain growth was apparent since the diffraction lines became spotty following an anneal at a very high temperature. (Fig. 4.3b)

c) Al-AlN films showed the AlN pattern only after being annealed up to 950°C, this may indicate that the thin Al film on top of the AlN was evaporated during the annealing process at temperatures higher than the melting point of Al (660°C) (Fig. 4.4b).

d) Amorphous oxide, hydroxide or a mixture of both did not change after annealing at above 900°C.

4.2.4 RHEED results from acid treated layers after annealing

Hydroflouric acid was used to remove the thin film encapsulant after annealing. The AlN layer was found to be easily removed by this treatment. A sample of GaAs was implanted with Sn⁺ using an ion dose of 5 x 10¹⁴ cm⁻² at 300 keV, encapsulated with AlN and then annealed at 1000°C. After annealing, the encapsulant was dissolved by treatment with HF for a few seconds. The RHEED pattern showed that the AlN had been dissolved and that most of the ion implantation damage to the GaAs crystal had been removed (Fig. 4.4a).

The encapsulating films which contained mainly Al and which gave oxide or oxynitrides when annealed in nitrogen, did not dissolve easily in concentrated HF. The RHEED patterns obtained from such films after HF treatment showed that the oxides or oxynitrides formed during annealing were still present. Al-AlN films showed traces of remaining encapsulant after annealing and etching (Fig. 4.5a).
4.2.5 The effect of water on good quality AaN films

An experiment was carried out to check the reactivity of good quality AaN thin films with water. A good quality AaN film giving a RHEED pattern as shown in Fig. 4.2a was boiled in water then examined again using RHEED. The RHEED pattern obtained for such a film showed a $\gamma$-A\textsubscript{6}O\textsubscript{13}OH pattern (see Fig. 4.5b). Measured d- spacings were found to be in good agreement with ASTM card no (21-1307) for $\gamma$-A\textsubscript{6}O\textsubscript{13}OH (see Section 4.4.3).

4.2.6 RBS analysis of as-deposited films on carbon

Films deposited on vitreous carbon substrates were analysed by Rutherford backscattering spectroscopy (RBS). The films were found to contain aluminium, nitrogen and oxygen only. A series of samples was examined and it was found that the nitrogen to oxygen ratio varied for different experiments. This variation indicated the non-reproducibility of the process for the formation of AaN films. Three main types of spectrum were observed. Fig. 4.6a shows an example of the first type in which only aluminium and oxygen were detected and which indicates the oxide or hydroxide nature of the layer. Fig. 4.6b is an example of the second type of spectrum in which oxygen, aluminium and some nitrogen were detected. This may indicate that the deposited layer contained a mixture of oxide and nitride. In the third type of spectrum shown in Fig. 4.6c the nitrogen peak and the aluminium are dominant but some oxygen contamination is apparent in the film. This oxygen contamination may have occurred due to slight changes in the operating conditions in the deposition chamber. Alternatively, it may be due to pick-up of oxygen by the AaN film during the delay between film formation and subsequent analysis (a few days).
a: RHEED pattern of metallic aluminium rich film obtained from unsuccessful deposition of AlN on GaAs. Arcing on the rings shows preferred orientation of (002) Al on(100) GaAs. The pattern is that of face centre cubic aluminium metal.

b: RHEED pattern of Al-AlN film obtained from partially reacted aluminium with N₂-NH₃ gas mixture rings belong to Al face and to AlN.

Figure 4.1
a: RHEED pattern from good quality AlN on (100) GaAs. Most of the evaporated aluminium is expected to react with the gas mixture to form AlN. The (002) reflection absent because the C-axis is parallel to the substrate.

b: RHEED pattern from amorphous surface layer. Possibly aluminium oxide or hydroxide formed because of a poor vacuum.

Figure 4.2
a: RHEED pattern of possible aluminium oxide pattern obtained from aluminium rich film annealed in nitrogen flow using graphite strip heater for (30 secs). This type of pattern predominates for all Al-rich films annealed using this method. This film proved impossible to remove by conc. HF.

b: RHEED pattern obtained from good quality film of AlN heated up to 1100°C, the observed structure is AlN, discontinuities of the rings is due to the formation of coarse grained crystals.

Figure 4.3
a: RHEED pattern from good quality AIN on GaAs annealed at 1000°C for 30 secs and the AIN film was removed after annealing using conc. HF revealing single crystal pattern of GaAs. This indicates the recovery of the damage caused to the GaAs crystal by the ion implantation with a dose of $5 \times 10^{14}$ Sn+ cm^{-2} at 60 KV.

b: RHEED pattern from good quality AIN film on (100) GaAs annealed at 950°C. Observed improved ring sharpness indicates better crystallinity due to the annealing process.

Figure 4.4
a: RHEED pattern from GaAs sample annealed at 950°C. The pattern shows spots from the single crystal GaAs. The traces of the remaining encapsulant after etching appeared as rings imposed on the single crystal pattern.

b: RHEED pattern obtained from an evaporated thin AlN film boiled in water (γ-AlOOH).

Figure 4.5
Fig. 4.6. RBS spectra obtained from evaporated AlN deposited on vitreous carbon. 1.5 MeV $^3$He$^+$ beam with a beam spot of 1mm$^2$ was used for the analysis.
4.3 Sputtered aluminium nitride

4.3.1 RHEED results

A series of experiments was carried out to sputter AlN films onto GaAs and glass substrates. Early sputtering experiments using an AlN target in nitrogen gas gave films with the RHEED patterns of amorphous material. A sputtered film obtained in a mixture of argon and nitrogen was polycrystalline AlN, as shown by the RHEED pattern in Fig. 4.7a. This textured film was identified according to the ASTM data Card No. 25-1133 for AlN. The observed broadening of the different rings is probably due to the distortion of the sputtered AlN crystal caused by the high speed at which it was deposited on the substrate. The orientation of the deposited AlN was varied and run dependent. The main observed epitaxial relationship of the AlN film grown on (100) GaAs is that the c-axis of the AlN film lay perpendicular to the substrate surface. Thick films of the order of 200nm and more proved to be deposited layers of crystalline AlN when examined by RHEED. This was true whether nitrogen or nitrogen/argon was used during sputtering. An unidentified RHEED pattern was also detected. This may have been due to the surface contamination of the target which required a long cleaning period before being used to coat the substrate with an AlN layer. Another example Fig. 4.7b shows a RHEED pattern obtained from the surface of a thick film of AlN (>1μm) sputtered in nitrogen/argon. In this figure the arcing indicates preferred orientation of the type (100). Some of the measured d-spacings from this pattern belong to AlN while others which cannot be identified may belong to other materials such as aluminium oxide or oxynitride.

4.3.2 X-ray diffraction results

Thicker films were sputter-deposited on GaAs and glass slides and were examined using CuKα radiation and a Philips X-ray diffractometer. Typical results obtained from such
films are shown in Fig. 4.8. Fig. 4.8a shows the results obtained from a film sputtered on GaAs using a nitrogen/argon mixture. Only AlN diffraction peaks are present (identified according to ASTM data Card No. 25.1133 for AlN), and the preferred orientation of the (002) plane of AlN on the (100) plane of the GaAs substrate is apparent. The single peak due to the (400) line of GaAs is dominant and can be obtained from (100) orientated single crystal GaAs. It appears at \( \theta = 66^\circ \) and has a "d" value of 0.141 nm.

The X-ray diffraction pattern (Fig. 4.8b) obtained from a film sputtered in argon gas showed that it was amorphous. This amorphous film had a metallic appearance and electron probe analysis showed that it contained N, O, Al and some argon. The presence of argon indicated that the argon ions had sufficient energy to enter the lattice during deposition. This energy may also have been sufficient to cause the break down of AlN molecules in the deposited thin film and to destroy the crystallinity of the deposited films. A standard X-ray diffraction pattern taken from powder AlN is shown in Fig. 4.8c for comparison.

4.3.3 Rutherford backscattering analysis

Backscattering spectra of the samples sputtered by either argon and nitrogen or argon/nitrogen mixture were analysed, using \(^4\)He\(^+\) ion beam, oxygen, nitrogen and aluminium were detected. The lowest oxygen content was found in those films which had been prepared by sputtering the target AlN in a mixture of nitrogen and argon gases. An RBS spectrum from such a film is shown in Fig. 4.11. Thin films sputtered in nitrogen or argon were shown to contain oxygen, nitrogen and aluminium.

4.3.4 Scanning electron microscopy and X-ray elemental analysis

Scanning electron microscopy provides information concerning the surface topography. Films sputtered in nitrogen or argon or mixture of nitrogen-argon showed smooth surfaces. The elemental analysis of the sputtered layers was carried out using a 10keV electron-beam. The characteristic X-rays from elements present showed that only oxygen, nitrogen and aluminium were present in those films sputtered in nitrogen or nitrogen/argon mixture. An example of this type of films is shown in fig. 4.9. However, Fig. 4.10 reveals the presence of traces of argon in the films sputtered in argon gas, but this is not seen in Fig. 4.9.
a: RHEED pattern from sputtered thin AlN film on (100) GaAs substrate using Nordiko sputtering machine (Film deposited under $3 \times 10^{-3}$ Torr gas mixture partial pressure and $N_2:Ar$ ratio 3:2).

b: RHEED pattern from surface of AlN film of 1.3μ thick on (100) GaAs showing preferred orientation on (100). Some of the arcs belong to AlN others are unidentified possibly Aluminium oxide or oxynitride (elemental analysis showed Al, O, N are only elements present in this film).

Figure 4.7
Figure 4.8 X-ray diffraction patterns of sputtered AlN thin film on (100) GaAs

a) nitrogen/argon mixture
b) argon gas
c) standard pattern from AlN powder
Fig. 4.9 X-ray spectrum obtained by electron probe micro analysis for sputtered AlN thin film on (100) GaAs. Sputtering was carried out by nitrogen-argon mixture at $3 \times 10^{-3}$ gas partial pressure and 300W reflecting power. Film thickness = 300nm. Electron beam energy = 10 keV. Counting time = 300 sec. Detected elements: Al, O, N, Ga, As only.
Fig. 4.10 X-ray spectrum obtained by electron probe micro analysis of AlN thin film sputtered by argon gas only - condition of sputtering was 3 x 10^{-3} gas partial pressure 300W reflecting power film thickness = 1.3μ, colour metallic, E-beam energy: 10 keV, Element detected: Al, O, N, Ar, Ga, As. Counting time = 300 sec.
Fig. 4.11 RBS spectrum obtained from sputtered AlN thin film using nitrogen-argon gas mixture and deposited on carbon substrate using 1.5 MeV 4H+ ions.
4.4 A\textit{\textsc{afn}} powder

The thermal stability of A\textit{\textsc{afn}} powder has been investigated using reflection high energy electron diffraction (RHEED) and X-ray diffraction. A\textit{\textsc{afn}} powder was treated thermally and chemically to assess its resistance to oxidation and to identify the phases formed. This was done not only to collect more information about the inertness of this compound but also to assist in the interpretation of the electron diffraction results obtained as a result of the annealing of the A\textit{\textsc{afn}} films. A comparison between these films and the sputtered or evaporated films was also of interest.

4.4.1 Oxidation resistance of A\textit{\textsc{afn}} powder

Table 4.1 shows the results obtained for A\textit{\textsc{afn}} heated in air for 3 hours. The X-ray diffraction analysis gives the composition of the bulk sample and the RHEED analysis gives that at the surface layer to a depth of a few nanometers. The typical RHEED pattern of the A\textit{\textsc{afn}} powder at room temperature is shown in (Fig.4.12a). For A\textit{\textsc{afn}} heated to 1000°C the RHEED analysis revealed the presence of an unidentified phase "x" (Fig. 4.12b) which is possibly oxide or oxynitride [see Section 6.4.1]. However, on heating to 1200°C, the A\textit{\textsc{afn}} was oxidized to \(\alpha\)-Al\textsubscript{2}O\textsubscript{3} (Fig. 4.12c) but still contained a second phase on the surface which had a strong unidentified diffraction line at 0.288nm (see Table 4.2).

4.4.2 Thermal stability of A\textit{\textsc{afn}} powder

The samples of A\textit{\textsc{afn}} heated in vacuo in quartz capsules for 24 hours at temperatures from 600-1400°C contained only A\textit{\textsc{afn}} when analysed by both X-ray diffraction and RHEED. Table 4.2 shows the d-spacings of phase "x" obtained from the RHEED
pattern of A\textsuperscript{2}N heated in air at 1000\degree C and also shows the
d-spacings obtained from A\textsuperscript{2}N heated in air at 1200\degree C and in
VACUO at 1400\degree C.

4.4.3 Reaction of A\textsuperscript{2}N powder with boiling water

The measured d-spacings of $\gamma$-Al\textsubscript{2}O\textsubscript{3} (Fig. 4.12d) obtained
from the surface of A\textsuperscript{2}N reacted with boiling water are
listed in Table 4.2 and the standard A\textsuperscript{2}N and $\alpha$Al\textsubscript{2}O\textsubscript{3} are
included for comparison.
a: Standard RHEED pattern taken from powder AIN at room temperature.

b: RHEED pattern from AIN powder heated at 1000°C.

c: RHEED Pattern obtained from AIN heated at 1200°C.

d: RHEED pattern obtained from AIN reacted with hot H2O (γ-A1OOH).

Figure 4.12
Table 4.1

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Phases present after heating for 3 hours</th>
<th>XRD analysis (bulk)</th>
<th>RHEED analysis (surface)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>AIn</td>
<td>AIn</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>AIn</td>
<td>AIn</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>AIn</td>
<td>phase &quot;X&quot;</td>
<td>(see also Section 6.4.1)</td>
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<tr>
<td>1200</td>
<td>α-Al₂O₃</td>
<td>phase &quot;X&quot; + α Al₂O₃</td>
<td></td>
</tr>
<tr>
<td>1400</td>
<td>α-Al₂O₃</td>
<td>α-Al₂O₃</td>
<td></td>
</tr>
</tbody>
</table>

*annealing in vacuo showed no sign of oxidation even for sample heated up to 1400°C for more than 24 hours.
# Table 4.2
Lattice d-spacings (nm). RHEED Patterns from surface of oxidized A\textit{f}N Powder

<table>
<thead>
<tr>
<th>Standards</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Standard RHEED Pattern of A\textit{f}N</strong></td>
<td><strong>A\textit{f}N heated to 1400°C in Vacuo</strong></td>
</tr>
<tr>
<td><strong>d(nm)</strong></td>
<td><strong>I</strong></td>
</tr>
<tr>
<td>0.346</td>
<td>S</td>
</tr>
<tr>
<td>0.272</td>
<td>VS</td>
</tr>
<tr>
<td>0.250</td>
<td>M</td>
</tr>
<tr>
<td>0.238</td>
<td>VS</td>
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<tr>
<td>0.183</td>
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<tr>
<td>0.175</td>
<td>M</td>
</tr>
<tr>
<td>0.159</td>
<td>M</td>
</tr>
<tr>
<td>0.155</td>
<td>S</td>
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<tr>
<td>0.144</td>
<td>S</td>
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<tr>
<td>0.131</td>
<td>S</td>
</tr>
<tr>
<td>0.118</td>
<td>M</td>
</tr>
<tr>
<td>0.115</td>
<td>M</td>
</tr>
</tbody>
</table>

**Comments**

| In good agreement with ASTM data Card No.251133 | In good agreement with ASTM data Card No.10-173 | Good agreement with A\textit{f}N at room temperature | Unknown phase "X" formed | Mainly \(\alpha-\text{Al}_2\text{O}_3\) some unknown phase "X" formed | \(\gamma-\text{Al}_4\text{O}_9\) Boehmite formed |

**Footnote**

d(nm) = inter planar spacing.
I = intensity.
Chapter 5

Results of ZrN

5.1 Introduction

In this chapter the experimental results obtained from ZrN thin films on GaAs will be presented in detail. This chapter includes results obtained using RHEED, SEM, Electron probe micro-analyser and RBS from ZrN films as deposited, annealed and etched to remove the layer.

