Formation of Silicon Based Ceramics by Mechanochemistry and Ion Implantation

by

Zhongli Li
(December 1998)
Canberra

A thesis submitted for the degree of Doctor of Philosophy of The Australian National University
The results presented in this thesis are author’s original research unless otherwise stated or acknowledged.

Zhongli Li
Acknowledgments

I am grateful to the staff and my fellow students of the department of Electronic Materials Engineering in the Research School of Physical Sciences and Engineering for their help during my studies.

First of all I would like to express my most sincere thanks to my supervisor Prof. Jim Williams, who has guided me into this exciting and enjoyable research field. His broad physical knowledge and great insight into experimental problems have benefited me during my study. Without his help and support this work definitely would not have been completed.

I wish to also thank Dr. Andrzej Calka for initiating this study and Prof. Barry Ninham, who provided me with the opportunity and motivation to do a PhD degree at ANU.

Sincere thanks to Dr. Jennifer-Wong-Leung, David Llewellyn and P.N.K. Deenapanray for collaborating on TEM and RBS analysis. I am grateful to Jennifer's stimulating discussion which gave me a better understanding of TEM micrographs.

To all members of the ball milling group, I am grateful for all their help, especially thanks to Drs. Nicholas Welham and Ying Chen for enriching suggestions.

Sincere thanks also to fellow PhD students who have already completed their studies: Drs. Genmiao Wang, Tony Puclin, Jonian Nikolov and Robert Corkery, for stimulating discussions, and to fellow PhD students who are still toiling away: Mr. Craig Johnson, Ms. Lan Fu and Shabih Fatima for helping with computer programming and their great friendship.

I would like to thank all the technical staff: Tom Halstead, Tony Kerr, Tony Watt, and Martin Conway for superb technical support in many different ways.
I would like to thank all the other people who contributed to the work of this thesis: Erdong Wu for his help on Mössbauer spectroscopy, Ms R. Chao and R. Bergman for elemental combustion analysis, members of the EMU in ANU and University of Sydney for helping with microstructural and elemental analysis.

I would like to express my most sincere thanks to my son Liang and my husband Beichao, whose outstanding understanding and mental support were essential for this thesis to be completed. I also would like to thank my brother and sisters for their support. Finally, I would like to devote this thesis to my dear parents. I wish them happiness in heaven.
Publications:

The publications directly related to this thesis:


5. Z. L. Li, J. Williams, D. J. Llewellyn and M. Giersig "Mechanochemical reaction and formation of an amorphous nitride phase during ball milling of Si in NH3", submitted to Appl. Phys. Letts.

6. Z. L. Li, J. Williams and D. J. Llewellyn, "Preparation of nanocomposite of Si3N4-SiC by ball milling", submitted to J. Appl. Phys.

Other ball milling publications:


Abstract

The development of silicon-based ceramics (e.g. Si₃N₄, SiC and their composites) is an active area of research because of the desirable properties of these materials. In addition, there is strong interest in improving the thermal, mechanical properties of these materials by optimum processing and also for reducing the production cost. Mechanical alloying (or ball milling) is a non-equilibrium process, which has recently been used successfully to synthesize a range of powders with nanometer scale microstructures. For example, the room temperature reaction of an elemental powder with a nitrogen-containing gas (or active carbon) can be directly induced by ball milling to form nitrides (or carbides). However, most previous ball milling studies have concentrated on transition metal nitrides and carbides. There have been few previous studies which have attempted Si₃N₄ or SiC formation using ball milling.

In this study, the detailed investigation of the formation of α-Si₃N₄, SiC and composite of Si₃N₄–SiC by mechanochemistry has been carried out. The mechanisms of reactions between silicon, carbon and gases (Si-NH₃, Si-C-N₂, Si-C), which can be induced by ball milling or so called mechanochemical reaction, are of particular concern. The results show that the final milling products are very sensitive to milling conditions, such as starting materials, milling ambient, milling temperature and milling energy. The investigation also focuses on the roles of iron, hydrogen and oxygen contamination from the milling ambient during milling. It is found that iron and hydrogen play crucial roles in the adsorption of nitrogen and the ultimate formation of α-Si₃N₄ during milling and subsequent annealing. However, oxygen inhibits the adsorption of nitrogen during milling.
The composite of Si₃N₄-SiC is also successfully formed by milling silicon and carbon powders in nitrogen gas and subsequent annealing. There is a threshold for the carbon starting content, above which nitrogen is adsorbed, and a Si₃N₄-SiC composite can only be formed when the carbon starting content is above this threshold. The presence of iron and the starting carbon phase are also important for composite formation. However, extended milling results in large nitrogen content and α-Si₃N₄ is favored on annealing rather than a composite.

The understanding of the mechanisms for nitride and carbide formation during the milling process is complicated due to the unavoidable presence of iron (and oxygen) contamination. Ion implantation is another non-equilibrium process for forming nitrides and carbides of silicon, used mainly in the semiconductor industry. This is a cleaner process than ball milling and, in this study, the implantation process has also been used to help understand the mechanism of ball milling. The results show that the formation of silicon nitride by both ball milling and ion implantation is quite similar: iron is found to enhance the crystallization of an amorphous Si-N phase formed during both ball milling and ion implantation whereas oxygen inhibits crystallization.
Contents

Chapter 1 General Introduction and Background .......... 1
  1.1 Introduction and Motivation for This Study .......... 1
  1.2 Background to Silicon Based Ceramics .............. 3
    1.2.1 Silicon Nitride (Si₃N₄) ....................... 3
    1.2.2 Silicon Carbide(SiC) ......................... 5
    1.2.3 Nano-Composites of Si₃N₄-SiC ................. 6
  1.3 Ball Milling ........................................ 7
    1.3.1 Extended Solid Solubilities .................. 9
    1.3.2 Disordering and Amorphization ............ 10
    1.3.3 Mechanochemical Reaction .................. 12
References ............................................. 18

Chapter 2 Experimental Techniques ...................... 22
  2.1 Uni-Ball Mill ...................................... 22
  2.2 Ion Implantation .................................. 24
  2.3 X-ray Diffraction .................................. 27
  2.4 Thermal Analysis .................................. 30
    2.4.1 Differential Thermal Analysis (DTA) .... 30
    2.4.2 Thermogravimetry Analysis (TGA) ...... 34
  2.5 Electron Microscopes ............................... 34
    2.5.1 Transmission Electron Microscopy (TEM) .. 35
    2.5.2 Scanning Electron Microscopy (SEM) .... 37
  2.6 Composition Analysis ................................ 37
  2.7 Rutherford Backscattering Spectrometry (RBS) ...... 38
  2.8 Conclusions ........................................ 42
References ............................................. 43

Chapter 3 Formation of Si₃N₄ by Ball Milling of Silicon in Nitrogen Containing Gases .... 44
Chapter 3 Preparation of Nanocomposite of Si$_3$N$_4$-SiC by Ball Milling

3.1 Introduction ................................................................. 44
3.2 Experimental Procedures .............................................. 44
3.3 Initial Milling at Room Temperature ............................... 46
   3.3.1 Milling of 3 g of Silicon ......................................... 46
   3.3.2 Milling of 1 g of Silicon in Ammonia ....................... 49
   3.3.3 Summary of Initial Observations ............................. 50
3.4 Initial Annealing Studies ................................................. 51
   3.4.1 Formation of Si$_3$N$_4$ ............................................. 51
   3.4.2 Composition and Phase Changes During Annealing .... 52
   3.4.3 Summary of Initial Annealing Studies ....................... 56
3.5 More Detailed Studies ................................................... 56
   3.5.1 Effect of Milling Conditions .................................. 56
   3.5.2 Role of Hydrogen, Iron and Oxygen ........................ 63
   3.5.3 Microstructure and Phase Changes during Milling and Annealing ........................................ 69
3.6 Reaction Mechanisms during Milling and Annealing .......... 76
   3.6.1 Amorphous Phase Formation during Ball Milling .... 76
   3.6.2 Processes during Annealing .................................. 78
   3.6.3 Thermodynamic Considerations .............................. 79
3.7 Conclusions ................................................................. 81
References ................................................................. 83

Chapter 4 Preparation of Nanocomposite of Si$_3$N$_4$-SiC by Ball Milling

4.1 Introduction ................................................................. 84
4.2 Experimental Procedures .............................................. 84
4.3 Results ................................................................. 86
   4.3.1 Silicon and Carbon (1:1) Milled in Vacuum ............. 86
   4.3.2 Silicon and Carbon (1:1) Milled in Nitrogen Gas ... 89
   4.3.3 Varying the Carbon Content ................................. 97
   4.3.4 Silicon Carbide Milled in Nitrogen ...................... 100
   4.3.5 Effect of Milling Atmosphere and Pressure ............ 103
4.4 Discussions ............................................................. 107
Chapter 5 Ion Implantation and Comparison with Ball Milling

5.1 Introduction and Background ................................................. 118
5.2 Experimental Procedures ......................................................... 120
5.3 Results and Discussions .......................................................... 122
  5.3.1 N⁺ as Nitrogen Source ......................................................... 122
  5.3.2 SiN⁺ Implantation as Nitrogen Source ................................. 138
  5.3.3 Comparison between Ion Implantation and Ball Milling 146
  5.3.4 Thermodynamics of Ball Milling and Ion Implantation 151
5.4 Conclusions ............................................................................... 153
References ......................................................................................... 155

Chapter 6 Conclusions .............................................................. 156

6.1 Summary and Conclusions ..................................................... 156
6.2 Future Work ............................................................................ 160
Chapter 1  General Introduction and Background

1.1 Introduction and Motivation for This Study

Silicon nitride (Si$_3$N$_4$) and silicon carbide (SiC) are two of the most promising non-oxide ceramic materials for high temperature structural applications. This potential arises because of their excellent mechanical performance and ability to operate under severe environments, for example, high-temperature strength, thermal stability, chemical stability, thermal shock resistance and oxidation resistance, etc. However, the fracture toughness of both monolithic Si$_3$N$_4$ and SiC is low. Much effort has been expended to improve toughness by development of nanostructured materials with the addition of appropriate second phases to induce reinforcing effects$^1$, $^2$, such as composites of Si$_3$N$_4$ and SiC. During the last 20 years, preparation techniques for Si$_3$N$_4$ and SiC (or their composites) have been explored and developed by many groups. Unfortunately, all manufacturing methods of producing such ceramics are conducted at high temperature. The common problems with such high temperature techniques are, firstly, that the technique is expensive$^3$; secondly, the consumption of energy during heating up to high temperature is substantial; thirdly, its multi-step character implies that the process is time consuming; lastly, operations involving liquids and gas can involve serious environmental hazards.