5.2 RHEED results

5.2.1 Results from as-deposited and annealed samples

Table 5.1 shows the electron diffraction results obtained from a series of ZrN films as deposited and annealed at various temperatures. The diffraction patterns reveal the crystallographic structure of the surface layer and provides information about the crystallinities and the phases present. The as-sputtered layer of ZrN, Tables 5.2 and Fig. (5.1a), shows a typical, fine structure of ZrN with a ring pattern and is in good agreement with the ASTM data card for cubic ZrN. After annealing at 500 and 600°C (Fig. 5.1b) the only observed change was that some arcing of the rings occurred indicating that the finely grained ZrN had become course grained as a result of annealing. At 700°C a change in the RHEED pattern was recorded and ZrO₂ was detected together with some faint rings of another phase (not identified). After annealing at a temperature of 800°C, RHEED showed clearly the monoclinic phase of ZrO₂, (Table 5.2 and Fig. 5.1c). However at 900°C this pattern changed to cubic ZrO₂, (Table 5.2 and Fig. 5.1d) and only the cubic phase of ZrO₂ was observed. The RHEED pattern from the annealed sample at 1000°C again shows clearly the
cubic phase of ZrO₂ plus some other rings which were found difficult to relate to any other ZrO₂ phase, but which were definitely not ZrN. This can be seen in Fig. (5.1e).

5.2.2 Etching characteristics

A series of diffraction patterns were obtained from the ZrN samples annealed in the temperature range of 500-1000°C. These samples were treated with HF acid to remove the ZrN layer after the annealing process. The ZrN layer should be easily removed by HF acid unless some change has occurred due to heat treatment whereby the ZrN is converted into a compound which is not easily etched. It can be seen from Table 5.1 and Fig. (5.1e), that the typical RHEED pattern for single crystal GaAs was observed from samples annealed up to 600°C after removing the ZrN layer. The RHEED pattern from the sample annealed at 700°C showed no ring or spot pattern. This is possibly due to contamination of the surface by an amorphous material which would mask the diffraction pattern. As can be seen from the SEM micrograph, at this temperature some islands of precipitates are left on the surface. Ring and spot patterns were detected for samples annealed at 800°C (Fig. 5.1f), with the rings belonging to ZrO₂ and the spots to single crystal GaAs and with the ring pattern identical to that observed before the acid treatment. Samples heated at 900°C and 1000°C showed no RHEED pattern. This may relate to the surface roughness of the examined samples which causes the scattered electrons to obscure the diffraction pattern.

5.3 Scanning electron microscopy

5.3.1 As deposited and annealed samples

ZrN layers on GaAs have been examined using the facilities in the Department of Materials Science and Engineering. SEM micrographs provided useful information concerning the surface topography of the deposited films and on the
Figure 5.1

Set of RHEED patterns obtained from ZrN thin films on GaAs annealed at different temperatures and showing changes occurring as a result of the annealing.

See next page for Figure 5.1 (d) (e) (f) and (g)
(d) annealed at 900°C for 30 secs.

(e) annealed at 1000°C for 30 secs.

(f) annealed at 600°C then treated with HF acid for 10 secs (showing the typical RHEED pattern of GaAs single crystal).

(g) annealed at 800°C and treated with HF acid for about 20 minutes showing rings from the remaining encapsulant and spots from the GaAs.
subsequent changes resulting from thermal treatment for 30 secs in the range of temperatures between 500-1000°C. The as-deposited layer had a smooth surface and no visible changes were observed after annealing up to 600°C (See Fig. 5.2a and Table 5.1). At higher temperatures of 700°C and above, the layer started to form bubbles (Fig. 5.2b). This is probably due to the vapour pressure of arsenic formed by the decomposition of GaAs. It can be seen Fig. 5.2c that some of the bubbles have burst. Oxidation has also started to occur as shown by the RHEED and X-ray elemental analysis results. The oxidation at the ZrN layer may have enhanced the out-diffusion of the arsenic into the coating layer. This phenomenon seemed to occur at temperatures between 700-1000°C.

5.3.2 Acid treatment of annealed films

Annealed films were treated with concentrated HF to remove the encapsulant and to reveal the substrate surface. It can be seen from Table 5.1 that the surface did not deteriorate at temperatures up to 600°C and that the GaAs surface remained smooth. At 700°C the SEM micrograph Fig. 5.3a showed that traces of the encapsulating layer remained. At temperatures greater than 700°C, some of the coating layer had not dissolved in the HF acid. This remaining layer may be an oxide or an alloy resulting from the reaction of the encapsulant layer with the substrate surface and this can be seen in Fig. 5.3b. This micrograph has been taken from a sample annealed at 800°C and then treated with conc. HF acid.

5.4 X-ray elemental analysis

5.4.1 As deposited and annealed films

Although the light element detector attached to the electron probe analyser in the Department of Materials Science and Engineering has not been extensively used, it has proved to
be very useful (in the present work) and important
information has been obtained, especially for films or bulk
materials containing oxygen and nitrogen. It is clear from
Table 5.1 and Fig. 5.4a that the elements present in the
coating layer and the GaAs substrate are Zr, Ga, As, O and
N. The Ga and As peaks are from the substrate and this was
confirmed by analysing a reference sample of GaAs before
coating.

Zr and N come from ZrN and the oxygen is either due to the
contamination which occurred during the deposition process
or absorption from the atmosphere. ZrN samples annealed at
700°C and above showed a decrease in the nitrogen peak and a
significant increase in the oxygen peaks. Nitrogen signals
were not detected from the spectra obtained from ZrN samples
annealed at 800°C-1000°C and the oxygen peak intensity
increased sharply. This can be seen in Fig. 5.4c.

5.4.2 Acid treated films after annealing

Table 5.1 shows that elements remaining after washing of the
annealed ZrN samples with concentrated hydrofluoric acid,
were Ga and As only. No signal from zirconium was detected
from samples annealed up to a temperature of 700°C. However,
it took a slightly longer time to remove the encapsulant
from the sample annealed at 700°C compared with those
annealed at lower temperatures. For the samples annealed at
800°C and above, some of the encapsulant remained
undissolved despite prolonged treatment in HF acid.
Fig. 5.4c shows a typical spectrum obtained from a ZrN
sample annealed at 800°C and treated with HF acid for about
20 minutes. In this spectrum a Zr signal can be detected.
This was confirmed by the SEM micrograph and the RHEED
pattern which both proved that some of the ZrN layer was
left on the surface. All the samples annealed at
temperatures between 800-1000°C gave similar results.
Figure 5.2

SEM micrographs of ZrN thin films on GaAs annealed at different temperatures showing changes of surface morphology as a result of the annealing process.
Figure 5.3

SEM micrographs of ZrN samples annealed and treated with HF acid to remove the encapsulant.
Fig. 5.4 X-ray spectra obtained by electron probe micro analyser provided with light element detector. The operating condition used was a 10 keV beam energy and a counting time of 300 secs.

(a) As deposited ZrN on (100) GaAs. Showing the elements present are Zr, N, O, Ga and As.

(b) Annealed at 800°C signals from Zr, O, Ga and As only detected.

(c) Annealed at 800°C for 30 secs then washed with HF acid for 20 minutes. Elements detected are Zr, O, Ga and As. Zr and O are probably from the remaining undissolved layer.
5.5 Rutherford backscattering analysis

The RBS technique was used to determine the elements present in the ZrN layer a) as deposited, b) after annealing. RBS provides information concerning the amount of the damage in the GaAs substrates and it can detect contamination of the surface after the removal of the encapsulant. Only a zirconium signal was detected from the as-deposited and annealed samples. Light elements such as oxygen and nitrogen are obscured by the yields from the Ga and As in the GaAs substrate.

ZrN layers annealed and then treated with HF to remove the encapsulant were examined and the results are shown in Table 5.1 and Fig. 5.5. These results show that no damage occurred to the samples annealed up to 600°C and the calculated damage parameters were similar to that for the GaAs substrate. The sample annealed at 700°C had a $X_{\text{min}}$ value of 8%. This value is slightly higher than that for good crystalline material, i.e. $X_{\text{min}} \approx 4-5\%$. This might indicate the presence of surface damage. The RHEED pattern obtained from the surface of this sample was also that of non-crystalline material.

Samples annealed at 800°C and 900°C gave RBS spectra from which calculated values for $X_{\text{min}}$ of 35% and 57% were obtained respectively. The samples also gave a Zr signal indicating the presence of some of the encapsulant. This result confirms those obtained by other techniques used and shows that some of the encapsulant remains and that the GaAs substrate becomes damaged.
Fig. 5.5 RBS spectra obtained from HF acid treated ZrN on GaAs (A) Random spectrum (B) ZrN/GaAs annealed at 900°C/30 secs (C) Annealed at 800°C/30 secs (D) Annealed at 700°C/30 secs (E) Annealed at 600°C/30 secs (F) Virgin sample of GaAs (G) Expanded spectra showing Zr signal from samples annealed at (1) 300°C and (2) 900°C.
<table>
<thead>
<tr>
<th>Anneal Temp.</th>
<th>X-ray elem. analysis</th>
<th>Elem. present in RBS</th>
<th>Phases present in RBS</th>
<th>Time needed to remove the layer</th>
<th>Results from acid treated films</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room</td>
<td>Zr,N,?O, Ga,As</td>
<td>Zr,N,?O, ZrN cubic</td>
<td>Zr,N,?O, ZrN cubic + arcing of rings</td>
<td>&lt; 10 secs smooth substrate surface</td>
<td>Layer removed Ga,As, Ga,As, Ga,As, Ga,As, No Patt contaminants surface</td>
</tr>
<tr>
<td>500</td>
<td>Smooth surface</td>
<td>Smooth surface</td>
<td>Smooth surface</td>
<td>&lt; 10 secs smooth surface</td>
<td>Layer removed Ga,As, Ga,As, Ga,As, Ga,As, No Patt contaminants surface</td>
</tr>
<tr>
<td>600</td>
<td>Smooth surface</td>
<td>Smooth surface</td>
<td>Smooth surface</td>
<td>&lt; 10 secs smooth surface</td>
<td>Layer removed Ga,As, Ga,As, Ga,As, Ga,As, No Patt contaminants surface</td>
</tr>
<tr>
<td>700</td>
<td>Bubbles started to form</td>
<td>Zr,N,?O, ZrN cubic + arcing of rings</td>
<td>Zr,N,?O, ZrN cubic + arcing of rings</td>
<td>&lt; 20 secs traces of islands left</td>
<td>Layer remained</td>
</tr>
<tr>
<td>800</td>
<td>Some bubbles have burst revealing the substrate</td>
<td>Zr,N,?O, ZrN cubic + arcing of rings</td>
<td>Zr,N,?O, ZrN cubic + arcing of rings</td>
<td>&lt; 20 mins Layer remained</td>
<td>Layer remained</td>
</tr>
<tr>
<td>900</td>
<td>Same as above</td>
<td>Zr,N,?O, ZrN cubic + arcing of rings</td>
<td>Zr,N,?O, ZrN cubic + arcing of rings</td>
<td>&lt; 20 mins Layer remained</td>
<td>Layer remained</td>
</tr>
<tr>
<td>1000</td>
<td>Same as above</td>
<td>Zr,N,?O, ZrN cubic + arcing of rings</td>
<td>Zr,N,?O, ZrN cubic + arcing of rings</td>
<td>&lt; 20 mins Layer remained</td>
<td>Layer remained</td>
</tr>
</tbody>
</table>
### Table 5.2

Lattice d-spacings (nm) taken from A RHEED patterns of the surface of ZrN as deposited and after annealing

<table>
<thead>
<tr>
<th>As deposited ZrN</th>
<th>After annealing ZrO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cubic</td>
</tr>
<tr>
<td>ASTM 35-753</td>
<td>Measured</td>
</tr>
<tr>
<td></td>
<td>Fig.5.1a</td>
</tr>
<tr>
<td>d(nm)</td>
<td>d(nm)</td>
</tr>
<tr>
<td>0.264</td>
<td>0.261</td>
</tr>
<tr>
<td>0.228</td>
<td>0.227</td>
</tr>
<tr>
<td>0.161</td>
<td>0.158</td>
</tr>
<tr>
<td>0.138</td>
<td>0.135</td>
</tr>
<tr>
<td>0.132</td>
<td>0.130</td>
</tr>
</tbody>
</table>

Extra lines were also found which are thought to belong to other ZrO₂ phases.
Chapter 6

Discussion

6.1 Introduction

This chapter begins with a discussion of the RHEED technique followed by a general discussion of the encapsulation of GaAs. The experimental results of the chemical reactivity of AIN powder are treated in Section (6.3). Discussion of the results of evaporated AIN are presented in Section (6.4) followed by the results of sputtered AIN and ZrN films in Sections (6.5) and (6.6) respectively.

6.2 RHEED

The RHEED apparatus has been improved and re-organised for this project. It was re-calibrated and the best operating conditions were chosen. The apparatus was adapted to study semiconducting materials after exhaustive attempts to achieve reliable results. The camera constant has been found using several standard materials. The accuracy has been checked, and was found to be within the accuracy limit of the RHEED method. The accuracy could be improved if careful measurements were taken, and the specimen size was similar to that of the standard materials (i.e. if "L" the distance from the specimen to the plate is kept constant).

The best results were obtained for different semiconducting materials and metal thin films when the operating voltage was fixed. The RHEED method is a direct and non-destructive technique, in which the specimen could be used again for further testing and measurements.

The RHEED method could be used for identification when an X-ray study is not possible. The X-ray method is more reliable and more accurate in identification of unknown materials, than the RHEED method. An accuracy of about 1-2% could be achieved by using this method[89,92].
The accuracy of the RHEED apparatus was checked by using the calculated camera constant and ring measurements obtained from aluminium sheet, a cobalt sample and titanium nitride (see Appendix 3). An error of less than 1% was achieved in the calculated d-spacings.

6.3 General review of encapsulation

6.3.1 Encapsulation of GaAs and III-V compounds

The most persistent problem in the ion implantation of III-V compounds is the need for effective and reliable methods of protecting these surfaces from thermal decomposition during annealing. This is a necessary process to remove the damage produced by the implanted ions and to make them electrically active[1].

III-V compounds exhibit preferential evaporation of the Group V constituent from unprotected surfaces. Such decomposition occurs at about 660°C for GaAs[16] and about 360°C for InP[17]. As a result of this process, the electrical and optical characteristics of the GaAs and InP surfaces can be seriously degraded. Some work has been carried out on capless annealing to avoid general problems associated with encapsulation.