Ball milling has recently been demonstrated to be a powerful technique for the synthesis of a wide range of metal and metalloid nitrides$^4$ and carbides$^5$. The room temperature reaction of an elemental powder with a nitrogen-containing gas or a carbon powder can be directly induced by ball milling. For instance, transition metal nitrides: TiN, ZrN, WN, MoN and Fe$_x$N$_y$, and carbides: TiC, V$_x$C, Cr$_x$C, Mn$_x$C, Fe$_3$C, have been broadly studied by many researchers$^4$, $^5$. However, only a few papers have reported the synthesis of silicon nitride and carbide by ball milling$^6$, $^7$. The results show that the Si$_3$N$_4$ and SiC phases are difficult to produce by ball milling and the end products are very sensitive to milling conditions. The aim of this thesis is to understand the mechanism of
formation of Si₃N₄, SiC and their composites induced by mechanochemical reaction, and to optimize the milling conditions for their formation.

The mechanochemical reaction between metal and a nitrogen-containing gas occurs at room temperature and, hence, the ball milling formation process is largely athermal. In this sense mechanochemical reactions can be considered to be non-equilibrium processes. Another non-equilibrium process for inducing compound formation at low temperatures is ion implantation. In this later process a fast ion beam of nitrogen, for example, is directed into a surface of a material such as silicon. When the concentration of nitrogen is high enough, a silicon nitride can be induced, although, an annealing treatment is normally required to obtain crystalline Si₃N₄. Ion implantation is a clean, vacuum process which is free of contamination. Hence, a comparison of ball milling, where contamination is unavoidable, with the ion implantation process, should be quite valuable in terms of better understanding the ball milling process. Therefore, nitrogen implantation of silicon, together with selective introduction of contaminants was also carried out as part of this study to compare with ball milling.

In this chapter, a brief overview is presented, covering the basic properties of Si₃N₄, SiC and their composites, and synthesis of Si₃N₄ and SiC by conventional techniques. Then follows a review of the synthesis of metastable materials by ball milling. This includes discussions of disordering and amorphization by ball milling, mechanochemistry and solid-gas reactions induced by mechanical action. Chapter 2 introduces the experimental techniques used in this study, and how to choose the right parameters for optimizing the experiments. Chapter 3 presents results of the formation of Si₃N₄ by ball milling silicon in ammonia and subsequent annealing. The effects of milling conditions and impurities are discussed in detail. Chapter 4 reports on studies of the formation of SiC and composites of Si₃N₄-SiC by ball milling elemental silicon and carbon in a nitrogen atmosphere. Chapter 5 explores ion implantation as an alternative means of fabricating Si₃N₄ and compares Si₃N₄ formation induced by the two different non-equilibrium processes: ball milling and ion implantation. Chapter 6 gives a summary of this thesis and recommendations for further work.
1.2 Background to Silicon Based Ceramics

1.2.1 Silicon Nitride (Si₃N₄)

The Si-N phase diagram is shown in Fig. 1.1. The solubility of nitrogen in liquid silicon at high temperature in equilibrium is extremely low. Only one compound (Si₃N₄) is found in this system. Si₃N₄ forms a covalent 3-dimensional hexagonal structure which can exist in both α and β crystallographic forms. Silicon atoms lie at the center of a tetrahedron with nitrogen atoms at each corner. Each nitrogen atom is shared between three tetrahedra so that each silicon atom has four nitrogen atoms as nearest neighbors and each nitrogen has three silicon atoms as nearest neighbors. Both the α and β crystallographic forms can exchange silicon and nitrogen atoms for other atoms without causing any major structural changes.

Silicon nitride has been known to chemists for over 80 years. Very early applications of Si₃N₄ were as thermocouple sheaths in the ferrous metal industries and as components for handling molten aluminum. First reports on silicon nitride as a
structural ceramic material, and on the formation of reaction bonded silicon nitride, appeared in the 1950's\textsuperscript{15}. Considerable interest in silicon nitride for its possible use for hot zone components in a range of high-temperature gas turbine and diesel engines\textsuperscript{16} has been maintained since the 1960's. However, large scale application of Si\textsubscript{3}N\textsubscript{4} has been severely limited by its difficulty of formation and its high cost. As a result, the major uses have been in niche areas where high cost for key components can be tolerated. Most of the current commercial applications for silicon nitride derive from its good combination of mechanical, thermal, and thermo-mechanical properties such as high strength at high temperature, low coefficient of thermal expansion, resistance to thermal shock, and resistance to oxidation and corrosion at high temperature. Detailed mechanical properties are given at reference\textsuperscript{17} and key properties of reaction bonded Si\textsubscript{3}N\textsubscript{4} are summarized in Table 1.1

<table>
<thead>
<tr>
<th>Property</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g.cm\textsuperscript{-2})</td>
<td>2.0-2.8</td>
</tr>
<tr>
<td>Expansion coefficient (20-1500 °C), (10\textsuperscript{-6}°C\textsuperscript{-1})</td>
<td>2.9-3.6</td>
</tr>
<tr>
<td>Volume resistivity ((\mu)m)</td>
<td>10\textsuperscript{-13}</td>
</tr>
<tr>
<td>Microhardness (vickers, MNm\textsuperscript{2})</td>
<td>1600-2200</td>
</tr>
<tr>
<td>Young's modulus (RT) (GNm\textsuperscript{2})</td>
<td>120-220</td>
</tr>
<tr>
<td>Fracture toughness (MNm\textsuperscript{3/2})</td>
<td>1.5-2.8</td>
</tr>
<tr>
<td>Flexural strength (RT), (MNm\textsuperscript{2})</td>
<td>150-350</td>
</tr>
</tbody>
</table>

Silicon nitride powder can be synthesized by several methods, some of which are already used for commercial production. Most industrial Si\textsubscript{3}N\textsubscript{4} powder is manufactured by either carbothermal nitridation of SiO\textsubscript{2}:

\[ \text{SiO}_2 + \text{C} + \text{N}_2 \rightarrow \text{Si}_3\text{N}_4 \] (above 1400 °C)\textsuperscript{18}.

or direct nitridation of silicon powder:

\[ \text{Si} + \text{N}_2 \rightarrow \text{Si}_3\text{N}_4 \] (above 1100 °C, with Fe as a catalyst)\textsuperscript{19}.

Si\textsubscript{3}N\textsubscript{4} also can be synthesized by liquid and gas reaction, e.g. by reaction of silicon tetrachloride and ammonia (one or both is liquid):

\[ \text{SiCl}_4 + \text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 \] \textsuperscript{20, 21, 22}.
Si₃N₄ powders must be consolidated to bulk material at high temperature before they can be used. However, Si₃N₄ consolidation is difficult because of the low self-diffusion coefficient of its constituents and high degree of covalent bonding. Thus, densification of Si₃N₄ is usually carried out at a high temperature (1400-1800 °C) through the addition of metal oxides such as MgO, Al₂O₃ and Y₂O₃. These sintering aids form a liquid phase at elevated temperatures and promote densification by means of solution-precipitation.

The behavior of the Si-N system, and the mechanism whereby silicon powder is converted into a sintered silicon nitride, has been a fascinating subject involving much research and development during the last 30 years. Despite this, a full understanding of the development of the silicon nitride microstructure has still to be achieved and more cost-effective methods of its production remain to be developed. In this latter regard, there are some emerging laboratory techniques for synthesis of Si₃N₄ including plasma synthesis, laser-induced reaction and mechanical alloying (the subject of this thesis). However, none of these methods has been fully developed or characterized.

1.2.2 Silicon Carbide (SiC)

Fig. 1.2 is a diagram of the Si-C binary system. Only one intermediate phase (SiC) is found. However, there are many different crystal forms of SiC falling into α- and β classes. High temperature hexagonal α-SiC has a high refractive index, high birefringence and strong dispersion: it can be subdivided into five poly types. The primary form of β-SiC is stable at low temperature and has cubic symmetry. SiC can be produced through many approaches. Most of the industrial SiC powders are manufactured by the Acheson process which involves carbothermic reduction of SiO₂ by carbon powders at temperatures reaching 2000-2300 °C for 30h:

$$\text{SiO}_2 + \text{C} \rightarrow \text{SiC} + \text{CO}_2 \text{ (gas)} \text{ (above 2000 °C)}$$

SiC is also synthesized through liquid phase reaction, e.g. by the reaction of SiCl₄, CCl₄ and Na in heptane at 230 °C:

$$\text{SiCl}_4 + \text{CCl}_4 + \text{Na} \rightarrow \text{SiC} \text{ precursor (amorphous)} + 8 \text{ NaCl}$$

$$\text{SiC} \text{ precursor (amorphous)} + \text{NaCl} \rightarrow \text{SiC} + \text{NaCl} \text{ (1500-1800 °C)}$$
1.2.3 Nano-Composites of Si₃N₄-SiC

Advanced ceramics such as Si₃N₄ and SiC have excellent properties in monolithic form. Nevertheless, material uniformity, reproducibility, reliability and brittleness are still problems to be dealt with for any type of ceramic-based material. Mechanical properties of monolithic ceramics, especially the fracture toughness, can be significantly increased by adding a second phase. High temperature mechanical properties such as flexural strength and creep resistance could also be improved with reinforcement by particle addition. In nano-composites, second phase nano-dispersions can be dispersed within the matrix grains or at grain boundaries, thus giving improved fracture toughness and strength. Particle and whisker/fiber reinforcements are
commonly used in order to improve strength and fracture toughness. The nanocomposite Si₃N₄-SiC is one of the most successfully developed composites for this purpose. Studies of structural development show that the added SiC nanograins are located within Si₃N₄ grains and also in grain boundaries. It is well known that the incorporation of SiC into an Si₃N₄ matrix influences the microstructure and increases the mechanical properties compared to those in pure Si₃N₄ material. The increased fracture toughness is shown in Table 1.2. Additional interest in composite materials is based upon the fabrication of very small grain size ceramics, particularly in the nanosize regime, which reduces the sintering temperature. Several methods to obtain nanocomposite Si₃N₄ -SiC have been reported. Typical methods include hot pressing amorphous Si-N-C mixtures prepared by chemical vapor deposition (CVD); mechanical mixing of Si₃N₄ and SiC powder, nitridation of SiC-based green compacts through hot isostatic pressing (HIP) and carbon coated on Si₃N₄ powder surfaces.