Capless annealing has been carried out in an arsenic ambient and in a face-to-face configuration[59]. Mixed results have been reported for the effectiveness of this method and surface defects were observed in samples treated in this way[97]. Because the capless technique allows decomposition to occur, even during rapid thermal annealing, at temperatures of 900-950°C[98], the technique is unlikely to be universally acceptable. In the future, it is expected that annealing temperatures in the range 1000-1100°C may be
required to activate high dose implants necessary for producing ohmic contact regions and this can be achieved only with the use of an encapsulant.

6.3.2 Deposition techniques and problems

Various encapsulants have been used in the past; films such as SiO₂, Si₃N₄, phosphorous or arsenic doped glass, and multilayers of, for example, SiO₂ and Si₃N₄, have been deposited by various techniques with the aim of finding a suitable thin film encapsulant able to withstand temperatures up to 1100°C.

In the case of SiO₂, many reports showed that considerable amounts of gallium diffuse out into the oxide from the GaAs substrate during annealing. However, there have been some recent reports of the use of SiO₂ up to temperature of about 1000°C[99] and 1100°C for short times[100].

The most widely used encapsulant, Si₃N₄, has been prepared in various ways such as by reactive deposition from a plasma of silane and nitrogen, r.f. sputtering from a Si₃N₄ target or chemical vapour deposition from a mixture of silane and ammonia (CVD). Plasma enhanced reaction (PECVD) between silane and nitrogen/ammonia at temperatures of about 200-350°C has the advantage of a low temperature of deposition and that a low oxygen content is attainable in such films[101].

However in the case of CVD Si₃N₄, it is necessary to heat the samples to the deposition temperature of about 650-700°C in a very short time (5-6 sec) which is difficult to do on an industrial scale. It has been reported that oxygen free Si₃N₄ films can be grown at 700°C and these films are satisfactory encapsulants for annealing Si implanted GaAs[101,102]. Also the CVD silicon nitride films prepared in the Department of Electronic and Electrical Engineering of the University of Surrey proved to be effective
encapsulants for all doses and implanted ions up to 950°C[98]. This type of film has been used up to 1200°C for very short times (3 sec) using electron beam annealing[34].

A comparative study of Si\textsubscript{3}N\textsubscript{4} films prepared either by sputtering from a target of Si\textsubscript{3}N\textsubscript{4} or reactively sputtered have contained an oxygen content of about 18\% for films sputtered from an Si\textsubscript{3}N\textsubscript{4} target and less for those which were reactively sputtered. These films will not be satisfactory until better control of the oxygen content can be achieved[2]. The oxygen distribution in the deposited films is said to be responsible for the out-diffusion of Ga or As[2,13,39].

PECVD Si\textsubscript{3}N\textsubscript{4} layers have been reported to be good up to about 1050°C[103]. The rapid thermal annealing technique was used to anneal GaAs samples implanted with Si\textsuperscript{+} ions up to doses of 7.5 \times 10\textsuperscript{13} cm\textsuperscript{-2}. It was also reported that the same cap does not work for those samples implanted with higher doses of Si. It is believed that when an amorphous layer forms due to the implantation of a high dose of Si, the PECVD Si\textsubscript{3}N\textsubscript{4} does not work because of the large strain at the Si\textsubscript{3}N\textsubscript{4}—GaAs interface.

There are very few publications on the composite Si\textsubscript{3}N\textsubscript{4}/SiO\textsubscript{2} cap. However transient annealing at a temperature of 900–1140°C for short times of 30 and 10 secs have been reported[104]. This composite encapsulant consisted of 0.1\textmu m of Si\textsubscript{3}N\textsubscript{4} and 0.4\textmu m of SiO\textsubscript{2}. Another report[31] has shown that good thermal stability and a tolerance of anneals up to 1100°C was achieved using a multi-layer encapsulant of Si\textsubscript{3}N\textsubscript{4}/SiO\textsubscript{2}.

6.3.3 The annealing temperatures and the required material

It is clear that in the future, high annealing temperatures (1100°C) may be required and this poses new problems compared with those prevalent in current industrial processing. However annealing at high temperatures requires
only short processing times[15,98]. Therefore a new process, generally referred to as rapid thermal annealing has been developed in recent years. This includes the use of graphite strip heaters, optical furnaces and scanning electron beams. Such processing is likely to produce new problems. For example, strain, slip due to temperature non-uniformity, thermal expansion coefficient mismatch, etc.

Despite the fact that Si$_3$N$_4$ is used practically on an industrial scale, several reports have shown that these films failed as a cap above about 950-1000°C, but this result may depend on the method of deposition and other parameters such as ion dose, material etc. Hence, research is being continued to find a better encapsulant, for example, AlN, ZrN, etc.

AlN has emerged as a new candidate to replace Si$_3$N$_4$; however these films have not been as extensively studied as Si$_3$N$_4$. Thus AlN has not been transferred to an industrial scale, but recently a great deal of interest has been shown by many research laboratories in its effectiveness as an encapsulant for GaAs. Conflicting results were reported about the quality of AlN thin films for encapsulants for GaAs. Eisen et al.[105] reported that r.f. deposited oxygen rich AlN was a suitable encapsulant with good adherence. Gamo et al.[43] have demonstrated the possible use of aluminium oxy-nitride encapsulants. They have reported electrical results which are superior to those obtained from samples capped with Si$_3$N$_4$. The AlON had a high oxygen content of about 82% of the nitrogen content. These films were r.f. sputtered from an AlN target. The annealing temperatures used in this study were 900°C and 950°C for a time of 10 minutes. Bierly et al.[42] have used aluminium oxy-nitride films produce by low energy ion beam sputtering. The ion beam used consisted of Ar and N$_2$ and the target was aluminium of 99% purity. These films can withstand temperatures up to at least 900°C without visual deterioration and minimal inter-diffusion with the gallium arsenide substrate. They have also reported that the ability of these films to serve as encapsulants appears to improve as films closer to pure AlN
are deposited. Oknomara's work demonstrated the superiorit of reactively sputtered AaN with a low oxygen content which was below the sensitivity of RBS analysis[41]. Furthermore, AaN films of thickness >1.2μm were successfully deposited with no peeling or cracking following an anneal to temperatures up to 1000°C. Ohnishi et al.[106] have used AaN films of 100nm in thickness for passivation and the anneals were performed using tungsten-halogen lamps in a nitrogen atmosphere at temperatures up to 1050°C. They applied the lamp annealing method to n+ layer formation for self-aligned, WSi-gate, GaAs MESFETs. They demonstrated good results and have shown that this method was very effective. Onodora et al.[45] have used the through AaN implantation technique, a 55nm thick AaN layer was reactively sputtered on a semi-insulating GaAs substrate. Then Si ions were implanted through the AaN, followed by annealing at 850°C for 15 minutes. During annealing the AaN acted as an encapsulant. Then the tungsten silicide gate, self-aligned GaAs MESFETs were fabricated. They suggested that the GaAs MESFETs fabricated by this method are important for ultra high speed GaAs VLSI circuits.

6.3.4 New thin films candidates

It is appropriate at this stage to point out that there have been several studies concerning thin film Schottky barrier contacts to GaAs. One of the main characteristics being sought for such films is the thermal stability and reliability when subjected to high temperatures.

Recently for example, TiW, TiN, Ta silicide, WN and TiW silicide have been studied producing promising results; good electrical properties for Schottky barriers were reported at annealing temperatures as shown in Table 6.1. These compounds were suggested to be suitable materials for the gate of a self-aligned gate GaAs MESFET.
Table 6.1 suggested that some of the materials may be useful as encapsulants as well as for forming good Schottky barriers to GaAs. For example, WSi$_x$ has been proved to be stable to temperatures of 1050°C for 6 secs. A problem with these metallic conducting materials may possibly be the difficulty in removing them without affecting the properties of the GaAs surface.

It is clear from this discussion that no optimum method for protecting compound semiconductor surfaces during annealing can be identified.

To monitor the effectiveness of various thin film encapsulants, it is necessary to develop methods for assessing the film and its structure. The need for detailed composition and structure information concerning the thin film in the as-deposited state (prior to annealing) is important. After the anneal both thin film encapsulant and substrate must be critically examined in order to determine the effectiveness of the cap.

6.4 The chemical reactivity of powder AlN

The behaviour of AlN under various conditions was studied. This includes:

a) Heating in air

b) Exposure to atmospheric air
c) Reaction with H₂O₂
d) Heating in vacuo

These conditions were considered to be more severe than those which might be encountered in annealing GaAs samples capped with AIN thin films. The goal of this study was to obtain information about AIN which would assist in the evaluation of the effectiveness of the AIN thin films prepared by various techniques and then annealed at higher temperatures. The RHEED pattern taken from AIN powder (as supplied) was that of crystalline AIN, (see Fig. 4.12a and Appendix 2). The calculated d-spacings were in good agreement with the ASTM Card No. 25-1133 for AIN[113]. No contamination or oxides were detected. This indicated the good chemical stability of AIN in air at room temperature. Surface oxides or contamination would have obscured the RHEED pattern. Such chemical stability has been reported previously[114-117]. However, oxide layers of a few nanometers were reported to form on AIN single crystals and powders[118]. Such an oxide layer would definitely have given its own pattern.

6.4.1 The thermal stability in air

The AIN pattern remained unchanged up to a high temperature when AIN was heated in air (Table 4.1) and thus demonstrated good oxidation resistance up to 1000°C. A surface phase change was observed using RHEED. The crystal underneath was found to be unchanged and gave the X-ray diffraction pattern of AIN. Since the powder was heated in air, it is possible that an oxy-nitride phase or possibly an oxide phase formed on the surface (see Fig.4.12b). This unknown phase named (X) is similar to that of a proposed second phase of AIN published recently (No. 34-669)[110]. Further investigation of this phase suggested that an AIN-Al₂O₃ spinel can be formed by hot compression of pure AIN and Al₂O₃. This is a more likely possibility rather than the formation of a new AIN phase. If a new AIN phase should form during the annealing at high temperature, then the AIN powders annealed
should have given the same phase when annealed in the range 600-1400°C in VACUO. One report[120] of heating the nitride in air suggested that the nitride passed through an intermediate stage of oxy-nitride during oxidation. Furthermore the Al-rich films annealed in nitrogen gave a pattern similar to that obtained by heating the AIFN powder at 1000°C. Further work is needed to investigate the nature of this phase properly. The oxides of aluminium have a phase transformation from (γ, χ, σ, θ, α), and it is well known that α-Al₂O₃ is the most stable phase of the aluminium oxides[121]. α-Al₂O₃ was clearly identified by X-ray diffraction analysis and RHEED in those samples annealed at 1200°C in air, hence the end product of the oxidation process of AIN is α-Al₂O₃. This is confirmed by both RHEED and X-ray diffraction results (Table 4.1 and Fig. 4.12c). However, the pattern from the surface still contains weak traces of the line at 0.288nm from phase (X). Results obtained from this work were found to be in agreement with the work of Laverenko et al.[117]. They have shown that the oxidation rate of AIN was very low and only 8% of AIN was oxidized when heated in oxygen at 1100°C. Another piece of work by Long and Foster[116] has demonstrated that high purity AIN was found to be very stable and chemically inert to acids and bases and also remained un-oxidized when heated in air up to 1000°C. Oxides were formed only when AIN was heated in wet air at 700°C. These results are also in agreement with the results obtained in the present work.

6.4.2 The chemical reactivity

To check the reactivity of AIN during exposure to atmospheric moisture, AIN was left in air for a long period of time (24 hours). The electron diffraction pattern obtained from these exposed powders was AIN only. This again indicated the stability of AIN powder towards the atmospheric moisture. An attempt to oxidize AIN powder with a strong oxidizing agent (H₂O₂) either by boiling or by leaving the powders overnight in the peroxide, did not result in any evidence that oxides of aluminium had formed.
In a low oxygen pressure atmosphere AlN powder was heated under very severe conditions at 1400°C for 24 hours and 72 hours, but under these conditions no changes were observed. The observed pattern was still that of AlN. Thus AlN is stable at very high temperatures provided the oxygen pressure is low. Note that 1400°C is higher than required for annealing ion implanted GaAs. The reactivity of AlN with water was determined in order to obtain information about the phase formed. It was also important to find out whether AlN would dissolve completely in water or whether only the surface would react forming a barrier to further reaction. Clear evidence that the reaction had occurred was the liberation of NH₃. Prolonging the reaction did not dissolve the AlN even when extra water was added and boiling was continued. This was due to the formation of an aluminium oxide hydroxide layer which protected the underlying AlN from further reaction. The RHEED pattern of Fig.4.12d is from the surface, whereas the X-ray pattern showing AlN only was obtained from the bulk of the material. It has been reported that when AlN reacts with water Al(OH)₃[122] is formed. However, recent work by Paleau et al.[115] suggests that Al₂O₃ is formed. As a result of the hydrolysis of AlN, Al₂O₃ was identified using Rutherford backscattering analysis. The present work showed the presence of crystalline γ-AlOOH on the surface of AlN[123]. The measured d-spacing from the surface pattern matched that of the γ-AlOOH from ASTM Data Card No. 21-1307[124]. The listed lines (Table 4.2) showed the pattern obtained is γ-AlOOH only. Aluminium oxides or hydroxide or oxy-nitride patterns are too different to be confused with this structure. Furthermore, the X-ray diffraction pattern obtained from the same sample showed extra faint lines at d = 0.611nm, 0.317nm, 0.185nm due to γ-AlOOH, in addition to a strong diffraction pattern belonging to AlN. Only the fourth strong line of γ-AlOOH at d = 0.235nm is not seen clearly because it is blurred by the strong-diffraction line at 0.237nm from AlN. Since the RHEED technique analyses the surface only, to the depth of a few nanometers and the XRD
demonstrated the presence of mainly AlN plus extra faint lines, it is believed that γ-AlOOH has formed on the surface only and was responsible for preventing further reaction. A similar RHEED pattern of γ-AlOOH was obtained by treating an AlN thin film with hot water. This again showed that the reaction of AlN with H₂O produces γ-AlOOH. This comparative study was found very useful and the information obtained can be used in principle to understand the behaviour of AlN and it may help in the interpretation of the results obtained using various methods of thin film preparation and annealing.

6.5 Evaluation of evaporated AlN films

It was thought that the reactive evaporation method would be rather simple compared to a complicated process like sputtering[125]. If the reaction between the aluminium atoms and the reactive gas molecules (nitrogen and ammonia) can be made to occur at a low substrate temperature this could make such a method rather attractive for industrial applications.

6.5.1 Deposition and mechanisms of the reaction

The early attempts to deposit AlN thin films by evaporating aluminium in an atmosphere of nitrogen and ammonia were successful, but such a deposition was onto a substrate heated to between 300-1200°C[126] or to about 500°C and above[125]. These temperatures are considered undesirable for III-V compounds. It has been reported that the deposition temperature of dielectrics must be as low as possible to avoid damaging the substrate and to avoid the diffusion of impurities and changes of the dopant distribution[2].

The experiments being carried out in the Department of Electronic and Electrical Engineering are designed and developed to deposit AlN films on substrates such as GaAs,
InP and on ternary III–V compounds without preheating to activate the reaction. The equation of the reaction can be expressed as:–

$$2Al + 2NH_3 \rightarrow 2AlN + 3H_2$$

6.1

The reaction takes place at substrate temperatures above 300°C[126]. In the present work we assume the reaction occurs in the gas phase prior to deposition onto a substrate which is not preheated, the result shown in Fig. 4.2a proved that such a reaction is possible and AlN had formed. The film had a polycrystalline structure. By comparison with the RHEED pattern obtained from AlN (Fig. 4.12a) and by measuring the interplanar spacings, the film was found to contain a pure phase of AlN. This structure was established first by using an electron transmission diffraction experiment[127]. In this case, the AlN films were deposited by using an aluminium target which was reactively sputtered in an argon–nitrogen mixture. It was suggested that such crystalline AlN films were stoichiometric. In the reflection diffraction mode the surface structure only can be detected. Therefore the composition of the underlying layer cannot be assessed using RHEED alone. The low oxygen content in the deposited films, analysed by RBS, may suggest that the majority of the film was AlN. The control of the reaction to deposit stoichiometric AlN seems rather difficult and the formation of such films of good quality, was found to depend upon many factors. A good quality AlN film is defined as containing mainly AlN, having an interface free of oxide or elemental aluminium and being capable of being removed by HF acid.

6.5.2 Deposition parameters

Experimentally, the best films were found to form when the pressure in the chamber was held at about $10^{-3}$ Torr, and the substrate was positioned at a distance greater than 5cm from the filament, because the mean free path of the aluminium atoms is between 5–7cm at a pressure of $10^{-3}$ Torr.
Factors affecting film reproducibility depend to a large extent upon the process parameters. These parameters include reactive gas pressure, the evaporation rate, the presence of oxygen, water vapour or the presence of other gases. Also some contamination from vacuum pump oil vapour which may diffuse into the chamber can be expected. These factors would effect the formation of stoichiometric or near stoichiometric AlN. If all contaminating gases are eliminated, the only possible reaction is between the aluminium atoms and the reactive gas mixture.

This reaction may follow Equation 6.1. Water molecules might enter the chamber in the carrier gas (in this case nitrogen) and either dissociate near the filament into oxygen and hydrogen, react with newly formed AlN or react directly with aluminium to form aluminium oxide hydroxide[123,129].

\[
2\text{Al} + 2\text{H}_2\text{O} \rightarrow 2\text{AlOOH} + \text{H}_2 \\
\text{AlN} + 2\text{H}_2\text{O (vap)} \rightarrow \text{AlOOH} + \text{NH}_3
\]

Unreacted aluminium may be present in excess at the surface, at the substrate film interface or throughout the layer. This may be caused by sudden changes in the filament current which will increase or decrease the evaporation rate. This excess of aluminium would attract oxygen or water vapour immediately on exposure to air. The possible absorption of water onto freshly prepared films through micropores has also been reported; this absorption, explained by capillary action of water vapour into the microvoids of the low packing density films, results in changes in refractive index[25,130]. This result was obtained using the nuclear reaction analysis technique which detects the presence of water by monitoring the hydrogen content of the film as a function of depth. In the present work, RBS results have shown the presence of oxygen in the deposited films and the amount of oxygen was found to vary from run to run, the lowest occurring in the good quality film of mainly AlN and also has no oxide or free aluminium at the interface.
The types of deposited films may be simply classified into three kinds:

a) Good quality films which may contain mainly AlN, see RHEED Fig. 4.2a and RBS Fig. 4.6c.

b) Intermediate quality films which may contain AlN, Al₂O₃, Al(OH)₃, Al. See RHEED Fig. 4.1b and RBS Fig. 4.6b.

c) Poor quality films which consist mainly of unreacted aluminium with small amounts of other compounds such as AlN, Al₂O₃, Al(OH)₃ etc. See RHEED Fig. 4.1a, RBS Fig. 4.6a.

The reactions, which probably take place inside the chamber, are as follows:

2Al + 4H₂O → 2Al(OH)₃ + 3H₂ (see above)  

If the water vapour dissociates near the filament into hydrogen and oxygen, aluminium oxide can form.

4Al + 3O₂ → 2Al₂O₃

Aluminium carbide has not been detected by electron diffraction, and none of the other techniques used can detect carbon easily. It has been reported that aluminium carbide (Al₄C₃) can be made by heating the two elements together above 1000°C[48]. No evidence for the presence of Al₄C₃ has been observed.

Aluminium may also possibly react with carbon monoxide or dioxide. These two compounds originate from the oil vapour which decomposes by heat into carbon or CO or CO₂.

In the presence of carbon

4Al + 3C → Al₄C₃

This reaction takes place as reported in[118]

2Al + CO → Al₂CO
The aluminium oxy-carbide has the same structure as that of AlN and it is believed that Al₂OC is soluble in AlN up to 14%. It is difficult to observe this compound since it has the same lattice spacings as AlN. Only a sensitive analytical technique which can detect the Al-C bond may reveal the presence of such a compound eg. IR or XPS etc. It was not possible to use such techniques in this work.

Traces of air in the chamber due to leaks in the vacuum system may allow aluminium oxy-nitride to form as follows:

\[
\text{Al} + \text{O}_2 + \text{N}_2 \rightarrow \text{AlO}_x\text{N}_y
\]

Aluminium oxy-nitrides exist in five phases, as reported in the powder diffraction file. None of these was detected by electron diffraction. Whether the oxy-nitride was present in small quantities beneath the surface or present at the interface is unknown. It is difficult to detect by the available techniques used in this work. Small amounts are not detectable by X-ray diffraction and RHEED only detects material in the first 5nm approximately.

The reactivity with atmospheric moisture

The reactivity of the deposited films to atmospheric moisture is not clearly established. The hydrolysis of the deposited films may occur inside the chamber during the evaporation process. This reaction can be expected as a result of the collision between aluminium atoms and the residual water vapour or water molecules carried by the carrier gas. The hot water vapour surrounding the filament, if present, would definitely react with newly formed AlN as well as the aluminium.

The composition calculations obtained from RBS spectra of films deposited onto carbon substrates have revealed that the film is composed of mainly AlN and AlOOH with an excess of aluminium. The hydrolysis of the films might occur during the film deposition, or after film exposure to
atmospheric moisture since the RBS analysis was carried out a few days after the deposition. These results were confirmed by theoretical simulation of the spectra using the Ziegler programme[25,128]. In this simulation it was found necessary to assume the presence of one atom of hydrogen for 2 atoms of oxygen in the films in order to fit the theory to the experiments, despite the fact that no backscattering yield can be obtained from hydrogen. The presence of hydrogen in the films affects the density and therefore decreases the backscattered yield of helium ions, reducing the peak heights in the spectra collected.

Paleau et al.[115] have suggested that the oxygen atoms located near the surface of the film of AIN arise probably from partial hydrolysis of the deposited material by atmospheric moisture before RBS analysis. It was suggested that alumina is formed as a passive coating which then protects the material from further attack by water vapour. Their AIN films were deposited by the reaction of aluminium tribromide and ammonia in hydrogen gas flow in the temperature range 400-900°C. This effect was not observed in this work.

Experiments carried out in our laboratory in order to check the AIN film reactivity with water have revealed that γ-AlOOH was formed as a result of such a reaction. A film consisting of polycrystalline AIN changed into γ-AlOOH after boiling in water. This can be seen from the RHEED pattern shown in Fig. 4.5b. This effect is also confirmed by repeating the experiment using AIN powder reacted with hot water, see Fig. 4.12d.

In order to protect the evaporated AIN films from attack by atmospheric moisture, the AIN film was coated with a thin layer of aluminium immediately after deposition. Thin aluminium layers soon oxidized to Al₂O₃ or AlOOH once exposed to air. It has been reported that aluminium reacts with H₂O to form aluminium oxide hydroxide or with O₂ to form Al₂O₃[129]. The oxide-hydroxide is not a stable
compound and decomposes on heating into $\gamma$-Al$_2$O$_3$ above 150°C[122]. The oxide film would prevent further oxidation and act as a protective coat.

6.5.4 The effectiveness as an encapsulant

For the past few years aluminium nitride has been used successfully as a cap for ion implanted GaAs in the Department of Electronic and Electrical Engineering of the University of Surrey. The method of annealing was to use a graphite strip heater to thermal pulse anneal with the maximum temperature being reached in about 5-10 seconds. The few reports published demonstrate that good electrical properties can be achieved using evaporated aluminium nitride as an encapsulant[25,128]. However, control of the AlN composition was thought to be the major problem affecting reproducibility. Optimum conditions for the preparation of a successful AlN layer have not yet been found which will allow the layers to act as good encapsulants up to temperatures of the order of 1100°C. When the cap is removed by HF acid a single crystal GaAs surface structure is revealed as in Fig. 4.4a. It was believed that the intermediate quality AlN might be converted into $\alpha$-Al$_2$O$_3$ after annealing to about 1100°C[25]. Some of these layers were found to be difficult to remove completely even when the treatment with HF acid was prolonged. The crystal was recovered from the implantation damage, but traces of the coating still existed on the surface (see Fig. 4.5a). A stable compound which had the structure of AlN-Al$_2$O$_3$ (Spinel) was formed during the annealing of the aluminium rich layer in a flow of nitrogen (Fig. 4.3a). This compound was first reported to form by hot compression of pure AlN and Al$_2$O$_3$. The measured interplanar spacings from RHEED patterns obtained from our samples was found to match well with those reported , [131,132]. This layer could not be removed using HF acid.
The coating layer which RBS analysis has shown to consist of a mixture of A\textsubscript{2}N and AlOOH with excess of aluminium acted as a good encapsulant. Detailed information of the proportion of each compound has shown that the composition is \( \approx 70\% \) A\textsubscript{2}N and \( \approx 25\% \) AlOOH with a small excess of aluminium\[25\]. However, the reported results by Pashly et al.\[133\] using sputtered aluminium oxy-nitride encapsulants were better than those obtained when a Si\textsubscript{3}N\textsubscript{4} cap was used. The composition of this encapsulant was 3 part A\textsubscript{2}N and one part Al\textsubscript{2}O\textsubscript{3} with slight excess of aluminium. Al\textsubscript{2}O\textsubscript{3} is also a refractory compound and Chue et al.\[134\] have indicated that Al\textsubscript{2}O\textsubscript{3} is a good mask against gallium and arsenic diffusion. However, the AlOOH decomposes thermally into \( \gamma \)-Al\textsubscript{2}O\textsubscript{3} which is soluble in HF acid, whereas \( \alpha \)-Al\textsubscript{2}O\textsubscript{3} is more stable and is not easily removed by HF acid.

Freshly prepared A\textsubscript{2}N deposited on GaAs and then annealed in the temperature range 900–1100°C in a nitrogen atmosphere showed no signs of oxidation. However, at high temperatures some sharpening of the diffraction arcs indicated that recrystallization of some of the A\textsubscript{2}N had occurred at 950–1100°C (Figs. 4.3b, 4.4b), but the A\textsubscript{2}N phase remained unchanged. Occasionally we have observed changes in colour of the cap, which may be due to the sudden exposure of the capped and annealed samples to atmospheric moisture before the samples have cooled down to room temperature. These changes of colour are attributed to the oxidation of the surface layer whether the surface layer consists of aluminium or aluminium nitride.

In order to improve the encapsulation performance of the evaporated A\textsubscript{2}N and to minimise the effect of composition variation of the A\textsubscript{2}N ratio to the other constituents of the film, it was suggested that a 30nm layer of Si\textsubscript{3}N\textsubscript{4} be deposited prior to the 60nm coating of evaporated A\textsubscript{2}N. A detailed study of the surface of the substrate after the removal of the capping layer has not been carried out to demonstrate the complete effectiveness of this encapsulant. However, the electrical properties were reported to be improved with better reproducibility\[128\]. The use of the
evaporated AlN film as a cap is still in the laboratory stage and does not fullfil the requirements of an ideal encapsulant. The method needs some improvements to ensure that a layer of the desired composition and properties can be deposited reproducibly. At this stage of the work we believe an improvement in the vacuum system is necessary. The optimum conditions of the evaporation rate and the reactive gas partial pressure must be determined. To increase the activity of the reaction, the deposition should be made on a hot substrate\[125,126\], but the III-V compounds are subject to decomposition if a preheating step is performed prior to deposition. Instead we suggest a heating of the reactive gas before admission to the chamber. Also to reduce the water vapour partial pressure inside the chamber the N$_2$/NH$_3$ mixture should be passed through potassium hydroxide to absorb the water in the gas mixture. This may increase the reaction rate between the aluminium and the nitrogen/ammonia mixture. This procedure should produce a layer consisting predominantly of AlN.
Experiments were performed to deposit A\textsubscript{2}N thin films from an A\textsubscript{2}N target by r.f. sputtering. The early work on the sputtering of A\textsubscript{2}N layers indicated the difficulty of preparing a pure stoichiometric layer. The available gases in which the sputtering was performed were argon and nitrogen. In the early experiments sputtering was performed in an atmosphere of argon gas only. The deposited films were amorphous when deposited in an argon or nitrogen atmosphere at low energy. The explanation for this may be that an oxide or hydroxide layer had formed on the surface of the target. Hence the low sputtering rate due to the low particle energy would not be enough to remove the oxide layer. Another possibility is that the sudden exposure of the film to atmospheric moisture might cause the hydrolysis of the A\textsubscript{2}N layer by absorption of water vapour from the atmosphere. Aluminium hydroxide is known to be amorphous at room temperature\cite{[135]}. The RBS results which showed the presence of Al, O, N indicated that the layer was not a pure A\textsubscript{2}N film. At higher sputter energies of 250-300W, a crystalline structure of A\textsubscript{2}N was obtained. This was synthesized in nitrogen alone or in a nitrogen/argon mixture i.e. by increasing the sputtering time (see Figure 4.6a). These results suggest that the amorphous oxide or hydroxide present on the A\textsubscript{2}N target is relatively thick and thus a longer cleaning cycle is needed to remove such oxides. Prior to deposition on GaAs results have shown that a direct reaction of A\textsubscript{2}N with hot water produces $\gamma$-AlOOH on the surface.

The thickness of these oxides is not known. The time needed to remove such undesirable layers which will depend on the sputtering conditions needs to be estimated in order to avoid contamination of the deposited layer. However, a crystalline A\textsubscript{2}N structure was detected by electron diffraction but it is still not clear whether the interface between the substrate and the deposited layer is free of
oxide. The X-ray elemental analysis using the electron probe shows an oxygen signal which suggests the presence of an oxide formed as a result of either:-

a) contamination of the target surface,

b) rupture of the AlN bond followed by the reaction of the aluminium with residual oxygen to form Al$_2$O$_3$ (small oxygen contamination in the sputtering gas),

c) or the possible hydrolysis of the film outside the sputtering chamber following deposition.

The amount of oxygen contained in the films seems to be at the lowest level for those films which were sputtered in an argon/nitrogen mixture. These films have a crystalline AlN structure but RBS spectra show they also contain a low oxygen content (see Figure 4.11). It is worth noting that the analysis of the layers by RBS or by electron probe elemental analysis was carried out a few days after the films were deposited (see Figure 4.9), whereas the RHEED analysis was carried out less than 24 hours after deposition. Thus partial hydrolysis of the films may have occurred when freshly deposited films were left in atmospheric moisture for a long time. A RHEED pattern obtained from a film left for a few days shows a poorer diffraction pattern than that obtained from the same sample just an hour after deposition. Such a pattern appeared cloudy which obscures partially the diffraction rings from the polycrystalline AlN phase.