Table 1.2 Comparing of Si₃N₄ and composite Si₃N₄-SiC

<table>
<thead>
<tr>
<th></th>
<th>Average grain size (µm)</th>
<th>Fracture toughness (MPa·m¹/²)</th>
<th>measured</th>
<th>calculated(Eq.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si₃N₄ (+1.5 w/o Al₂O₃+6 w/o Y₂O₃)</td>
<td>0.37 ± 0.27</td>
<td>4.7± 0.3</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td>Si₃N₄+10 v/o SiC</td>
<td>0.36 ± 0.24</td>
<td>4.4± 0.1</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td>Si₃N₄+20 v/o SiC</td>
<td>0.36 ± 0.24</td>
<td>6.4± 0.5</td>
<td>6.2</td>
<td></td>
</tr>
</tbody>
</table>

Mechanical ball milling has great potential for production of large quantities of nanosize ceramic powders which may lead to a variety of processing flexibility such as superplasticity, low sintering temperature and simultaneous densification and shape-forming ability.

1.3 Ball Milling

Ball milling has recently been demonstrated to be a powerful technique for non-equilibrium processing (alloying, compound synthesis and reduction). In the ball milling
process involved in mechanical alloying of metals, the powder particles are trapped between colliding balls or between ball and vial, and are subjected to a severe plastic deformation accompanied by hardening and a local rise in temperature. Particles are repeatedly flattened, fractured and often cold-welded, depending on their mechanical properties. In time, powder particles with a characteristically lamella structure are formed. The lamellar structure is increasingly refined during further milling. Furthermore, inter-diffusion between the constituent layers of the lamellar becomes active as the local temperature of the particles increases or is significantly enhanced by a high density of defects. As a result, a balance between coalescence and fragmentation is achieved during ball milling which leads to a rather stable average particle size and a uniform composition. As a result of the non-equilibrium, somewhat athermal processes occurring during ball milling, non-equilibrium material compositions and microstructures often develop that cannot be produced by conventional processing techniques. Another important feature of mechanical ball milling is that it can change the reactivity of solids due to either increases in the system free energy or decreases in the activation energy for chemical reactions, for example, by the accumulation of non-equilibrium defects and the creation of atomically clean surfaces. The activated clean surfaces have a great affinity for gas adsorption when the powder particles are exposed to a reactive gas environment. Solid-gas reaction may subsequently take place under a mechanical external force. When chemical reactions are induced, the process is referred to as mechanochemistry.

Recent investigations have shown that milling conditions such as milling mode, milling time, milling temperature, milling atmosphere, milling speed, the nature of the balls, starting materials, and the ball-to-powder mass ratio are important parameters for determining the milling process and the end milling products. Milling mode is a combined description of milling energy and the milling force involved in the milling processes. In general, the mechanical alloying or mechanochemical reaction processes take place much more quickly under higher energy milling conditions. However, higher contamination from milling media is usually obtained for higher milling energy. There are mainly two types of energy transfer occurring during
milling, involving impact force and shearing force. It has been reported\textsuperscript{61} that impact force leads to cold welding in ductile materials, which results in the formation of alloys, while, on the other hand, the shearing force controls mainly the fracture process, leading to the refinement of particle size. For brittle materials, high energy impacts also favor fracturing. Milling temperature is a most controversial parameter as determined from conflicting reports\textsuperscript{62, 63, 64}. However, there is agreement that milling temperature can strongly affect inter-diffusion, defect creation and relaxation during milling. The effects of milling atmosphere can be divided into two categories: reactive and non-reactive atmosphere. Non-reactive environments such as vacuum or Ar gas protects milled powders from oxidation\textsuperscript{65, 66}. Gas molecules can be adsorbed onto fresh particle surfaces created during milling, substantially lowering the gas pressure in an enclosed mill. Adsorption of reactive gases during milling in a reactive gas atmosphere, such as nitrogen, hydrogen and ammonia, may enhance the grain refinement and amorphization\textsuperscript{67, 68} or induce mechanochemical reactions\textsuperscript{69}. The properties of the starting materials are also obviously important. The composition\textsuperscript{70} and chemical affinity\textsuperscript{71} of starting materials play a significant role in the milling process and the determination of end products.

Mechanical ball milling was originally used in the late 1960’s and early 1970’s by Benjamin, Volin and Bomford\textsuperscript{72, 73, 74} for the development of dispersion-strengthened Ni and Al based superalloys. This project was ultimately unsuccessful\textsuperscript{75}. However, a number of key ideas developed during this effort to offer an alternative way to achieve the original goal. In particular, ball milling was envisaged to be capable of producing a wide range of metastable phases, such as extended solid solubilities\textsuperscript{76}, gross disordering, amorphization, mechanochemical reactions and solid-gas reactions, thus opening up many possibilities for materials synthesis.

1.3.1 Extended Solid Solubilities

Extended solid solubilities have been noted in the process of studying amorphization in several alloying systems. Schwarz \textit{et al}\textsuperscript{77} found that the solubility limit of Ti in fcc Ni was approximately 28 at\% on ball milling Ti and Ni powders. The
equilibrium solubility of Ti in Ni is only a few percent. It was suggested that this increased solid solubility was associated with the formation of a metastable amorphous phase. Hellstern et al. found an extended solid solubility of Al in bcc Nb of about 30 at% for ball milling of elemental Nb and Al powders. The stable equilibrium diagram for Al-Nb indicates Al solubility of <10 at% for temperatures below 1000 °C.

1.3.2 Disordering and Amorphization

It is well known that large strains and plastic deformation (>20%) can destroy long range chemical order in ordered alloys. As in the case of extended solid solubilities, most of the studies of disordering by ball milling have so far been in conjunction with experiments on amorphization. Amorphization can be obtained by ball milling either elemental powders (mechanical alloying, MA) or intermetallic compounds (mechanical milling, MM). The first example of amorphization of intermetallic compounds by MM was reported by Ermakov et al. in the Y-Co and Gd-Co systems. The first suggestion that MA might produce amorphous material was made by White during a study of the synthesis of superconducting Nb3Sn via MA and subsequent thermomechanical treatment. The first definitive study of amorphization by MA was carried out by Koch et al. in the easy-glass-forming alloy system Ni-Nb. In this experiment, powders of Ni and Nb were milled together in a high-energy ball mill. The as-milled product was appropriately examined and identified by X-ray and Mössbauer techniques and exhibited the characteristics of an amorphous material. The driving force for this reaction was initially postulated to be the gain of free (strain) energy by alloying the elements, while nucleation of the crystalline intermetallic compounds with an even lower free energy was kinetically suppressed. Since then, a number of alloys have been amorphized by MA.

In order for amorphization to occur by MM of an equilibrium intermetallic compound, the free energy of the crystal must be raised to that of the corresponding amorphous alloy. Defects introduced by the deformation during milling must be responsible for raising the free energy of the crystalline compound. Energy can be stored in defects such as vacancies, interstitials, dislocations, grain boundaries and other...
atomic disorder involving strain energy. The question here is what defects are controlling a given reaction? It has been reported that the free energy difference between the crystalline compound and an amorphous metallic alloy is typically 5-20 kJmol\(^{-1}\) \(^9\). A maximum value for the stored energy associated with a very high dislocation density of about 10\(^{14}\) cm\(^{-2}\) in cold-rolled NiTi was estimated to be 2.2 kJmol\(^{-1}\) by Koike \textit{et al}\(^9\), which is minor compared with that required for a crystalline to amorphous transformation. During ball milling, the crystalline size may be reduced to nanocrystalline dimensions and Yamada \textit{et al}\(^1\) have suggested that nanocrystalline boundaries may be responsible for driving the crystalline to amorphous phase transformation in Ti-Ni. Seki and Johnson\(^2\) have suggested that the amorphization of the CuTi\(_2\) intermetallics by milling was driven mainly by the energy stored in antiphase domain boundaries. The contribution from dislocations was estimated to be 1 kJmol\(^{-1}\). The remainder of stored energy required for amorphization (the enthalpy of crystallization =11 kJmol\(^{-1}\)) was believed to come from the disordering at antiphase boundaries. Bakker and coworkers\(^3\) have argued that anti-site chemical disorder is the main source of energy storage in ball milled intermetallics. They suggest that amorphization results when the free energy of the disordered compound exceeds the free energy of the amorphous state. Thus it appears that anti-site disorder and grain boundary energy of nanoscaled grains are the important defects which can drive the crystalline-to-amorphous transformation by MM.

Most studies described above involve mixtures or alloys of transition metals. Relatively less research on amorphization by mechanical treatment has been carried out on other materials and elements such as silicon. However, there have been a few studies of structural changes which occur due to milling of silicon\(^4\)\(^-\)\(^6\)\(^-\)\(^6\). Gaffet and Harmeling\(^4\) first reported on the partial amorphization of elemental silicon (about 10% of the volume) by ball milling. Based on experimental investigations (SEM, EDX, XRD, TEM, DSC), they claimed that the transition occurred during a continuous refinement of the grain size of the particles and a change in the lattice parameter of silicon lattice which leads to destabilization of the diamond structure. Bokhonov \textit{et al}\(^5\) subsequently also observed partial amorphization of milled silicon and suggested this
occurred during MA due to the formation of amorphous SiO, which is structurally similar to amorphous silicon. The effect of oxygen on the amorphization process was more directly reported by Millet et al\textsuperscript{7}. However, the later results showed a poor correlation between the level of oxygen contamination and the formation of the amorphous phase, although oxygen did appear to play a role in amorphization. On the other hand, the subsequent crystallization temperature of the amorphous silicon during annealing increased with the percentage of oxygen. It was suggested that the presence of oxygen appeared to stabilize the amorphous silicon induced by ball milling. A more recent study carried out by Shen et al\textsuperscript{96} indicated that most of the amorphous silicon is concentrated near the surface of the milled particles, while the grain size of the inner nanocrystalline silicon ranged from 3 to 20 nm. The crystallite-refinement-induced amorphization mechanism was first suggested by Gaffet and Harmeling for milled silicon\textsuperscript{94}: there is a critical grain size below which the crystal to amorphous transition is favored.

### 1.3.3 Mechanochemical Reaction

Increasing attention has also been paid to chemical processes driven by external mechanical energy; so called mechano-chemistry. Mechanochemistry is described as a process where chemical reactions develop under the influence of a mechanical action and where the mechanical action changes the reactivity of solids\textsuperscript{98}. Thus the reaction can occur at temperatures much lower than they would normally occur under thermal equilibrium. Some examples from the literature are given below, with particular emphasis on carbides and nitrides.

It was suggested that high energy states induced by MA increase the chemical reactivity, and high temperature chemical reaction can take place at room temperature by high energy ball milling. For example, reaction between Al and graphite leading to the formation of Al\textsubscript{4}C\textsubscript{3} was observed by Jangg and was called reaction milling\textsuperscript{99}. Following the finding by Jangg, the formation of high temperature phases, such as metal carbides and silicides by milling transition metals with active carbon (or graphite) and silicon, was reported by several authors\textsuperscript{100, 101}. Such reactions to form ceramics and
silicides normally take place at elevated temperature. However, owing to enhanced reactivity due to the refined grain size and accumulated lattice defects during ball milling, reaction can be expected to take place at much lower temperatures. For example, Cocco et al.\textsuperscript{102} found reactions between Ti and Si\textsubscript{3}N\textsubscript{4} took place at room temperature after a certain period of milling, forming TiN and Ti-silicides such as Ti\textsubscript{5}Si\textsubscript{3} and TiSi\textsubscript{2}.

The first solid-gas reaction induced by ball milling was produced more or less by accident\textsuperscript{103}. In this case, the milling of erbium in molecular nitrogen, which had been selected as an inert medium, unexpectedly showed the formation of an erbium nitride. Many of the early examples of solid-gas reaction induced by ball milling were inadvertently found to occur during amorphization studies. For example, the mechanical alloying of elemental Cr and Cu-Cr alloy in nitrogen atmosphere was reported by Ogino et al.\textsuperscript{104}, who found that large amounts of nitrogen were absorbed during milling in Ar-air and Ar-N\textsubscript{2} atmosphere, resulting in significant grain refinement and subsequent amorphization of chromium and Cr\textsubscript{70}Cu\textsubscript{30}. It is highly probable that amorphous nitrides were formed in such cases. Aoki et al.\textsuperscript{105} also reported nitrogen-induced amorphization of Ti-Zr powders during mechanical alloying and formation of an amorphous nitride phase a-TiZrN\textsubscript{0.3}. In general the amorphization of pure metals or binary alloys from the same group in the periodic table and exhibiting compete solid solubility such as Ti-Zr, V-Nb, and Ni-Pd is hard or impossible by ball milling or rapid quenching without the presence of contaminants. However, the synthesis of an amorphous metal nitride such as a-TiZrN\textsubscript{0.3} can be achieved by a combination of alloying (Ti-Zr) and chemical reaction (N\textsubscript{2}.Ti, Zr). Koch et al.\textsuperscript{81} prepared amorphous Ni\textsubscript{60}Nb\textsubscript{40} from elemental powders by MA in air and helium atmosphere. The crystallization features and the position of the maximum of the principal peak in the X-ray diffraction pattern are different, due to the different oxygen concentrations in the alloys. Wang et al.\textsuperscript{106} studied effects of different atmosphere on the mechanical alloying of Ni\textsubscript{60}Ti\textsubscript{40} composite powders. The results show that there are different transformation paths when this material is milled in different atmospheres. These last two studies clearly indicate enhanced oxidation induced by ball milling. Although the above studies only reported the results of amorphization of
materials by solid-gas reaction induced by ball milling, they clearly involved mechanochemistry and nitride/oxide formation. However, the understanding of the gas adsorption and reaction processes during the milling were not examined. The aim of the present work is to study the mechanism of the gas adsorption induced by ball milling, to examine the effects of milling conditions on solid-gas reactions, and to understand the mechanism of compound formation under a reactive atmosphere, such as nitrogen and ammonia.

In many of the above, early examples of gas-solid reactions by mechanical alloying, the formation of a nitride (or oxide/hydride) was not the main objective of the study. However, a number of transition metal nitrides have been purposely synthesized by ball milling. The first such report on nitride formation by mechanical alloying was by Calka\textsuperscript{107}, who found that TiN and ZrN can be directly formed after milling elemental powders Ti and Zr in nitrogen gas at room temperature. He suggested that the rough, clean surfaces created by ball milling absorb nitrogen and the mechanical action induces the dissociation of molecular nitrogen. Furthermore, the rate of generation of the clean surface is critically dependent on the shearing action of the balls during milling. One year later, many other nitrides were synthesized by ball milling of elemental powders in a nitrogen atmosphere, such as VN, BN, WN by Calka \textit{et al}\textsuperscript{108}, Ti\textsubscript{2}N, Fe\textsubscript{2}N, Fe\textsubscript{4}N by El-Eskandarany \textit{et al}\textsuperscript{109}. Using ammonia as a source of nitrogen to synthesize metal nitrides by ball milling was first carried out by Koyano\textsuperscript{110} and Calka\textsuperscript{111}. More recently, the use of NH\textsubscript{3} as a nitrogen source during milling has attracted considerable interest as a result of the enhancing role of H in the reaction process\textsuperscript{112}. Under ball impact, NH\textsubscript{3} dissociates into hydrogen and nitrogen atoms. Both nitrogen and hydrogen are adsorbed by the elemental powder and, when the nitride forms, hydrogen is eventually evolved as hydrogen gas. The pressure change during milling was measured by Chen \textit{et al}\textsuperscript{112}, who found that for milling of titanium in ammonia, the pressure first decreased then increased again as hydrogen gas was liberated.

A dynamic study of nitride formation induced by ball milling was carried out by Ogino \textit{et al}\textsuperscript{113}. They studied elemental Ti, Zr, Nb, Ta, Sr and Mo powders milled in N\textsubscript{2} atmosphere. Their results suggested that the nitriding rate increases with an increase in
the enthalpy of nitride formation. They suggested that the nitrogen absorption in the powders occurs at the instant the ball collision occurs and the quantity of nitrogen adsorbed by one collision event is nearly proportional to the mechanical energy supplied to the powder. Ogino et al.\textsuperscript{114} reported that the nitriding reaction kinetics are a function of milling energy for Ti and Ti-Al systems in a nitrogen atmosphere. In addition, a more detailed study of the milling dynamics, together with the relation between milling condition and the rate of solid-gas reaction has been carried out by Calka and Nikolov\textsuperscript{115,116}. They found that when Ti and Fe are milled under different milling modes in a nitrogen atmosphere, the mode involving shearing force is the most promising one for creating solid-gas interactions, because the rubbing action of a shearing-force exposes fresh surfaces to reactive gases.

More detailed studies of the effect of the solid-gas reaction process on milling conditions, such as milling atmosphere and milling temperature, were carried out by Chen and co-workers. For example, the synthesis of iron nitride was carried out in different nitrogen sources (NH\textsubscript{3} and N\textsubscript{2})\textsuperscript{117}. They suggested that ammonia is a more efficient nitriding source for the formation of iron nitride than nitrogen gas and the presence of hydrogen appears to play a catalytic role in assisting the nitriding reaction during the ball milling of a gas-solid mixture. A comprehensive study of the catalytic role of hydrogen was carried out in the Ti-NH\textsubscript{3} system during ball milling\textsuperscript{112}. The formation of an intermediate hydride TiH\textsubscript{1.5} converts the ductile Ti metal to a more brittle metal hydride, which enhances the rate of fracturing and particle size reduction\textsuperscript{118}. The TiH\textsubscript{1.5} decomposes during prolonged milling and forms TiN subsequently.

A systematic study of nitride formation induced by mechanochemical reaction covering more than 20 elemental powders has recently been carried out by Nikolov as part of a PhD program\textsuperscript{119}. The major achievements of his study are shown in Table 1.3, which indicates that the mechanochemical reaction and phase transformation processes can end in very different milling products, depending on the milling system and milling parameters. However, the gas-solid-state reactions occurring during milling are not completely understood. The reaction mechanism between elemental solid and gases is sensitive to many parameters such as type of elemental solid, composition of nitriding
atmosphere and pressure, milling energy, mode of milling (impact to shearing ratio), milling temperature, surface properties and others.