In the experiment carried out to prepare a thick layer (about 1μm) suitable for X-ray diffraction analysis, the diffraction peaks (Figure 4.8) were found to belong to AlN and only one diffraction peak of GaAs (400) at 0.164nm was obtained. Since the GaAs has a (100) surface orientation only the (400) diffraction peak would be expected from a single crystal. This result is typical of a (100) oriented face centre cubic structure. The AlN film examined by X-ray diffraction showed a preferred orientation relative to the substrate and the orientation relationship was 002 AlN/100 GaAs. This means that the C-axis of the AlN crystals is perpendicular to the GaAs surface. The RHEED pattern
(Figure 4.7b) taken from the surface of the film shows the same effect clearly. Not surprisingly the electron diffraction analysis has revealed the presence of A\textsubscript{1N}, together with extra rings possibly due to presence of an oxide. RHEED is sensitive to surface layers of about 5 nm thick whereas the X-ray diffraction is sensitive to layers \( \approx 1 \) \( \mu \)m thick\[74,85\]. Thus RHEED has the advantage of detecting a small amount of surface material which cannot be detected by X-ray diffraction. The results suggest that the A\textsubscript{1N} layers are not stoichiometric and possibly that oxygen is incorporated in the layers to produce an oxynitride\[103\] so that the freed aluminium atoms can combine with oxygen to form \( \text{Al}_2\text{O}_3 \). In the chosen experimental conditions of an Ar/N\(_2\) sputtering gas mixture, it is suggested that the aluminium produced as a result of the breakdown of the A\textsubscript{1N} target would react with the reactive gas mixture to form A\textsubscript{1N}. However, the argon gas alone has produced films with the metallic cluster. Thus the argon ions seem to be energetic enough to break the A\textsubscript{1N} bond to produce an Al-rich film. This effect is well known as preferential sputtering when the low mass constituent is preferentially sputtered\[136\]. As shown from X-ray diffraction (Figure 6.1) an amorphous layer was obtained which means that the crystallinity of the film has been destroyed under heavy bombardment of the deposited layer at the target and possibly the deposited film on the substrate by the energetic reflected ions. The pattern was taken from a metallic like film of thickness about 1\( \mu \)m. This film when analysed by the electron probe (see Figure 4.10) showed the presence of Al, N, O, Ar, As and Ga. The presence of the argon in the deposited film can be explained by the theoretical model shown in Figure 6.1. This model explains the mechanism of sputtering and throws light on the process which takes place in the sputtering chamber. The experimental results presented in this work are in good agreement with the model. The ion trapping of the energetic ions by the target explains the presence of the argon in the film\[136\].
Figure 6.1. General ion-surface interaction process (according to ref. 136).
In general the deposited layers were found to be composed of aluminium oxide and aluminium nitride; however, some of the films were found to be predominantly A\&N.

Some of the sputtered A\&N layers were used as encapsulants for III–V semiconductors. However, the sputtered layer failed to protect the ion-implanted GaAs samples during annealing. The failure of the cap is attributed to an interface reaction between the layer and the GaAs substrate. The most likely reaction is that aluminium or aluminium oxide deposited initially reacts with the GaAs. One report has suggested the composition of layers formed by sputtering from a compound target of A\&N is A\&N contaminated with oxygen, i.e. an oxynitride[105]. This is in agreement with the results obtained in this work. The elements present were Al, N, and O but the exact composition could not be determined from the RHEED and X-ray data.

6.7 Zirconium nitride films

6.7.1 General

The effectiveness and thermal stability of zirconium nitride thin films has been investigated in detail. The published data suggest that zirconium nitride is the most thermodynamically stable mononitride. ZrN is a hard and high melting point material. In addition the thermal expansion coefficient is close to that of GaAs i.e. $(7.24 \times 10^{-6} \, ^\circ C^{-1}$ for ZrN and $6.9 \times 10^{-6} \, ^\circ C^{-1}$ for GaAs). The fact that ZrN is soluble in concentrated HF acid is also regarded as an advantage for an encapsulant, since HF does not react with GaAs. In view of the above, it was thought worthwhile to investigate the possible application of a ZrN thin film as a protective coating for ion implanted GaAs during the annealing process. The typical annealing method used in this study was a rapid thermal process in a flow of nitrogen gas. This was done in order to reduce the oxygen presence in the annealing chamber. The ZrN layers were sputter deposited by Dowty Electronic Limited. Their
interest is in the use of ZrN for tribological applications. Thus the thermal stability, oxidation and phase transformation are of great importance for their goals. Our interest is in the behaviour of the coating layer during rapid thermal annealing of ion implanted GaAs at a high temperature. The reported literature says that the existence of the higher nitride of zirconium is doubtful. A compound like Zr$_3$N$_4$ is not a true compound but zirconium metal in which the nitrogen is dissolved interstitially. Only ZrN has been positively identified[50].

The ZrN may be formed by reactive sputtering as follows:

$$2\text{Zr} + \text{N}_2 \rightarrow 2\text{ZrN}$$  \hspace{1cm} 6.9

However, the ZrN thin film under study is not oxygen free. It may be partially poisoned by the low oxygen partial pressure during deposition. Hafnium, which is often found as an impurity in zirconium was not found in the ZrN film. However, in the work of Krusin et al.[52] such an impurity was detected by RBS analysis. They reported that the presence of 0.5% hafnium is unavoidable as a contaminant in a zirconium target. It is known that zirconium metal has a strong affinity for oxygen. Duckworth et al.[96] studied a zirconium layer on a quartz substrate, they found that oxygen contamination was present throughout the deposited layer.

6.7.2 RHEED observation

Pre-examination of the as-deposited ZrN films using RHEED has shown that the surface structure is a polycrystalline ZrN phase. The main d-spacings of ZrN (see Table 5.2) have been measured using a camera constant of 2.35(nm x mm). The measured d-values were found to be in good agreement with those of ZrN reported in the ASTM powder diffraction file. This pattern (see RHEED Figure 5.1a) remained unchanged up to 600°C and only arcing of the diffraction rings was observed as shown in Figure (5.1b). This effect occurred as
a result of the thermal treatment which produced a preferred orientation of the ZrN film due to the annealing cycle[137]. The first major change detected was from a sample annealed at 700°C which gave a RHEED pattern of the single ZrO$_2$ cubic phase. It can be seen from the SEM micrograph (Figure 5.2b) that the surface had changed and bubbles had formed at this temperature. The electron probe analysis of the elements present showed a sharp increase in the oxygen peak coupled with a sharp decrease in the nitrogen peak (Figure 5.4b). This shows that some of the nitride layer was oxidized. In contrast the electron diffraction pattern obtained from a sample annealed at 800°C (Figure (5.1c)) shows that different phases are present and a large number of diffraction lines were observed. Some of the measured lines were found to be close to those of the monoclinic phase ZrO$_2$ (see Table 5.2). One of the characteristic features of the monoclinic structure is the large number of diffraction lines[137]. It has also been reported that ZrO$_2$ normally crystallizes in the monoclinic structure[52]. Other unidentified lines probably belong to other zirconium oxides. Figure (5.1d) shows a diffraction pattern taken from a sample annealed at 900°C. The pattern was identified as ZrO$_2$ of cubic structure, as the measured d-values were close to that of ZrO$_2$ - Card No 27-997, (see Table 5.2). Figure (5.1e) taken from the surface of the sample annealed at 1000°C shows the cubic phase and some unidentified faint rings. The rings from cubic ZrO$_2$ are sharper due to the recrystallisation effect and the faint rings are believed to belong to another phase or phases of ZrO$_2$. The results obtained from this work are in agreement with the work of Krusin et al.[52], who investigated the oxidation of ZrN films in dry oxygen. They reported a mixture of oxides were formed as a result of the oxidation process with the cubic and monoclinic phases predominating. It was suggested in that study that a metastable phase of cubic ZrO$_2$ transformed into a monoclinic form on heating. The X-ray diffraction analysis which was performed on a series of samples, identified the presence of a cubic phase of ZrO$_2$. It is known that ZrO$_2$ can change its structure from amorphous to
cubic via the tetragonal to monoclinic structures [130] during annealing in the range from room temperature up to 1000°C.

We were able to remove the ZrN layer from samples heated up to 600°C easily. RHEED patterns obtained from the exposed GaAs surfaces were that of high quality single crystals with Kikuchi lines. This typical pattern is usually obtained from a clean smooth GaAs surface. These results were confirmed by RBS in which the damage parameter $X_{\text{min}}$ was similar to the value from a virgin GaAs sample analysed in the same run. No zirconium or oxygen signals were detected from this sample and a SEM micrograph showed no visible damage (see Figure 5.3a). Above this temperature some of the layer remained unetched. The RHEED results from the sample annealed at 700°C and then etched were those usually obtained from a contaminated surface. Compounds such as GaZr or ZrAs were reported in the literature, but unless a crystalline structure forms, it is difficult to identify the presence of such a material. The other possibility is that another undissolved amorphous oxide remained on the surface. Figure (5.1g) shows a ring pattern plus spot pattern obtained from samples annealed at 800°C and etched with HF acid. The ring pattern is similar to that obtained from the surface before etching (Figure 5.1c). This confirms the presence of oxides which are difficult to remove by the HF acid. The spot pattern however is that of the GaAs substrate. It is believed that the electron beam was incident on the part of the surface which was a burst bubble or blister. This area of the surface was cleaned by HF acid which also removed the gallium or native oxides exposing the fresh GaAs surface (See SEM Micrograph Figure 5.3b). The absence of Kikuchi lines indicates surface roughness due to the decomposition of the GaAs at this annealing temperature.

The RHEED patterns from samples annealed at 900°C and 1000°C after acid etching were not clear. This effect is due to the scattering of the electrons from the highly damaged
The scanning electron microscopy results in conjunction with the electron probe proved very useful in the evaluation of the ZrN layer performance during heat treatment. SEM micrographs (Figure 5.2a) showed that smooth surfaces with no visible changes were produced from samples annealed up to 600°C. Surface morphology remained similar to that obtained from reference samples coated with a ZrN layer. However, the electron probe showed the presence of nitrogen, oxygen and zirconium from the film, the oxygen peak seemed rather small and remained the same up to 600°C. This result suggests an oxygen contaminated ZrN layer was synthesized. However, at this stage, the elemental analysis was used as a qualitative test rather than a quantitative one. No oxygen signal was detected from the GaAs reference sample using the electron probe, only arsenic and gallium signals being recorded. This confirmed that the oxygen contamination was from the film and not from the substrate. The first sign of change on the surface was observed following an anneal at 700°C. This change appeared in the SEM as gas bubbles accumulated at the surface. The formation of the bubbles may be explained by the surface expansion due to oxide formation[138]. We believe that the gas bubbles are filled with arsenic gas since this temperature is slightly above the critical decomposition temperature of GaAs. One author[51] suggested that diffusion occurs through the grain boundaries of the ZrN layer. Others reported that arsenic diffuses into the encapsulant through columnar pipes[31]. Samples annealed at temperatures between 800-1000°C showed more burst bubbles. The damage seems to be temperature dependent since at high temperatures more bubbles have burst and the damage inflicted on the layer was increased. We believe that the layer is oxidized completely and it can be seen from Figures 5.2c and 5.3b that the layer remained
undissolved after HF treatment. Using the microprobe zirconium and oxygen signals were detected from samples annealed at 800°C and above. This confirmed the electron diffraction results which showed that phase transformations occurred as a result of the oxidation process. The results obtained by SEM and the electron probe are in agreement with RBS data (Figure 5.5) which showed a zirconium signal from the samples annealed at 800-1000°C followed by etching in HF acid. These results proved that the capping layer was not removed completely and the layer had suffered a severe change after oxidation.

6.7.4 Rutherford backscattering

Following the annealing of the samples coated with ZrN up to 600°C followed by etching the cap in HF acid, a $X_{\text{min}}$ of 6% was measured which demonstrates the quality of the crystal at the interface. A similar $X_{\text{min}}$ value was obtained from a virgin GaAs sample examined at the same time and proved that no serious damage had occurred to the surface. At elevated temperatures such as 700°C, a $X_{\text{min}}$ value of 8% indicated that damage had been introduced or decomposition had occurred. This may be explained by the evaporation of the arsenic from the surface (see SEM micrograph Fig. 5.2c). The SEM micrograph and electron diffraction pattern showed the presence of a damaged, contaminated surface. The $X_{\text{min}}$ values obtained from samples annealed between 800 and 1000°C (Figure 5.5) showed that the damage occurring at the GaAs surface increased as a result of increasing the temperature. Only zirconium signals were detected in addition to the gallium and arsenic from the GaAs substrate. Since oxygen has a lower mass than the Ga and As, its signal is masked by the signals from the bulk GaAs.

No published work on the possible application of ZrN layers as protective coatings for III-V compounds during annealing have been reported in the literature. However, recently a few papers have been published on the possible application of ZrN as an oxygen diffusion barrier in an aluminium
metalization scheme for silicon devices. The ZrN was sputter deposited, prior to the aluminium, onto a silicon wafer. The annealing of these films showed that ZrN acts as a good barrier against aluminium and silicon diffusion during a 30 minute anneal at up to 550°C. The layer failed completely at 600°C when a ternary compound of $Z_3 Al_4 Si_5$ was reported to form[51]. The same authors have reported the oxidation behaviour of ZrN thin films in an oxygen atmosphere. They found that oxidation of the ZrN films occurred between 475°C and 650°C and that the process is dependent on the temperature. ZrO$_2$ was detected both in the cubic and monoclinic phases[52]. In this work a transient annealing method in a chamber flushed with nitrogen was used and was expected to prevent oxidation. Surprisingly, the ZrN cap failed at a low temperature which was mainly attributed to oxidation of the film as a result of the thermal treatment. This oxidation is presumed to be the result of the presence of residual oxygen and/or water vapour in the chamber and the result of outgassing of the graphite strip and its surroundings.
General conclusions and future work

7.1 Introduction

In this chapter the final conclusions to be drawn from this work are presented. Suggestions for future work are also included.

7.2 RHEED

The RHEED apparatus which had been lying idle for some time was dismantled and rebuilt with many improvements. The operating conditions were improved in the following ways:

a) Beam alignment: Better optical axis was achieved.

b) Aperture diameter: A small aperture was made to reduce size of main beam.

c) Recorded details: Pattern size increase from 50% to about 75% of the total film size.

d) Vacuum: Improved, and time needed to achieve the operating vacuum was lowered from 8 hours to 2-3 hours.

e) Filament life: The improved vacuum and the adaption of suitable cooling time periods has meant that filament life has been extended from 1 month to more than a year.

f) Operating voltage: Previously the maximum voltage was 35kV, in the present work 60kV, 50kV and 40kV were tried and the 40kV voltage was chosen as satisfactory results were obtained at this voltage.

g) The camera constant was found, and the error was checked using different materials and was less than 1%.
The protection of III-V compounds semiconductors during annealing is of great important since the annealing process after ion implantation causes surface degradation of the implanted material. The typical annealing temperature is high enough to cause significant changes to the substrate material. Annealing temperatures around 900°C and above were found to be necessary[1,2,5,98]. However, temperatures as high as 1150°C have been used in order to remove the damage caused by ion-implantation[25]. The extent of the damage depends upon the dose, the substrate material, the implanted ions and the implantation energy. This is well explained in several reviews[2,58,98]. Encapsulation is provided to protect the III-V semiconducting material during the annealing process, although some work on capless annealing is reported to have had some success[1,2,73]. Nevertheless protection by encapsulation is the predominant process in the semiconductor industry.