In this thesis, the silicon-gas (N₂, NH₃) and (silicon + carbon)-gas (N₂, NH₃) systems were chosen to extend the early studies of the effect of milling conditions, not only because Si₃N₄ and SiC are promising non-oxide, high-temperature ceramic materials, but also because the end products of these systems are very sensitive to milling conditions such as milling energy, milling temperature, atmosphere and impurities, and hence are very difficult to produce. Unlike transition metal nitrides, the only report that has been published on the synthesis of Si₃N₄ by ball milling has been from our laboratory. This thesis reports on a detailed investigation of Si₃N₄ formation during ball milling of silicon in an ammonia environment and subsequent annealing. The main aims were to understand the mechanism of mechanochemical reaction in the Si-N system and to optimize the milling conditions for the silicon nitridation reaction. The role of hydrogen and iron in the process is also of particular concern. Furthermore,
the formation of the Si$_3$N$_4$-SiC composite was investigated by milling silicon and carbon in nitrogen gas atmosphere and subsequent annealing. The effect of carbon and iron is discussed.

Ion implantation of nitrogen into silicon was also studied to compare with nitriding results from ball milling. A brief literature review of ion implanted nitridation will be left until Chapter 5. Suffice it to say here that the non-equilibrium mixing and athermal reaction of nitrogen with silicon during implantation and subsequent annealing would appear to have some similarities to the non-equilibrium ball milling process. However, ion implantation is a "cleaner" process than ball milling, and therefore may allow contamination effects during ball milling to be clarified.
References:

Chapter 1 General Introduction and Background

49 C. Herring, J. Appl. Phys. 21, 301 (1950).
60 C.C. Koch, Nanostructure Mater. 9, 13 (1997).
Chapter 1 General Introduction and Background

Chapter 1 General Introduction and Background

Chapter 2 Experimental Techniques

As introduced in Chapter 1, this thesis is focused on an investigation of the mechanism of formation of Si-based ceramic materials by mechanochemical reaction during ball milling. The experiments were carried out under different conditions, such as milling time, energy, temperature and atmosphere. The as-milled and subsequently annealed samples were investigated by X-ray diffraction (XRD), thermal analysis (DTA, TGA), combustion elemental analysis, electron microscopy (SEM, TEM, STEM), Mössbauer spectroscopy and Rutherford backscattering (RBS). For comparison, ion implantation experiments were also carried out as an alternative method to produce and analyze the same ceramic materials. This Chapter describes the basic principle of the above experimental techniques and equipment, and gives examples of data using typical experimental parameters used in this study.

2.1 Uni-Ball Mill

To study the formation of silicon nitride-based ceramics by mechanochemistry, the type and operation of the ball milling device is very important. Three types of devices are generally used for research into mechanical alloying: attritors\(^1\), rotating mills\(^2\) and vibratory mills\(^3\). In each mill design, the central event which determines the microscopic deformation, welding and fracture behavior is the ball-powder-ball or ball-powder-cell-wall collision. For example, a vibratory mill (containing several tens of balls) is a high speed and high energy mill due to the three dimensional motion and high frequency of balls and powders. Attritors contain typically many more balls and the greatest number of collisions occurs between the balls and powder and the collisions are at low energy. In comparison with the vibratory mills and attritors, rotating mills contain few balls and they operate at reasonably high speed. All the ball milling experiments carried out in this thesis were performed on a home-built rotating milling device (Uni-Ball Mill)\(^4\), which was specially designed for magnetically controlled ball
The balls are made of magnetic steel with varying diameters (1”, ½” and 1/3”). The balls are confined in a vertical cell whose rotation is variable through a range of 10–300 rpm. The milling cell is made of non-magnetic stainless steel, and has a small volume of 300 ml. The cell can be sealed under vacuum (10⁻³ Pa) or a positive gas pressure (maximum 500 kPa) by an “O” ring seal and a valve. An attached pressure gauge is used to monitor the pressure change during milling in a gas atmosphere. A heater can be mounted on the back wall of the cell allowing experiments to be carried out from room temperature up to 200 °C. The temperature is monitored by Cr-Al thermocouple which is connected to a temperature controller. A liquid nitrogen (or other cooling agent) bath is available as an option for milling at below ambient temperature. The typical feature of this mill is that external magnets are placed near the milling cell to control the ball movement, and hence the impact force and the milling energy. The position of magnets can control the mode of milling from predominantly shearing force mode to high impact force mode. The milling mode can strongly influence the milling process and, in some cases, determine the phase and
Chapter 2 Experimental Techniques

microstructure of the final product. Calka et al. have carried out a systematic series of experiments to determine the effects of magnet position. Their results, using a perspex cover and a high speed camera, have shown that when a single magnet is placed at the bottom of the milling cell (M₁ in Fig. 2.1), the magnet field holds the balls mainly in the bottom parts of the milling cell, generating a shearing force between ball and the cell. When the magnet is placed at the side of the milling cell (M₂), the balls are pulled up by this magnet, and fall to provide a high impact force to the powder. When two magnets are placed at positions M₁ and M₂, it is possible to provide an impact force of about 50 times the gravitational force, thus giving very high energy milling conditions. In general, highly energetic mills produce the end product more rapidly. However, the Uni-Ball Mill is a very low efficiency mill (small number of impacts per second) compared with a SPEX mill (vibratory) or a Fritsch mill. For example, using high energy milling (Spex 8000 vibration mill), Le Caër et al. have synthesized various carbides and silicides by milling metallic elemental powders with graphite or silicon for up to several tens of hours. However, similar processes take place after several hundred hours of milling using the Uni-Ball Mill. It should be stated that the level of iron contamination is very sensitive to the milling conditions and to the powders and gases in the mill. For example, for milling of silicon in ammonia, a major focus in this thesis, iron contamination appears to be a problem. Silicon and iron easily react with each other forming iron silicides during milling. These unwanted phases strongly affect the end products of milling. High energy milling usually increases iron contamination so that a compromise is often used in arriving at experimental conditions. For silicon milled in ammonia (Chapter 3), the shearing force mode was used to minimize the reaction between silicon and iron contamination. For a mixture of silicon and carbon milled in nitrogen (Chapter 4), iron contamination is small and, for efficient milling, the high impact mode was used.

2.2 Ion implantation

Ion implantation is a non-equilibrium process which incorporates impurities into a solid by bombardment with energetic ions, and results in the near surface modification
of the material. The basic ion-solid interaction processes are\(^8\): i) ion implantation can lead to the build up of a concentration profile of foreign atoms within a solid, thus altering the near-surface composition; ii) a fast ion can lead to the displacement of several tens, and even hundreds, of lattice atoms within a volume surrounding the ion trajectory, and create considerable structural damage to the material; iii) following bombardment with many ions, significant sputtering of the surface (removal of surface atoms) can have occurred; iv) solid atoms can be transported within the dimensions of the collision cascade at temperatures below those at which normal diffusion processes would operate.

Three ion implanters were used in this study: The Mk4 Lintott implanter at Harwell, a 1.7 MV NEC tandem implanter at ANU and a 150 keV implanter at ANU. The Harwell implanter can deliver positive ions at high current. The ANU implanters use a negative ion source and have implantation temperature control from liquid nitrogen temperature to a few hundred degrees centigrade. All of the implanters have similarities in their basic operation systems, and a schematic illustration of the 1.7 MV machine is shown in Fig. 2.2. The negative ions are produced in the ion source which is floated to a high voltage (up to 100 keV negative). The ions are focused into a beam and only those ions with a particular mass-to-charge ratio are allowed to pass through the magnetic analyzer. After further acceleration in the high voltage tank (up to 1.7 MV), the negative ions can undergo a charge exchange in the high voltage terminal, converting them to positive ions. They are then accelerated out of the terminal to earth gaining twice the terminal energy (for ions with one positive charge). Another magnet is then used to transport a well-focussed beam of selected energy and charge state onto the sample. The ion beam is then deflected by a varying electric field in the scanning unit so it can uniformly cover a desirable target area which is confined by an aperture. The implantation dose is monitored by a current integrator connected to the target and secondary electron emission is suppressed by applying a voltage (-300 V) to a cylindrical shield surrounding the target. In this study the 1.7 MV tandem was used for implanting 70-300 keV Si\(^+\) ions to amorphize the silicon wafers (see Chapter 5). With reference to Fig. 2.2, the 150 keV implanter at ANU does not have a second HV stage.
nor a second magnet. The Harwell machine has a positive (Freeman) ion source and also no HV and second magnet: it also has a slightly different beam scanning mechanism.

![Schematic block diagram of the ANU 1.7 MV tandem ion implanter](image)

*Fig. 2.2 A schematic block diagram of the ANU 1.7 MV tandem ion implanter*
In this study, the ion implantation of 30-40 keV N$_2^+$ or N$^+$ into Si (100) wafers was carried out at Harwell. During nitrogen implantation to doses typically of $10^{16}-10^{18}$ cm$^2$, the sample temperature rose to between 150 and 500 °C, depending on the dose rates used. To better simulate the ball milling case, the implantation of 125 keV Fe$^+$ and 120 keV SiN into Si(100) wafers was carried out on the 150 keV machine at ANU. Silicon nitride (ball milled) powder was used as the SiN source by pressing it with Ag powder into a Cu cathode. Further details of the implantation set up are given in Chapter 5.

2.3 X-ray Diffraction

X-ray diffraction plays a major role in examining the structural evolution during ball milling and during subsequent annealing. In this work, X-ray diffraction patterns were taken at room temperature on a standard X-ray diffractometer (Philips PW1120) with Co k$\alpha$ radiation ($\lambda=0.1789$nm). The arrangement of the XRD set up for powder diffraction is shown in Fig. 2.3. The sample is mounted at the center of the focusing circle. The sample to detector distance remains unchanged during rotation of the detector, thus maintaining a parafocusing geometry. Note also that the sample surface always forms the angle $\theta$ with the central incident ray, while the diffracted beam forms an angle $2\theta$. The linkage between the detector and the sample, therefore, must maintain a 2:1 rotational ratio. When X-rays fall on a polycrystalline sample, diffraction only occurs when Bragg's law is satisfied:

$$n\lambda=2d\sin\theta, \quad [1]$$

where: $n$ is an integer number(1, 2, 3), $\lambda$ is the wavelength of incident X-rays, $d$ is the interplanar spacing of the atomic diffracting planes, and $\theta$ is the Bragg angle (the angle between the incident X-rays and atomic planes).

The relations between different crystal structures of materials (e.g. fcc, bcc, hcp) and $d$ spacing or diffraction angle $2\theta$ have been published as powder diffraction files. The structure and phase can be identified by comparing the experimental d-spacing or $2\theta$ with the files. In this thesis, the structure and the phases of the investigated sample are identified by comparing with published JCPDS-ICDD data files.
The shape and intensity of diffraction peaks are influenced by instrumental as well as sample characteristics. The time constant $RC$ and detector scanning speed are the main factors for instrumental peak broadening. In general, large $RC$ and rapid scanning speed may cause two adjacent peaks to overlap and the peaks shift to a higher angle. For almost all examples in this thesis the analysis is not limited by the instrument but rather by the nature of the sample and limitations of the XRD method. It is well known\cite{1} that the shape and width of X-ray diffraction peaks are determined by the crystalline (grain) size, lattice strain and defects. For instance, small grain size, lattice strain and a large density of defects will result in the broadening of the diffraction peaks and peak shape changes as well. The broadening from both small crystal size and strain can be assumed to be the linear addition of the two contributions\cite{13,14,15}, that is:

$$B_g(2\theta) = B_p(2\theta) + B_s(2\theta) = 0.9\lambda / D\cos\theta + \eta\sin\theta / \cos\theta$$

[2]
where $B_{g}(2\theta)$ is the overall broadening, $B_{p}(2\theta)$ is the broadening due to crystal size, $B_{s}(2\theta)$ is the broadening due to internal strain, $\lambda$ is the wavelength of the X-ray radiation, $D$ is the average dimensions of crystalline particles, $\theta$ is the Bragg angle, and $\eta$ is the effective internal strain. From formula [2], the smaller the particle size and the higher the level of strain, the broader are the diffraction peaks. If $D$ is too small and/or $\eta$ is too large, $B_{g}(2\theta)$ is very large and adjacent peaks may overlap to give a high background to the XRD spectrum. For instance, ball milled samples are often fine powders and contain lattice strain as well as defects. In this case, the XRD spectrum will give indistinct peaks with a high background. Fig 2.4 illustrates how the shape and intensity of diffraction peaks are affected by grain size and strain. The samples were prepared by milling pure silicon in nitrogen atmosphere for different times. Before milling, the silicon diffraction peaks are sharp and have high intensity which indicates that the particle size is large. The main peaks appear at $2\theta = 33.15, 55.53, 66.22$, which are typical of the diamond cubic lattice of silicon and the absolute angles are representative of the respective lattice spacing between lattice diffracting planes. After

![Fig. 2.4 Typical XRD spectra for Si milled in nitrogen for various times.](image-url)
ball milling for 24h, the particle size is reduced and disorder (strain energy) is stored in the particles. Broadened diffraction peaks are observed and the intensity of the peaks is reduced. Further milling up to 168h introduces more strain to the particles and the particle size further decreases. A high background to the XRD pattern is also obtained. The question here is: what is the real structure indicated by this high background? Is it an amorphous phase or a crystalline phase with nano-scale grains after milling? It is obvious that the XRD technique cannot give the full structural information for heavily deformed, nanosize or amorphous samples. From this point of view, TEM was used to further study samples with a high background X-ray diffraction pattern.

2.4 Thermal Analysis

Thermal analysis is a technique that measures changes in some physical parameter of the system as a function of temperature. Often the measured physical parameter is heat release or uptake and, when this changes significantly as a function of temperature, useful information concerning structural or phase changes is obtained. Thermal analysis most commonly employs one of two methods: differential thermal analysis (DTA), and thermogravimetry analysis (TGA). These two methods are used extensively in this thesis and are outlined below.

2.4.1 Differential Thermal Analysis (DTA)

Differential thermal analysis (DTA) is a thermal technique in which the heat effects, associated with physical or chemical changes, are recorded as a function of temperature or time as the substance is heated at a uniform rate. In this technique, a sample and a reference are heated in the one furnace, with the sample temperature continuously compared with that of the reference material. The difference in the temperature $\Delta T$ is recorded as a function of furnace temperature or time. Whenever a sample undergoes a change in rate of heat up take (or enthalpy) either exothermic or endothermic, such as a chemical reaction, fusion, crystalline structure inversions, decomposition and dissociation reactions, heat is either absorbed or
lubricated. A substantial difference will then result between the sample and reference temperatures. This temperature difference $\Delta T$ (called the DTA signal) is recorded as a peak on the DTA curve.

Various factors affect the experimental results. They include instrumental factors and sample characteristics. The instrumental factors are furnace size and shape, furnace atmosphere, sample holder material and geometry, heating rate, speed and response of the recording instrument. The sample characteristics are particle size, thermal conductivity, heat capacity, packing density, swelling or shrinkage of the sample, and sample size. In this study, the DTA experiments were carried out using a Shimadzu DTA-50 analyzer. The samples were ball milled powder and the most important variables affecting the data are the heating rate, sample size and furnace atmosphere, in addition to the real heat changes in the sample.

2.4.1.1 Heating rate

In general, an increasing heating rate will shift the peak maxima to higher temperatures and will increase the peak height. The higher heating rate will also decrease the resolution of two adjacent peaks and baseline drift may be appreciable. Slow heating rates will reduce the baseline drift and peak height. At very low heating rates, the peaks become very small and broad and the analysis is time consuming. In this study, reactions occurring during heating are the decomposition of Fe(N) and crystallization of amorphous Si$_x$N$_y$H and Si-C-N phases (Chapters 3 and 4). An acceptable heating rate of 20 °C/min was used for most experiments except for activation energy analysis, where different heating rates were used, as indicated in Chapter 3.

2.4.1.2 Furnace atmosphere

A dynamic gaseous atmosphere was employed in this study. In general, it is advantageous that an appropriate gas flow is used for a period before and during heating
in order to ensure removal of all unwanted gases from the voids in the sample. The gas flow rates may cause the DTA peaks to shift\(^6\). A suitable gas flow must, however, be such that the thermal regime in and around the sample is not interfered with. The composition of the atmosphere depends on the problem being investigated. In this study, as-milled powder is very sensitive to oxygen upon heating. To suppress the reaction between the sample and the gaseous atmosphere (air) which can markedly displace peaks, an inert gas (argon) was used with a flow rate of 50 ml/min. In some cases, for studying the effect of gaseous atmosphere, nitrogen gas or air were used (see Chapter 3 and 4).

2.4.1.3 Sample size

A ideal sample would be infinitely small. Small samples yield smaller but narrower peaks and reduce the probability of overlap between neighboring effects\(^7\). In this respect there is, superficially, a compensating effect between sample size and heating rate. Small samples, like slow heating rate, also reduce baseline drift and peak height. For some reactions (e.g. decomposition reactions), peak temperatures are affected by sample size. In order to produce comparable results, all sample sizes in a particular series were kept small and of the same magnitude.

The DTA parameters used in this study are: heating rate 20 °C/min and gas flow rate 50 ml/min. Each sample was heated twice. The first run revealed the thermal changes during heating. For the second run it was assumed that no further thermal changes occurred during heating and this second curve was used as a baseline, by subtracting it from the first run.

It should be pointed out that, in many cases, the use of only a single thermal technique may provide insufficient information to completely solve the problem at hand. For example, an exothermic peak in the DTA curve may be caused by a crystalline phase transformation or, perhaps, a solid-state chemical reaction. As with other instrumental methods, complementary or supplementary information, as can be supplied by the use of other thermal methods, may be needed. Other techniques such as
X-ray diffraction, elemental analysis and TEM were used to aid in the interpretation of results in this thesis. For example, Fig. 2.5 shows the DTA curve of silicon milled in nitrogen atmosphere for 168h. There are two exothermic peaks observed. First, a broad exothermic peak occurs between room temperature and 1000 °C, and a second (sharp) exothermic peak at a temperature of 736 °C overlapping with the first (broad) exothermic peak. These peaks are difficult to interpret without knowing the results from other analysis methods. As discussed before, ball milling reduces particle size and introduces defects and strain into particles which can be observed as a high background to the X-ray diffraction patterns. The first broad exothermic peak on the DTA curve most likely corresponds to grain growth and structural relaxation, such as strain relief and annealing out of some defects, since the high background to X-ray diffraction patterns has disappeared after annealing to 1000 °C. The second exothermic peak is more difficult to interpret than the first one. Sharp silicon X-ray diffraction peaks with low background are observed after the sample is annealed at temperatures higher than

![Graph showing DTA curve of Si sample milled in nitrogen for 168h](image-url)
the peak temperature, whereas quite broad peaks were observed at temperatures lower than the peak temperature. This indicates that this exothermic peak may be associated with some chemical reaction, or with crystallization of some amorphous silicon fraction if some amorphization takes place during milling. After many experiments, Gaffet et al.\(^8\) suggested that partial amorphization of silicon was obtained after silicon ball milling for about 95h, and this amorphous phase crystallized upon annealing. Thus, this sharp exothermic peak is probably associated with crystallization of amorphous silicon.

2.4.2 Thermogravimetry Analysis (TGA)

TGA is a technique whereby a sample is continuously weighed as it is heating at a constant rate\(^6\). The resulting weight change vs. temperature curve so obtained gives information concerning the thermal stability and composition of the original sample, the composition and thermal stability of intermediate compounds, and the composition of the residue\(^6\). As for DTA, the experimental results are also affected by instrumental factors and sample characteristics. In general, a lower heating rate definitely decreases the apparent decomposition temperatures and the temperature at which the reaction is completed is lowered also. The detection of intermediate compounds in the weight loss curve is also dependent on the heating rate employed. Typically, higher heating rates can result in intermediate effects not being observed.

The parameters of TGA used in this thesis are: heating rate of 20 °C/min, argon gas flow rate of 80 ml/min.