A variety of materials have been investigated to determine their suitability as encapsulants. Among those studied are thermally grown oxide, aluminium, silicon oxide, all proved to be only partly successful in preventing the dissociation of GaAs[1,2,25,98]. Silicon nitride is the most widely used material despite difficulties in achieving reproducibility of the reactively sputtered and CVD silicon nitride layers. More recently work has been reviewed on using SiO₂ as an encapsulant and some reports suggested that silicon oxide can also withstand high annealing temperatures[99,100]. Other new materials have been investigated such as AlN or composite materials, for example Si₃N₄/SiO₂ [1,31,47] or Si₃N₄/AlN[25,128] However more recent reports have shown a growing interest in refractory metal silicides as thermally stable Schottky barriers for GaAs which may also serve as encapsulants[106,110,112].
Evaporated AIN was the first material used as an encapsulant for ion implanted GaAs. The evaporated films were examined and found to consist mainly of aluminium, oxygen and nitrogen. The presence of oxygen was shown to be due mostly to hydrolysis of the films on exposure to the atmosphere. The protection of these films with a layer of aluminium prevented hydrolysis and showed that the as-deposited layers were mainly AIN with a low oxygen content[25].

Films with or without excess of aluminium at the surface were used to anneal ion implanted GaAs successfully to temperatures as high as 1000°C.

Difficulties in controlling the deposition process meant that a small amount of aluminium was sometimes deposited onto the surface of the GaAs substrate without reaction with NH₃, forming a thin aluminium layer underneath the AIN films. Such films were found to be difficult to remove because of the reaction of the aluminium layer with the GaAs surface. Thus, the reproducibility of good quality AIN was difficult to control. Nevertheless a "sandwich" encapsulant consisting of a very thin layer of Si₃N₄ (≈300nm) followed by a layer of evaporated AIN solved the problem of reproducibility and encapsulants produced in such a manner withstood temperatures as high as 1140°C[25,128].

Powdered AIN

AIN powder proved to be resistant to oxidation in air up to ≈1000°C and when heated in an inert atmosphere up to 1400°C, the AIN powder did not react with the low oxygen pressure prevailing. AIN proved to be stable under non-oxidizing conditions up to 1400°C and this was at least 200°C higher than might be required in practice for annealing GaAs. Oxidation of AIN results in the formation of α-Al₂O₃ at temperatures of about 1200°C. AIN reacts with water to form α-AlOOH.
7.6 Sputtered AlN

The sputtered AlN layer used as an encapsulant did not exhibit good encapsulation properties, since it tended to react with the GaAs surface in most cases. There is a possibility that this interface reaction was due to the presence of free aluminium or aluminium oxide. The experimental conditions for production of a good encapsulant containing mostly AlN or an AlN layer at the interface has to be determined in order to improve the encapsulation behaviour of sputtered AlN. It is also necessary to ascertain the maximum amount of oxide which may be present in the AlN layer which does not effect the performance of the AlN cap.

7.7 ZrN thin film coatings

ZrN layers have failed to protect GaAs substrates at temperatures above 700°C. The oxidation of the layer at about 700°C has proved that ZrN cannot be used as an encapsulant to protect GaAs during annealing at high temperature (i.e. 900°C and above) and the oxide was found difficult to remove. However, a ZrN film could be used as a passivation coat for GaAs ICs up to a temperature of about 600°C.

7.8 Suggestions for future work

7.8.1 Evaporated AlN

The results obtained for evaporated AlN encapsulants have shown promise. However, evaporated AlN is still only used on a laboratory scale and improvements to the method are necessary to produce reliable and reproducible AlN layers with low oxygen contamination. This might be carried out by:
1) Providing a better vacuum system to reduce the oxygen pressure in the reaction chamber

2) Optimizing the experimental conditions i.e. controlling the evaporating rate of the aluminium and determining the relative reactive gas pressure to produce a good quality AIN film containing a minimum amount of oxide.

3) Minimizing the effect of possible hydrolysis of the film by keeping the coated samples in a dry atmosphere prior to annealing or by carrying out the annealing as soon as possible after deposition.

7.8.2 Sputtered AIN

The results presented in this work do not mean that work on sputtered AIN should be abandoned. It is important to improve the experimental conditions and this may be carried out as follows:

1) Using research grade sputtering gases.

2) Ensuring the dryness of gas pipes which must be free of any moisture which has possibly accumulated during successive sputtering.

3) Ensuring the dryness of the chamber walls which could absorb water vapour during periods of inactivity. This could be done by baking the chamber.

4) Using a satisfactory cleaning cycle for the target to remove any oxide or hydroxide present on the surface.

5) Increasing the pump-down time or improving the base pressure to reduce the oxygen presence. To achieve this we suggest sputtering a highly reactive metal such as Ti to reduce the residual oxygen while keeping the shutter closed to protect the sample surface from contamination.

6) Finding the best sputtering conditions to produce good quality AIN with minimum oxide contamination or free aluminium. This may be done by changing the sputtering energy and the sputtering gas partial pressure of a single gas used or the mixture of gases.
7.8.3 ZrN layers

The ZrN layers proved unreliable and it is not considered worthwhile to do further work on this material since reports in the literature have shown that the ZrN oxidizes at about ≈680°C[49,120].

7.8.4 Possible new encapsulants

Among new materials likely to be considered are the silicides. The literature has shown that some are thermally stable and can withstand high temperatures especially if the material can be used for device fabrication without the need to remove the silicide after annealing.
a) Polycrystalline pattern of GaAs obtained from mechanically damaged sample, used for calculating camera constant.

b) Schematic diagram of polycrystalline GaAs. Indexing of the pattern.
a) Standard RHEED pattern of AIN powder (99%) and 50μ particle size. The d-spacings were obtained by measuring the radii of the rings (r) and converting these to d-spacings using the camera constant (Camera const. = dr). The spottiness of the rings is due to the relatively large crystal size of the AIN powder.

b) Indexing of main d-spacings of AIN pattern.
a) RHEED pattern of TiN thin film prepared by annealing a thin titanium film on Si substrate. The annealing carried out using lamp annealing method in nitrogen flow.

b) Indexing of d-spacings of TiN pattern.
Titanium nitride

A TiN thin film of metallic gold colour was prepared by incoherent lamp annealing of Ti film on silicon. The annealing was performed in a nitrogen flow and the result of thin process was silicide and nitride formation. The silicide formed self aligned to the silicon gate and the nitride formed above the silicide acted as a diffusion barrier[139]. The RHEED pattern of TiN was used to check the accuracy of camera constant after five years work.

Table A

<table>
<thead>
<tr>
<th>Lattice d-spacing (nm)</th>
<th>RHEED pattern of TiN thin film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured</td>
<td>Standard X-Ray Diffraction</td>
</tr>
<tr>
<td>d(nm)</td>
<td>I</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>0.243</td>
<td>VS</td>
</tr>
<tr>
<td>0.2107</td>
<td>S</td>
</tr>
<tr>
<td>0.151</td>
<td>VS</td>
</tr>
<tr>
<td>0.129</td>
<td>m</td>
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<tr>
<td>0.122</td>
<td>m</td>
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<td>m</td>
</tr>
<tr>
<td>0.097</td>
<td>m</td>
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<tr>
<td>0.091</td>
<td>m</td>
</tr>
<tr>
<td>0.087</td>
<td>m</td>
</tr>
</tbody>
</table>

Footnote

vs = very strong.
S = strong.
m = medium.
w = weak.
d(nm) = interplanar spacing.
I = intensity.
hkl = Miller indices of set of interplanar spacings.
References


List of Publications


FORMATION OF TITANIUM DISILICIDE BY ELECTRON BEAM IRRADIATION UNDER NON STEADY STATE CONDITIONS

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ABSTRACT
Titanium disilicide was formed by multiply-scanned electron beam irradiation of titanium films of nominal thickness 1200Å on silicon substrates. Samples were annealed at power densities of 2 to 52.5Wcm$^{-2}$ using times in the range of 1 to a few hundreds seconds. Rutherford backscattering analysis was used to study the metal redistribution and to estimate the approximate compositions and thicknesses of the films. Compounds were identified by X-ray and electron diffraction. Sheet resistance was measured by the four probe technique and surface topography inspected by scanning electron microscopy.

The silicide thickness achieved depends only on annealing time for power densities in the range of 20 to 50Wcm$^{-2}$ and hence is independent of heating rate and peak temperature during the heating cycle.

INTRODUCTION
Titanium disilicide is a prospective candidate for formation of contacts and interconnects in VLSI technology [1]. This compound has a lower resistivity than metallic titanium: typically 13 - 25µΩcm, depending on the fabrication method [1].

Extensive studies on the annealing of titanium films deposited onto silicon substrates [2] [3] [4] and multilayer structures [5] [6] have been reported. Most of this work concerns isochronal furnace annealing although there are some reports on laser [7] [8] and electron beam annealing [9].

The results on isochronal furnace annealing suggest that once the critical temperature for titanium disilicide formation (600°C [3]) is exceeded the reaction proceeds very rapidly [7] and that it is diffusion controlled with the mobile species being silicon [11]. Silicon atoms diffuse through titanium disilicide easily and a compound layer forms at the compound-metal interface [1].

In terms of annealing time, the furnace and laser methods are at the opposite extremes, (tens of minutes to tens of nanoseconds respectively). The work reported in this paper is the result of a study of an intermediate annealing regime where the time is the order of seconds. A raster-scanned electron beam with a high power density is used to elevate the specimen temperature rapidly above that required for the formation of titanium disilicide.

EXPERIMENTAL
Titanium films of thickness 1200Å were evaporated in UHV onto 3" silicon (100) single crystal wafers, and also onto 1μm of polysilicon on SiO$_2$ on...
a single-crystal substrate. Uniformity of the thickness of all the titanium films was better than 10% across a wafer, and oxygen contamination was below the sensitivity of Rutherford backscattering analysis (<5%). The wafers were cleaved into ~7 x 7mm squares for annealing and analysis.

Annealing was carried out in vacuum of 10^-6 Torr using a commercial Lintech electron beam facility [12]. A 30kV electron beam was raster scanned at frequencies of 70Hz and 25kHz over an area 30 x 30mm, the power density being controlled by varying the electron beam current. The samples were mounted on a thin molybdenum plate, (as shown schematically in Fig. 1), supported at two corners by small silicon chips and held in place by thin molybdenum spring clips. This plate was supported on the water-cooled stage by three ball-bearings. This system was chosen to approximate perfect thermal insulation of the sample from the heat sink and to provide the sample with a hot background established by the simultaneous irradiation of the molybdenum plate.

![Figure 1. Schematic of sample mounting system.](image1)

![Figure 2. RBS spectra of samples annealed at a power density of 23.4Wcm^-2 for 4 secs. (a) 5 secs. (b) and 6 secs (c) reference spectrum (d)](image2)

Films deposited on single-crystal substrates were annealed at power densities of 41, 31.5, 23.4 and 15.2Wcm^-2. A few samples were also annealed at 6, 5, 4, 3 and 2Wcm^-2. Films deposited on polycrystalline silicon were annealed at power densities of 52.5, 31.6, 23.4, 13.5 and 6Wcm^-2. Annealing times ranged from 1 to several hundreds of seconds.

Rutherford backscattering analysis with 1.5MeV He^+ ions was used to study titanium redistribution and to assess the chemical composition of the reacted films. This analysis was performed twice on each sample, once immediately after annealing and then after removal of any unreacted titanium with a selective etchant (H_2O_2 : NH_4OH : H_2O [13]). Sheet resistance measurements were also carried out before and after etching.

Selected samples were inspected by X-ray and glancing angle electron diffraction (RHEED) in order to determine the chemical composition of reacted films. Surface textures were studied using scanning electron microscopy.
RESULTS

Figure 2 shows the RBS spectra for samples annealed at power density 23.4 W/cm² for 4, 5 and 6 secs. (spectra a, b and c respectively) compared to a reference spectrum for an unannealed sample (d). Spectrum c typifies a film with a composition of 33% titanium and 67% silicon and a thickness of ~2500Å. X-ray diffraction confirmed that this layer is TiSi₂; however, RHEED revealed that some Ti₅Si₃ is also present.

In Figure 3 the TiSi₂ layer thickness formed on single crystal substrates is plotted as a function of annealing time for several power densities. The TiSi₂ thickness was calculated from the RBS data using the Bragg's rule for compound stopping power, Ziegler's stopping power for elemental titanium and Santry et al.'s stopping power for elemental silicon.

Figure 3. Thickness of compound, ΔW, formed upon annealing versus annealing time for power densities of 15.2 W/cm² (A), 23.4 W/cm² (B), 31.5 W/cm² (C) and 41 W/cm² (D). Solid lines represent calculated thicknesses at the same power densities assuming diffusion controlled growth.

The two important features of Figure 3 are:
(i) after a certain critical time which must elapse before any reaction takes place the silicide thickness is proportional to annealing time,
(ii) for the three highest power densities (B, C and D) the reaction is almost independent of power density; however the lowest one (A) indicates a slower reaction rate.

Essentially similar results were obtained on polycrystalline substrates.

Figure 4 shows the typical behaviour of sheet resistance R as a function of annealing time at a constant power density, in this case 31.5 W/cm². The sheet resistance initially increases from 70Ω/µ for an unannealed film to about 130Ω/µ after 2.5 secs annealing, then dramatically decreases to 0.5Ω/µ after 4 secs. Upon longer annealing the sheet resistance of a film on a single crystal substrate changes very little (curve a), whereas on a polycrystalline substrate, it increases. By measuring of the sheet resistance after removal of any unreacted titanium, the bulk resistivity may be deduced. This shows a similar time dependence with a minimum value of (12 ± 1.2) μΩcm.

The texture of reacted films is strongly dependent on the substrate type and the annealing conditions. This is demonstrated in Figure 5. For a fully reacted film on a single crystal substrate, a fine, rather feature-
less texture is observed (a and b). Similar textures are produced on a polycrystalline substrate when the titanium film is partially reacted (c and d), whereas fully reacted films show catastrophic deterioration of their surfaces (e and f). This behaviour is characteristic of all films on polysilicon annealed at between 13.5 and 31.5 Wcm\(^{-2}\): also, surprisingly those annealed at 6 and 52.5 Wcm\(^{-2}\) showed surface textures similar to c and d.

![SEM surface textures](image)

Figure 5. SEM surface textures for:
Ti/single crystal: fully reacted (a), etched (b); Ti/polysilicon: partially reacted (c), etched (d); Ti/polysilicon fully reacted (e) and (f)

In Figure 6, the lowest value of sheet resistance attained at each power density is plotted for both types of substrate. Films grown on single crystal silicon always yielded slightly lower values than those on a polycrystalline substrate. Above about 15 Wcm\(^{-2}\) the sheet resistance is independent of power density.

**DISCUSSION**

The annealing conditions applicable in this series of experiments are best represented by a heating/cooling curve of the type shown in Figure 7a.

![Heating/cooling cycle](image)

Figure 7. Heating/cooling cycle calculated for a power density of 31.5 Wcm\(^{-2}\) (a). Asymptotic temperature dependence on power density (b) calculated with assumptions given in the text. The dashed line shows the critical temperature for TiSi\(_2\) formation. Accepted room temperature values of
0.45 for silicon [16], 0.5 for titanium [17] and 0.4 for molybdenum [17] to 1 at 1000°C [16].