2.5 Electron Microscopes

Electron microscopes were developed because of the limited image resolution in light microscopes, which is imposed by the wavelength of visible light. Electron microscopes have revolutionized our understanding of materials by completing the processing-structure-properties links down to atomic levels\(^9\). There are basically two types of electron microscopic techniques, scanning electron microscopy (SEM), and transmission electron microscopy (TEM).
2.5.1 Transmission Electron Microscopy (TEM)

The key features of modern TEM are described as follows. The electrons emitted by a filament at high voltage are accelerated to earth and focussed, via a double condenser lens system with field-limiting apertures, onto the specimen. An image from the specimen is obtained on a fluorescent screen via a three- or a four-lens magnification system. The microscope may operate to produce either a diffraction pattern from a specific region of the specimen (typically <0.5 μm in diameter) or one of several types of image. For example, a bright field (BF) image is taken from the transmitted beam, a dark field (DF) image is obtained from a diffracted beam, a weak beam (WB) image is formed in DF using a faint diffraction spot, and normally has a higher resolution than conventional BF image and DF image. In all cases where quantitative information about the microstructure of the material is required, detailed correlation is made between the diffraction pattern and an image. Fig. 2.6 shows the TEM micrograph and selected area diffraction pattern of a typical ball milled sample (SiCN1-3, Table 4.1). The bright field image in Fig. 2.6(a) shows that there is some crystalline structure (from contrast variations) in the as-milled powder. The selected area diffraction pattern shows well defined diffraction rings, Fig.2.6(c), which can be indexed as α-SiC and α-Fe. The dark field image was taken from a (220) ring of SiC and shows the microstructure of SiC crystallites (bright regions) in that orientation, Fig. 2.6 (b).

As mentioned before, the X-ray diffraction technique is limited in its ability to characterize fine milled powders. TEM was employed as a supplemental tool to characterize the phase and structure in cases where there was a featureless or high background X-ray diffraction pattern. The TEM sample was prepared by dispersing as-milled powder in methanol with an ultrasonic bath, and spreading the dispersant on 3 mm diameter carbon grids. The structural state was investigated by indexing the selected area diffraction pattern. Both bright field and dark field image techniques were used. High resolution TEM observation was also carried out in collaboration with Dr. M.Giersig. Most of the TEM experiments were carried out using a philips 350 keV microscope at ANU, and high resolution TEM was carried out at Melbourne university on a Jeol 400 keV high resolution microscope.
Fig. 5.5 TEM micrograph and selected area diffraction pattern of a typical ball milled sample. (a) BFI, (b) DFI, (c) selected area diffraction pattern
Chapter 2 Experimental Techniques

TEM observation was also used for examining ion implanted samples. For studying the near surface implanted layer, the samples were made as cross-sectional transmission electron microscopy (XTEM) samples. The XTEM samples were made by first cutting the samples into small pieces $3 \times 1 \text{ mm}^2$, and glued together with the surfaces of interest face-to-face. The sample was then polished on both sides until the cross section was about 60 $\mu$m. The samples were then dimpled on one side using a gatan dimpler until the center of the sample was about 20 $\mu$m thick. The sample was then glued on a 3 mm diameter copper ring and placed in an ion beam miller for further thinning. The ion beam miller is a Gatan duo mill and the samples were thinned on both sides by sputtering with a 4-5 keV Argon ion beam incident at an angle of $15^\circ$ to the surface of the sample.

The TEM experiments carried out in this thesis were in collaboration with D. Llewellyn and Dr. J.Wong-Leung for ball milled and ion implanted samples, respectively.

2.5.2 Scanning Electron Microscopy (SEM)

The SEM has been widely used for the investigation of material morphology\textsuperscript{20}, surface damage\textsuperscript{21}, structural defects\textsuperscript{21}, thermal stress fracture and mechanical fracture\textsuperscript{22}. In the current study, it was found\textsuperscript{23-24} that the particle morphology and size distribution are directly dependent on the sample type and milling conditions. The particle morphology and size distribution of ball milled powder have been monitored using a Cambridge S360 scanning electron microscope. The powder samples were gold coated in order to remove charging effects from insulating powders.

2.6 Composition Analysis

As discussed in the following chapters, the adsorption and chemical reaction of gases (nitrogen or ammonia) is a key factor during milling. Chemical composition analysis provides important information on monitoring such adsorption during milling. Combustion elemental analysis (for detection of H, N and C) and Energy-Dispersive X-
ray analysis (EDXA) (for Si, Fe and other heavier elements) were used to provide composition. Combustion elemental analysis is in fact a modified gas analyzer where the sample is combusted and the gases, after scrubbing and reduction, are separated on a gas chromatograph column and measured by a detector. A Carbo-Erba (model 1106) instrument was used in this work. A SEM equipped with an EDXA detector was also used for composition analysis. The EDXA detector collects the characteristic X-ray signal for different elements and gives information on composition when calibrated with standards. A Tracor Northern 5500 energy-dispersive X-ray detector (Be window, 147 eV Si(Li) detector), mounted on the Cambridge S360 SEM, was used for detecting X-rays from heavier elements than oxygen, such as iron and silicon. A VG601UX STEM was also used for composition analysis for selected samples at the University of Sydney. In some cases, the amount of oxygen was determined by Rutherford backscattering spectrometry (RBS) which is described below.

2.7 Rutherford Backscattering Spectrometry (RBS)

RBS is an ion beam analysis technique widely used in solid state research. The method of RBS is based upon Coulomb interaction of a charged moving particle (usually He$^+$ accelerated through 2 million volts) with an atom of the substance under investigation. An important feature of RBS is its ability to determine the composition of the specimen. The main concepts of the method are described as follows. Assume that a collimated beam of accelerated particles with mass $M_1$ (He mass 4 in this study), atomic number $Z_1$ (2 for He), and energy $E_0$ (2 MeV) is directed on the surface of the object under investigation, e.g. a fairly thin film of material with atoms of mass $M_2$ and atomic number $Z_2$. Some of the ions ($\sim 10^8$) in the beam will be scattered from the surface or the whole thickness of film if it is thin and the beam loses negligible energy in travelling through the film. Therefore, the backscattered energy $E_b$ is given by:

$$E_b = K_{M2} E_0$$

Here $K_{M2}$ is the kinematic factor, defined as the ratio of energy of the particle after elastic interaction with atom of mass $M_2$ to its value before collision ($E_0$). If the energy distribution of these back scattered ions is measured, a peak appears on the
backscattering energy spectrum in the region of energy $K M_{2} E_{0}$. If a series of elements were located in the thin film, then each element would produce a peak at an energy equal to the kinematic factor for that element multiplied by the primary-beam energy. Thus, each surface contaminant can be identified by its backscattered energy in the RBS spectrum. The actual composition can be determined by the ratio of the heights of each element through the simulation of the spectrum by a RUMP analysis program\textsuperscript{27, 28}. For example, Fig. 2.7 shows the RBS random spectrum of 30 keV $N_{2}^{+}$ implanted Si (Chapter 5). The $He^{+}$ ions scattered by nitrogen and silicon at the surface were detected at channels 210 and 320, respectively (shown by arrows). Note that the nitrogen and silicon signals in Fig. 2.7 are not sharp peaks: the silicon signal extends back to zero backscattered energy because the sample is thick and the beam loses energy in travelling through it. On the other hand, nitrogen is distributed within a reasonably thin film and its signal has a width (spread of backscattered energies). The lighter nitrogen signal
overlaps with the heavier silicon signal. The surface composition as simulated by RUMP is Si$_3$N$_6$. Other features of Fig. 2.7 are illustrated below.

Another important advantage of RBS is depth information. As an accelerated ion beam travels through a material, it continuously loses energy ($\Delta E_{in}$). If it scatters from some depth it loses more energy ($KM^2E$) in the scattering event and then loses further energy as it returns through the film to the surface ($\Delta E_{out}$). Thus, the energy of backscattered particles can also locate the depth below the surface, $X$, from which they are scattered, according to the following

$$E_b = KM^2 (E_0 - \Delta E_{in}) - \Delta E_{in},$$

where $S_{in}$ and $S_{out}$ are the rate of energy loss with depth on the incident and exit path, respectively. From equation [4], differences in the backscattered energy for scattering from the same mass can be converted to depth. For example, Fig. 2.7 shows that the nitrogen (note the width of the nitrogen peak) is distributed from the surface (channel 210) to some depth at channel 160. The height of the silicon signal coming from the nitride layer is lower than from the underlying silicon (see insert) and this height (or ratio of Si:N heights) gives the film stoichiometry, which can be simulated by the RUMP program. The depth of the structure can be determined from the energy width of each channel by also using the RUMP simulation program.

Fig. 2.7 also shows a so called channeled spectrum. In this case, the incident ion beam is aligned with the atom rows along the $\langle 100 \rangle$ direction in the silicon crystal, as shown schematically in the insert. For channeling conditions, the backscattered height is much reduced when a single crystal is damage-free but scattering of the ion beam is enhanced if atoms in the crystal are displaced from their regular lattice positions. If the lattice is completely distorted, the random and channeled spectrum will be identical. In Fig. 2.7, the channeled spectrum shows that the height of the nitride layer (both the silicon signal and nitrogen signal) is identical with that of the random case, hence no channeling effect. At a depth just below the nitride layer there is a sharp damage peak in the underlying silicon crystal due to implantation damage. Below this the silicon yield drops in the channeled spectrum because of the good quality silicon single crystal.
Chapter 2 Experimental Techniques

Fig. 2.8 Schematic showing the geometry of the RBS system

The RBS experiments were carried out on selected ball milled samples for monitoring of powder composition. For ion implanted samples, the RBS (with channeling) was used to determine the composition and depth of ion implanted layer and the depth of implantation damage.

In this study, a back angle detector is set at an angle of 168° with the respect to the incident beam of 2 MeV He⁺ ions for backscattering measurements, see Fig. 2.8. A glancing angle detector is set at angles ranging from 98 to 110° for glancing exit angle measurements to enhance near-surface depth resolution. The current on target was kept at 50-70 nA. For ion implanted samples, both channeled and random spectra were taken.
For random spectra, the samples were tilted 5° off around the y-axis and about 0.5° around x-axis from the channeling direction.