(iv) since Debye temperature for silicon is 658°K [18], the specific heat is temperature dependent and may be calculated from the approximate formula according to Wolf [19].

(v) the conduction energy loss from the irradiated area on the molybdenum plate and from the specimen to the hot stage is estimated to be 10%.

A computer program was written to calculate numerically a predominantly radiation limited heating/cooling cycle. Calculated asymptotic temperatures compare well with experimental values measured by infra-red pyrometry in the range 8 to 23Wcm⁻², as shown in Figure 7b. The theoretical thermal cycle was then used to calculate the silicon diffusion length in the silicide, which for a diffusion controlled process is representative of the compound thickness formed [20]. The results of this calculation are superimposed on the experimental data in Figure 3. Good agreement is obtained between experimental and calculated values for the initial delay in compound formation. However, the general character of the theoretical curves is entirely different from experimental results. For power densities above 15Wcm⁻², the process is clearly not diffusion controlled: the sample temperature is high enough that silicon transport from the substrate to the silicide-metal interface is not the rate determining factor. Below 15Wcm⁻², the experimental lower reaction rate observed indicates that silicon diffusion may play some part in limiting the silicide growth.

CONCLUSIONS

It has been shown that titanium disilicide formation may be achieved by raster-scanned electron beam irradiation of titanium films on silicon substrates.

Titanium disilicide formed on single crystal substrates is comparable to furnace-annealed material in terms of low resistivity and good surface quality: however, on polycrystalline substrates the surface is frequently badly cracked, possibly owing to differential thermal expansion between TiSi₂ and polysilicon.

It is not clear yet whether this method of TiSi₂ formation is suitable for device fabrication, particularly in the case of titanium on polysilicon. However, one may hope to improve the quality of these films by a careful choice of titanium and polysilicon thicknesses such that all the polycrystalline material is consumed during TiSi₂ formation.

ACKNOWLEDGEMENTS

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19. ibid.
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The thermal stability of AIN powders and thin films has been investigated using reflection high-energy electron diffraction (RHEED) and X-ray diffraction. AIN powder was treated thermally and chemically to assess the oxidation resistance of this compound and to identify the phases formed. The results show that AIN is stable up to 1000°C in air and remains stable up to 1400°C in vacuo. γ-AIOOH is formed when AIN is treated with water at 100°C but AIN does not react readily with atmospheric moisture at room temperature. The thermal stability of thin films of AIN on GaAs has been evaluated at temperatures between 900 and 1100°C in a nitrogen atmosphere. It was found that AIN did not oxidize under these conditions. Pure AIN is a suitable encapsulant for GaAs at high annealing temperatures in an inert atmosphere.

1. Introduction

Aluminium nitride is currently of great interest as an encapsulant to protect ion-implanted GaAs during annealing. The chemical reactivity of AIN under these conditions is thus of practical importance. Kubaschewski and Evans [1] have reported that AIN decomposes when heated in air at 940 to 950°C whereas Lyutaya et al. [2, 9] state that AIN oxidizes when heated in air above 800°C. In addition, the oxidation of crystals of AIN has been studied by Slack and Chelly [3] who found that at room temperature a protective oxide layer, about 10 nm thick, formed on single crystals of AIN in 1 day. Lavrenk et al. [4] showed that the oxidation rate of sintered AIN in oxygen at 800 to 1100°C was very low and that at 1100°C only 8% was oxidized. Thus it was thought necessary to investigate the stability of AIN under conditions likely to be encountered as a result of encapsulation and annealing of ion-implanted GaAs. X-ray diffraction (XRD), and reflection high-energy electron diffraction (RHEED) have been used to study treated AIN powders and thin films were used to investigate bulk and surface phases formed.

2. Experimental details

AIN powder (99%) was supplied by Koch Light Limited (UK) and had a particle size of 50 μm and a dark grey colour, and by Alfa Products (West Germany) which had a light grey colour and a finer particle size. XRD analysis was carried out using a Debye–Schererr camera of 11.486 mm diameter CuKα radiation and glass specimen capillaries of 0.5 mm diameter. The RHEED analysis was carried out using an operating voltage of 40 kV at background pressure of 3 to 5 × 10⁻⁴ torr. The sample holder was an aluminium block (2 cm × 1 cm × 1 cm) with a wide, shallow groove into which the powder was pressed. The surface was made as smooth as possible before analysis.

Samples of AIN powder contained in porcelain boats were heated in air in a muffle furnace for 3 h at temperatures from 600 to 1400°C. The samples were allowed to cool in the furnace before being analysed. Other samples of AIN powder were placed in quartz capsules 7 cm long and 2 cm diameter, which were evacuated to about 10⁻⁴ torr and sealed. These capsules were heated in a muffle furnace for different times at temperatures [3] from 600 to 1400°C, and then allowed to cool in the furnace.

In order to study the wet oxidation of AIN and to identify any oxidation products, AIN powder was treated with 30 wt% hydrogen peroxide. About 0.5 g AIN was placed in a 250 ml beaker with 125 ml H₂O₂ solution, covered with a clock glass and either (a) heated to boiling point for 10 min, or (b) stirred for 5 min and left at room temperature for 24 h. The suspensions were then filtered and the residues left to dry uncovered at room temperature for 24 h. The reaction of AIN with water was studied by placing about 0.5 g AIN into 125 ml water and boiling for 10 min, when ammonia gas was liberated and a white precipitate formed which was removed by filtration and then dried for 24 h in air. Thin films of AIN were prepared by vacuum evaporation of aluminium metal in an atmosphere of nitrogen and ammonia [5]. The annealing of AIN films was carried out using a graphite strip heater for a very short time (30 sec) in flowing nitrogen and at a temperature of 900 to 1100°C. This process is typical for the rapid thermal annealing of ion-implanted GaAs.

3. Results

Table I shows the results obtained for AIN heated in air for 3 h. The XRD analysis gives the composition of the bulk sample and the RHEED analysis gives that of the surface layer to a depth of a few nanometres. The typical RHEED pattern of the AIN powder at room temperature is shown in Fig. 1. For AIN heated to 1000°C the RHEED analysis revealed the presence of an unidentified phase (X, Fig. 2) which is possibly an oxide or oxynitride. However, on heating to 1200°C, the AIN was oxidized to γ-Al₂O₃ (Fig. 3) but still
**Table II**

<table>
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<th>Temp (°C)</th>
<th>Phases present after heating for 3 h</th>
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<tbody>
<tr>
<td>600</td>
<td>AIN</td>
</tr>
<tr>
<td>800</td>
<td>AIN</td>
</tr>
<tr>
<td>1000</td>
<td>AIN</td>
</tr>
<tr>
<td>1200</td>
<td>$\alpha$-Al$_2$O$_3$ phase X + $\alpha$-Al$_2$O$_3$</td>
</tr>
<tr>
<td>1400</td>
<td>$\alpha$-Al$_2$O$_3$</td>
</tr>
</tbody>
</table>

*Annealing in vacuo showed no sign of oxidation even for samples heated to 1000°C for more than 24 h.

contained a second phase on the surface which had a strong unidentified diffraction line at 0.288 nm (see Table II).

The samples of AIN heated in vacuo in quartz capsules for 24 h at temperatures from 600 to 1400°C contained only AIN when analysed by both XRD and RHEED. Table II shows the $d$-spacings of phase X obtained from the RHEED pattern of AIN heated in air at 1000°C and also shows the $d$-spacings obtained from AIN heated in air at 1200°C and in vacuo at 1400°C. Measured $d$-spacings of $\gamma$-AlOOH (Fig. 4) obtained from the surface of AIN reacted with boiling water, are also listed in the table and the standard patterns of AIN and $\alpha$-Al$_2$O$_3$ are included for comparison. RHEED patterns from thin films of AIN on (100) GaAs are shown in Fig. 5. The diffraction pattern from the as-deposited AIN film (Fig. 5a) reveals the polycrystalline structure of the deposited layer and shows the presence of AIN only. This type of film, when annealed at 950°C, gave the RHEED pattern shown in Fig. 5b. Sharpening of the rings is clearly observed, but no change in the structure has occurred. An AIN thin film of the same type annealed at a higher temperature (1100°C) gave the diffraction pattern shown in Fig. 5c. Again, the diffraction lines are those of AIN alone, clearly demonstrating the oxidation resistance of the AIN thin film. However, some of the rings are "spotty" and this phenomenon may be explained as being due to recrystallization occurring in the layer at this temperature.

**4. Discussion**

AIN powder proved to be resistant to oxidation in air at temperatures up to about 1000°C. At higher temperatures an unknown phase, X, was formed on the surface. This phase could be an oxide or oxynitride of aluminium. The unknown phase, X, and $\alpha$-Al$_2$O$_3$ seem to be related structures, but phase X is not $\alpha$-Al$_2$O$_3$ since the strongest line of $\alpha$-Al$_2$O$_3$ (0.346 nm) is absent in phase X. Furthermore, phase X was formed when thin films of aluminium were annealed at about 1000°C in nitrogen containing traces of air. On heating to 1200°C in air, AIN was transformed completely into $\alpha$-Al$_2$O$_3$, although the pattern from the surface still contains weak traces of the line at 0.288 nm. When heated to 1400°C in evacuated capsules (10⁻⁴ torr) AIN powder did not react at the low oxygen pressure prevailing.

Thin films of AIN deposited on GaAs and then annealed in the temperature range 900 to 1100°C in a nitrogen atmosphere showed no sign of oxidation. However, at higher temperatures some sharpening of the arcs occurred. The appearance of spots in the arcs indicated recrystallization of some of the AIN at 1100°C. The stability of AIN at lower temperatures under various conditions was also investigated. AIN did not react with the oxidizing agent hydrogen peroxide, again indicating the stability of AIN towards oxidation. However, AIN reacted with hot water and the surface was converted to AlOOH (boehmite). Polycrystalline AIN did not form a surface oxide in air at room temperature, although Slack and Chelly [3] have reported that powders and single crystals form a protective layer of oxide 5 to 10 nm thick. Such a crystalline oxide was not detected in the...
<table>
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<th>Standards</th>
<th>Standard RHEED pattern of AIN, room temp.</th>
<th>Results</th>
<th>AIN heated to 1400°C in vacuo</th>
<th>AIN heated in air at 1000°C</th>
<th>AIN heated at 1200°C in air</th>
<th>AIN reacted with H₂O at 100°C</th>
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*vs = very strong; s = strong; m = medium; w = weak.

In good agreement with ASTM data card no. 25-1133

The aluminium oxide hydroxide pattern obtained from the reaction with water showed that AIN does not dissolve readily in water to form aluminium hydroxide. The formation of the crystalline layer of AlOOH prevented further reaction of the AIN with water. It had previously been reported that treatment with water gave either Al(OH)₃ [6]:

\[
\text{AIN} + 3\text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{Al(OH)}_3
\]

or α-Al₂O₃ [7]

\[
2\text{AIN(s) + 3H}_2\text{O(g) \rightarrow NH}_3(g) + \alpha-\text{Al}_2\text{O}_3(s)}
\]

The present work shows that the probable reaction is:

\[
\text{AIN} + 2\text{H}_2\text{O} \overset{100^\circ \text{C}}{\rightarrow} \text{NH}_3 + \text{AlOOH}
\]

5. Conclusions

AlN is suitable as an encapsulant for GaAs under non-oxidizing conditions up to 1400°C; this is at least 200°C higher than might be required in practice for annealing GaAs. Some recrystallization of the AlN thin film occurred between 950 and 1100°C. Polycrystalline AlN is also stable at room temperature under normal conditions of use.

Acknowledgements

The authors would like to thank Mrs P. Bills and Dr D. Lewis from the Chemistry Department for their useful comments. They also would like to thank Mr S. Greaves for carrying out the X-ray analysis.

Figure 4 RHEED pattern obtained from AlN reacted with hot H₂O (γ-AlOOH).

Figure 5 RHEED patterns obtained from thin AlN films on (100) GaAs. (a) As-deposited by vacuum evaporation of pure Al metal in N₂-NH₃ mixture at 3 x 10⁻³ torr. (b) Annealed at 950°C for 30 sec. (c) Annealed at 1100°C for 30 sec.
References


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EVAPORATED ALUMINIUM NITRIDE ENCAPSULATING FILMS

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AlN films were deposited onto GaAs and vitreous carbon substrates held at room temperature, by reactive evaporation of aluminium in the presence of nitrogen and/or NH₃ gas mixture. These films and their combination with very thin layers of Si₃N₄ were successfully used as encapsulants for GaAs and were found to withstand annealing temperatures of up to 1100 °C. Films grown by this novel method were analysed by Rutherford backscattering spectrometry and reflection high energy electron diffraction. Oxygen, nitrogen and aluminium were the only elements detected in the encapsulants. However, the best encapsulants were found to have the lowest oxygen content. The deposition conditions were found to be very important in preventing the reaction of the films with the surface of GaAs during heat treatment.

1. INTRODUCTION

To prevent the decomposition of GaAs and other III-V compounds during heat treatment at high temperatures, it is necessary to protect the surface with a stable dielectric film deposited at low temperature. Many papers have reported the use of SiO₂⁴ and Si₃N₄²⁻⁷ as encapsulants. However, it has been demonstrated that SiO₂ and oxygen-contaminated Si₃N₄ allow gallium to out-diffuse from GaAs surfaces⁸ and also silicon to diffuse from Si₃N₄ into GaAs during annealing⁸⁻¹¹. Despite the fact that Si₃N₄ is reported to provide better surface protection than SiO₂¹², oxygen contamination is still a problem in layers of Si₃N₄ grown by sputtering and chemical vapour deposition (CVD).

Recently, several papers have reported studies of AlN and aluminium oxynitride films⁹,¹⁰,¹³⁻¹⁵ for use as GaAs encapsulants. AlN is thermodynamically more stable, and it has been shown that r.f.-sputtered AlN layers have a thermal expansion coefficient close to that of GaAs¹⁰ (6.6 x 10⁻⁶ °C⁻¹ for AlN, and 6.9 x 10⁻⁶ °C⁻¹ for GaAs). Therefore, the interfacial stress is minimized during heating. Okamura et al.¹⁰ have reported the use of reactively sputtered AlN films for annealing silicon-implanted chromium-doped semi-insulating GaAs at temperatures up to 1000 °C with minimal thermal conversion effects. The oxygen content in
these films was below the detection limit of Rutherford backscattering measurement using 350 keV helium ions. Prior to this, Gamo et al.\textsuperscript{16} studied AlO\textsubscript{x}N\textsubscript{y} deposited by sputtering, and the presence of oxygen in the layers was not detrimental to the attainment of electrical activity from selenium-implanted GaAs.

Recently, we have used evaporated AlN films produced by a novel method described in this paper to obtain high carrier concentrations and good mobilities in GaAs implanted with Sn\textsuperscript{+} and Se\textsuperscript{+} to a dose in the range from 1 \times 10\textsuperscript{14} to 1 \times 10\textsuperscript{15} ions cm\textsuperscript{-2}. An annealing temperature of 1000 °C for 20 s is used to achieve a sheet resistance as low as 30 Ω/□\textsuperscript{17–19} for a 5 \times 10\textsuperscript{14} Sn\textsuperscript{+} cm\textsuperscript{-2} (300 keV, room temperature) dose, using a graphite strip heater. In this paper the preparation and characterization of these evaporated AlN films is presented. The impetus in the investigation into new dielectric films was the need to achieve carrier concentrations high enough to permit fabrication of non-alloyed ohmic contacts required in the development of GaAs integrated circuits.

2. EXPERIMENTAL METHODS

The experimental apparatus used for the deposition of evaporated AlN films was a simple evaporator with some modifications (Fig. 1). It consisted of a chamber where a vacuum of 10\textsuperscript{-6} Torr could be realized by means of a rotary and diffusion pumping system, and a tungsten filament heated by a 100 A power supply. NH\textsubscript{3} was transported into the chamber by bubbling nitrogen through aqueous NH\textsubscript{3}. Pure aluminium was melted and evaporated from a tungsten filament in the chamber held at a pressure of about 10\textsuperscript{-3} Torr. The flow rate of the nitrogen–NH\textsubscript{3} mixture was adjusted continuously to keep the pressure constant in the chamber, which was

Fig. 1. Schematic diagram of the evaporator used to deposit AlN: A, gauge; B, aqueous NH\textsubscript{3}; C, flowmeter; D, tungsten filament; E, shutter; F, sample holder; G, gas inlet; V, valve; DP, diffusion pump; RP, rotary pump.
continuously pumped. The evaporated aluminium reacted with NH$_3$ to deposit AlN onto substrates held at room temperature.

Films deposited onto vitreous carbon substrates were analysed by Rutherford backscattering spectroscopy (RBS). The energy spectrum of 1.5 MeV $^4$He$^+$ ions backscattered from a film surface area of diameter 1 or 2 mm at a scattering angle of 150° was recorded to determine the composition of the AlN layers, applying standard backscattering analysis techniques$^{20}$. The evaporated AlN layers were also analysed using the reflection high energy electron diffraction (RHEED) technique operated at 40 kV and at a background pressure of $(3-5) \times 10^{-5}$ Torr.

3. RESULTS

3.1. Characterization of the deposited AlN films

3.1.1. Rutherford backscattering spectroscopy analysis

RBS analysis of different evaporated films identified aluminium, nitrogen and oxygen as the only elements present. The backscattering spectra obtained from the evaporated films deposited onto vitreous carbon substrates are shown in Fig. 2, where the arrows refer to the presence of a given element on the sample surface. The relative amounts of nitrogen, oxygen and aluminium were estimated for all the films and found to change from run to run. The quantity, uniformity and film thickness depended strongly on the position of the substrate in the chamber during deposition. Films with excess aluminium (Fig. 3) were generally deposited close to the tungsten filament containing the evaporating aluminium. This was so, because the evaporated aluminium atoms impinged directly onto the substrate without reaction with the NH$_3$ gas. Good quality films were deposited onto substrates positioned at a distance greater than 5 cm from the tungsten filament, because the mean free path of aluminium atoms is approximately 5 cm at a pressure of $10^{-3}$ Torr$^{14}$. Figure 4 shows that aluminium was present in excess at the surface of the film and at the substrate film interface. This might also have been due to sudden changes of filament current resulting in changes in temperature of the aluminium to produce either an increase or decrease in the evaporation rate.

The amount of oxygen present in all the films whose spectra are shown in Fig. 3 was approximately constant and was uniformly distributed through the layers. Its presence is thought to be due to hydrolysis of the thin films by atmospheric moisture prior to RBS analysis. This is demonstrated in Fig. 5, which shows a spectrum obtained from an evaporated AlN film similar to those in Fig. 3, with the exception that the AlN film was coated with a thin layer of aluminium immediately after AlN deposition. The amount of oxygen in this case is small compared with that observed in the films of Fig. 3. Therefore, the oxygen was mainly absorbed by the AlN films once exposed to atmosphere. Composition analysis showed that the film was mainly AlN with an excess of aluminium and a thin (about 100 Å) oxide layer on the aluminium surface (shown in Fig. 5 by the surface oxygen peak). This oxide layer (Al$_2$O$_3$), once formed, coats the film, preventing it from further oxidation.

Composition calculations on the spectra of Fig. 3 revealed that the films were mainly composed of AlN and aluminium oxide hydroxide (AlOOH) in the proportions indicated in the figure. These results were confirmed by theoretical
Fig. 2. RBS spectra of 1.5 MeV helium ions backscattered from (a) 3000 Å evaporated AlN on vitreous carbon, showing partial hydrolysis (65% AlN plus 35% AlOOH plus excess aluminium), and (b) 4800 Å evaporated AlN on vitreous carbon, showing that thicker films were less hydrolysed compared with (a) and with spectra of Fig. 3 (85% AlN plus 10% AlOOH plus excess aluminium).
Fig. 3. RBS spectra obtained from various AlN films. (a), (b) and (c) are spectra obtained from evaporated AlN films deposited onto vitreous carbon placed at different positions in the evaporation chamber between the tungsten filament and the NH$_3$ gas inlet: (a) close to the NH$_3$ inlet; (b) at a distance intermediate between (a) and (c); (c) close to the tungsten filament. The amount of aluminium increased from (a) to (c). (d) Simulated spectra for the conditions of Fig. 3(b) above. Spectrum 1 was obtained for a film which did not contain any hydrogen. Spectrum 2 was obtained for a film which contained hydrogen. It was found necessary to assume the presence of one atom of hydrogen for two atoms of oxygen to fit theory to experiment.
Fig. 4. RBS spectrum of 1.5 MeV helium ions backscattered from an evaporated AlN film with an excess of aluminium at both the carbon–film interface and the surface of the film.

Fig. 5. RBS spectrum of 1.5 MeV helium ions backscattered from an evaporated AlN film coated with aluminium immediately after AlN deposition. The amount of oxygen is reduced compared with that present in the films of Fig. 2 and Fig. 3. This demonstrates that oxygen comes mainly from hydrolysis of the AlN films by atmospheric moisture.
simulations of the spectra using the Ziegler program\textsuperscript{21}. It was found necessary to assume the presence of one atom of hydrogen for two atoms of oxygen in the films in order to fit the theory to experiment, despite the fact that no backscattering yield can be obtained from hydrogen. The presence of hydrogen in the films affects their density, and therefore decreases the backscattered yield of helium ions, reducing the peak heights in the spectra collected (see Fig. 3(d)).

Films of thickness less than 1000 Å were found to be completely hydrolysed (Fig. 3) whereas thicker films were only partially hydrolysed—as shown in Fig. 2, in which a spectrum obtained from a 3000 Å evaporated AlN film is presented. The nitrogen peak in this case is complicated by overlap with the oxygen peak. It is apparent that the addition of the nitrogen and oxygen creates the step structure observed in the backscattering spectrum. Composition analysis in this case showed that there were nearly equal amounts of oxygen and nitrogen in the evaporated film and that it was mainly composed of AlN (about 70\%) and AlOOH (about 25\%) with an excess of aluminium.

3.1.2. Dissolution and quality of evaporated AlN films

Prior to any heat treatment, all deposited AlN films were easily removed from the surfaces of the GaAs and the vitreous carbon samples in hydrofluoric acid, regardless of their quality, composition or thickness, and dissolution was spontaneous. However, after heat treatment at high temperatures (about 1100 °C), dissolution was not spontaneous, and films containing excess aluminium at the film–GaAs interface were difficult to remove. In this case the film had reacted with the GaAs surface, forming a compound—possibly GaAlAs, which is not easily attacked by hydrofluoric acid. The same type of films on vitreous carbon were analysed by RBS and showed no change in their composition, and were easily removed in hydrofluoric acid.

It was found that good quality encapsulating layers dissolved readily in hot distilled water, whereas poor encapsulant layers (i.e. aluminium rich) were not readily soluble in hot distilled water. Thus a simple qualifying test was adopted to judge whether films were likely to be successful as encapsulants for GaAs, i.e. whether the films were soluble in hot water before any heat treatment. The films of Fig. 4 failed this qualifying test.

Evaporated AlN films were also deposited onto semi-insulating GaAs and analysed by RBS before and after heat treatment. Figure 6 shows spectra taken from two samples which were coated with evaporated thin films from two different runs. Spectrum a was taken from a film which passed the simple qualifying test described above and was easily removed in hydrofluoric acid before and after the heat treatment. The figure shows no out-diffusion of gallium or arsenic into the cap after the anneal. Spectrum b, however, was taken from a film which failed the qualifying test and could not be removed in hydrofluoric acid after the heat treatment. Spectrum b indicates that gallium and arsenic have out-diffused into the film, presumably forming a structure or compound which is not readily soluble in hydrofluoric acid.

After heat treatment at 1150 °C a change in film colour was observed for those films with an aluminium encapsulant (Fig. 5). This was a result of the evaporation of the excess aluminium from the surface of the film (detected on the glass viewer of the
annealing chamber) and/or reaction of excess aluminium with nitrogen and oxygen to form more AlN or Al₂O₃. RBS analysis of such a film showed that the composition had changed from that of Fig. 5 to that of Fig. 3. Thus the aluminium encapsulant had been removed from the surface of the AlN film, exposing it to atmospheric hydrolysis. No evidence of gallium or arsenic out-diffusion into the AlN cap was observed from RBS data.

The uniformity and quality of the films were difficult to control using the present system. However, when pure NH₃ was used instead of bubbling nitrogen though aqueous NH₃, the film uniformity and deposition rate were improved and no longer depended on the position of the samples in the evaporator. The film composition, however, did not change from that obtained with aqueous NH₃.

3.1.3. Reflection high energy electron diffraction observation

Figure 7 shows the RHEED patterns of evaporated AlN on GaAs(100) and vitreous carbon. Analysis of the patterns showed that the surface layer consisted mainly of polycrystalline AlN (Fig. 7(a)) corresponding to the RBS spectrum in Fig. 2. All the measured d spacings correspond to those of AlN (see Fig. 7(f)) and did not change after heat treatment in nitrogen. Films containing an excess of aluminium (Fig. 3 and Fig. 5) showed the RHEED pattern in Fig. 7(b), where extra rings of fairly weak intensity were due to a thin aluminium film on the evaporated AlN surface. These extra rings, however, disappeared from the pattern in Fig. 7(c)
obtained from the same film annealed in nitrogen at a temperature of 1150°C. As observed with RBS, the excess aluminium had evaporated and/or reacted with nitrogen to form more AlN. Oxide films showed the pattern in Fig. 7(d) which is characteristic of an amorphous structure. As mentioned above in the section on RBS results, the encapsulant failed on GaAs owing to the presence of excess aluminium which resulted in a chemical reaction between the films and GaAs at high temperature. Figure 7(e) shows an unidentified RHEED pattern from a thin layer of encapsulant after such a failure.

3.2. The activation of Sn⁺⁺ and Se⁺⁺-implanted GaAs

To evaluate the evaporated AlN film performance as an encapsulant material for GaAs, and to prove its effectiveness, Hall effect and resistivity measurements were performed on high dose Sn⁺⁺ and Se⁺⁺-implanted GaAs at room temperature, with an energy of 300 keV. The results of these investigations have been published elsewhere [17–19]; however, a summary of the results is presented here. Thermal pulse annealing using a graphite strip heater, an electron beam heater and an incoherent light heater produced high percentage electrical activities for high doses (more than $1 \times 10^{14}$ ions cm$^{-2}$). Initially, the evaporated AlN films of Fig. 2, with and without a protective aluminium top film, were used as encapsulants to achieve a resistivity of

Fig. 7 (continued).
Fig. 7. RHEED patterns from AIN films: (a) good quality thin film of AIN prepared by evaporating pure aluminium wire in N\textsubscript{2}–NH\textsubscript{3} mixture onto semi-insulating GaAs(100) substrate at room temperature; (b) evaporated AIN with excess aluminium on GaAs(100) (extra rings from aluminium metal pattern); (c) thin AIN plus aluminium film annealed at 940 °C, showing AIN pattern only (no extra rings; probably excess aluminium evaporated); (d) amorphous material, probably Al\textsubscript{2}O\textsubscript{3}, formed at the surface of aluminium-rich film; (e) unidentified pattern, probably of an aluminium oxide obtained from a film which failed and reacted with the GaAs surface when annealed at 1150 °C; (f) schematic diagram of the main AIN lattice spacing according to ref. 22, for comparison.

40 \Omega/\square from Sn\textsuperscript{+} implants\textsuperscript{17}. The encapsulant withstood annealing temperatures as high as 1000 °C for 20 s without any sign of cracking or peeling. However, the CVD Si\textsubscript{3}N\textsubscript{4} cap was observed to fail above 950 °C. Evaporated AIN proved to be superior to CVD Si\textsubscript{3}N\textsubscript{4} when implant activations were compared as a function of temperature\textsuperscript{23}. A double-layer cap\textsuperscript{18,19} consisting of 300 Å of CVD Si\textsubscript{3}N\textsubscript{4} covered with 600 Å of evaporated AIN (Fig. 8) allowed temperatures up to 1100 °C to be used, with improved reliability over single-layer caps. The lowest sheet resistance of 28 \Omega/\square\textsuperscript{18} was measured from a sample implanted with a dose of $1 \times 10^{15}$ Sn\textsuperscript{+} cm\textsuperscript{-2}, annealed at 1090 °C for 28 s using a double-layer cap. Using this procedure, electron concentrations of about $10^{19}$ cm\textsuperscript{-3} were obtained from both selenium and tin implants.
DISCUSSION AND CONCLUSIONS

This is the first report of the use of evaporated AlN as an encapsulant for ion-implanted GaAs. The evaporated films were characterized and found to consist mainly of aluminium, oxygen and hydrogen. The presence of oxygen was shown to be due mostly to hydrolysis of the films on exposure to the atmosphere. The protection of these films with a layer of aluminium prevented hydrolysis and showed that the as-deposited layers were mainly AlN with a low oxygen content (see Fig. 5). Films with and without excess aluminium at the surface were used to anneal ion-implanted GaAs successfully to temperatures as high as 1000 °C. Thus, films with no protective aluminium overlay, such as those of Fig. 3 consisting mainly of AlN and AlOOH, can withstand high annealing temperatures despite the presence of a high oxygen content. It is likely that water is lost from the hydrolysed layers during annealing, so that the net oxygen content is reduced. No gallium or arsenic out-diffusion into the encapsulant was observed by RBS.

Difficulties in controlling the deposition process meant that a small amount of aluminium was sometimes deposited onto the surface of the GaAs substrate without reaction with NH$_3$, forming a thin aluminium layer underneath the AlN films. Such films were found to be difficult to remove after heat treatment, because of the reaction of the aluminium layer with the GaAs surface. To avoid this problem, a double-layer encapsulant was developed which consisted of 300 Å of CVD Si$_3$N$_4$ deposited at 635 °C for 15 s, followed by 600 Å of evaporated AlN. This combination withstood annealing temperatures as high as 1100 °C$^{18}$ and produced the lowest resistivity ever recorded from tin-implanted GaAs (see Section 3.2). This double-layer cap provided a more reproducible and reliable method for protecting the GaAs surface during high temperature annealing than a single layer of AlN or Si$_3$N$_4$. (The
CVD Si$_3$N$_4$ layers fail at temperatures of 950°C and above when used alone. Finally, unlike the case of Si$_3$N$_4$, the presence of oxygen in the AlN layers seemed not to affect significantly the quality of the layer as an encapsulant.

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