2.8 Conclusions

This chapter has given a brief description of the various experimental techniques and how they were typically used in this study. Further details are given in the following chapters. In the case of ion implantation, a brief review of the literature for nitrogen implantation studies in silicon is given in Chapter 5.
References:

1. Spex shark mill
Chapter 3 Formation of Si₃N₄ by Ball Milling of Silicon in Nitrogen Containing Gases

3.1. Introduction

This chapter presents a detailed study of α-Si₃N₄ formation by ball milling of silicon in an ammonia or nitrogen environment under different milling conditions and subsequent annealing. The effects of many milling and annealing parameters on the end products are investigated. Initial studies showed that the formation of α-Si₃N₄ occurs after milling in ammonia (following subsequent annealing), but apparently not in nitrogen gas. This indicates that the presence of hydrogen may be important for formation of α-Si₃N₄ during milling and annealing. The role of oxygen (contamination) in the milling process is also of concern. Furthermore, since iron can enhance the nitridation reaction in the conventional high temperature process, this investigation is also focused on the understanding of the role of iron during milling. Indeed, in our milling situation, iron contamination (from the milling media) is introduced into the system progressively during milling. It is found that hydrogen, oxygen and iron play crucial roles in the formation of an amorphous SiₓNᵧH phase during milling and crystallization of α-Si₃N₄ upon annealing. The composition, phases and microstructure after milling and phase evolution during annealing are also studied. It was found that the end products are also sensitive to milling conditions, such as milling energy, time and temperature. After a detailed investigating of all the above issues, the results and specific observations are used to establish the mixing and reaction processes which occurred during milling and annealing, and an attempt made to understand the variety of non-equilibrium processes which take place.

3.2. Experimental Procedures

The ball milling process was carried out using a home built horizontal milling device, as described in Chapter 2. High purity silicon semiconductor wafers and iron
powder, with a purity of 99%, was used as starting materials. Four hardened steel balls, together with silicon powder under 500 kPa pressure of anhydrous ammonia or nitrogen gas were sealed in a stainless steel cell. Two amounts of silicon were used as starting material: 1 and 3 g. With 500 kPa of ammonia, there is a slight excess of nitrogen with respect to silicon for stoichiometric Si₃N₄ formation for 1 g of silicon. However, for 3 g of silicon to form Si₃N₄ only about 1/3 of the required nitrogen is available in a single charge. So, in some cases, the milling process was disrupted several times to introduce fresh ammonia gas into the cell: the cell was first evacuated to a pressure of 10³ Pa before recharging with fresh ammonia and then the milling process continued. In order to minimize the introduction of oxygen into the system during recharging with ammonia, the gas tube connected to the cell (which was sealed by a valve) was repeatedly evacuated and purged with ammonia before opening the valve. The pressure of the cell was monitored by an attached pressure gauge. An external magnet was placed at the bottom of the cell to supply a predominantly shearing force, and the mill rotation speed was 110 rpm for most experiments. The milling was performed at two temperatures: room temperature and 100 °C. A heater was attached to the milling vial for the higher temperature (100 °C) case and the temperature was measured by a Cr-Al thermo-couple. Annealing was carried out in a Carbolite tube furnace with high purity nitrogen or argon flowing through the tube at a rate of 0.5 l/min during heating.

The structural evolution of the powder was monitored by means of an X-ray powder diffractometer equipped with Co Kα radiation. The thermal properties were investigated using a Shimadzu DTA-50 / TGA-50 thermal analyzer. The chemical composition was determined using combustion elemental analysis (Carlo Erba 1106) and energy-dispersive X-ray analysis (EDXA) on a Cambridge scanning electron microscope (SEM). Rutherford backscattering analysis (RBS) was also carried out on selected samples for monitoring of powder composition. The combustion elemental analysis provides carbon, nitrogen and hydrogen in terms of weight percent of the sample, and the EDXA gives the silicon, iron and chromium atomic ratios. For most cases it was assumed that oxygen was not present
within the powders since RBS analysis indicated that oxygen was less than 5 at%. Assuming that carbon, nitrogen, hydrogen, silicon, iron and chromium are the only elements existing in the powder, the elemental atomic percentages for each of these elements was then calculated.

3.3. Initial Milling at Room Temperature

3.3.1 Milling of 3 g of Silicon

In a first series of experiments, silicon powder from wafers (3 g) was milled for various times in either ammonia or nitrogen gas. Fig. 3.1 shows the typical pressure changes (as measured by the attached pressure gauge) during milling in ammonia and in nitrogen gas. In the ammonia case, the pressure is almost constant for about the first 25h of milling, then increases gradually up to 96h. In some cases, (e.g. with 1 g of silicon powder) the pressure was actually observed to decrease initially. Based on previous studies of metal
powders milled in ammonia gas, this suggests the likely production of hydrogen gas from dissociated ammonia. In the case of milling in nitrogen, the pressure only increases slightly at an early stage of milling, which is most probably caused, by a small temperature increase during milling. This indicates that nitrogen gas adsorption and dissociation is less efficient than ammonia.

Table 3.1 Composition of as-milled samples in different ambient. (3g Si)

<table>
<thead>
<tr>
<th>Milling Ambient</th>
<th>Milling Time(h)</th>
<th>N (at%)</th>
<th>H (at%)</th>
<th>Si (at%)</th>
<th>Fe (at%)</th>
<th>Cr (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>48</td>
<td>25</td>
<td>24</td>
<td>50</td>
<td>1</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>72</td>
<td>34</td>
<td>13</td>
<td>48</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>118</td>
<td>34</td>
<td>13</td>
<td>44</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td>N₂</td>
<td>48</td>
<td>0</td>
<td>---</td>
<td>100</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>168</td>
<td>2</td>
<td>---</td>
<td>98</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

Table 3.1 shows the composition of the above as-milled samples after various milling times. It indicates very low nitrogen content for milling in nitrogen gas but a high nitrogen and hydrogen content in as-milled powders for milling in ammonia. The nitrogen and hydrogen contents change as milling progresses, with the nitrogen content increasing and hydrogen decreasing. The gradually decreasing hydrogen content in the powder during milling confirms that the ammonia was first adsorbed by the powder and decomposed either on the surface of and/or within the powder. It is also interesting to note a significant level of iron (and chromium) contamination from the milling media for milling in ammonia. After 118 h milling, the level of iron contamination is close to 7 at%. Taking account of the increasing iron content, the ratio of N: Si for milling in ammonia increases and is 0.50, 0.70 and 0.77 for 48h, 72h and 118h milling, respectively. This indicates that nitrogen is insufficient for complete formation of stoichiometric Si₃N₄ after milling. For milling in nitrogen gas, there is little change in the very low nitrogen and iron (chromium) content with increased milling time.
Fig. 3.2 XRD patterns of samples milled in NH$_3$ for various times (3g Si).

Fig. 3.2 XRD patterns of samples milled in N$_2$ for 168h and subsequent annealing at 1100 °C in Ar.
Chapter 3 Formation of Si$_3$N$_4$ by Ball Milling of Silicon in Nitrogen Containing Gases

Fig. 3.2 presents the XRD results of the above samples milled in ammonia. The intensities of silicon and iron diffraction peaks decrease and increase, respectively, with increasing milling time. Eventually, the silicon peaks are replaced by a broad, diffuse background, indicative of an amorphous-like structure, together with broadened α-Fe and γ-Fe peaks. The appearance of γ-Fe suggests that some nitrogen may have been adsorbed along with iron contamination. For the sample milled for 118h, there is some evidence from weak XRD peaks for FeSi$_2$ formation during milling. The nitrogen milling case is shown in Fig. 3.3. Following milling, only silicon peaks are observed, consistent with the data of Fig. 3.1 and Table 3.1, where low nitrogen content exists in the as-milled powders.

3.3.2 Milling of 1g of Silicon in Ammonia

Table 3.2 shows the composition of 1 g of silicon (as-milled) after different times: 48, 117, 168h. The nitrogen content tends to increase and hydrogen content decreases with increasing milling time for the as-milled sample, which is consistent with the 3 g silicon case. The ratios of N : Si are 1.13, 1.11 and 1.46. The nitrogen content is much higher compared with the case of 3 g of silicon. For the 168h milled sample, the nitrogen content is higher than that required for stoichiometric Si$_3$N$_4$.

Fig. 3.4 shows the XRD patterns of 1 g of silicon milled in ammonia for different times. The silicon diffraction peaks gradually broaden and decrease with increasing milling time. After 168h milling, a highly diffuse background structure is observed, with almost

<table>
<thead>
<tr>
<th>Milling Time(h)</th>
<th>N at%</th>
<th>H at%</th>
<th>C at%</th>
<th>Si at%</th>
<th>Fe at%</th>
<th>Cr at%</th>
</tr>
</thead>
<tbody>
<tr>
<td>48</td>
<td>33</td>
<td>34</td>
<td>1</td>
<td>29</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>117</td>
<td>30</td>
<td>36</td>
<td>1</td>
<td>28</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>168</td>
<td>41</td>
<td>16</td>
<td>3</td>
<td>28</td>
<td>9</td>
<td>2</td>
</tr>
</tbody>
</table>
Chapter 3 Formation of Si₃N₄ by Ball Milling of Silicon in Nitrogen Containing Gases

Fig. 3.4 XRD patterns of samples milled in NH₃ for different times (1g Si)

complete disappearance of silicon peaks. As indicated earlier, this suggests the formation of an amorphous-like phase (SiₓNᵧH) in view of the high nitrogen and hydrogen adsorption. There is no evidence for direct iron silicide formation during milling, indicating sufficient nitrogen may be important for suppressing the formation of iron silicides. Both γ-Fe and α-Fe were observed in the samples after 48h milling.

3.3.3 Summary of Initial Observations

From the above analysis, crystalline α-Si₃N₄ is clearly not formed during ball milling. However, a possible amorphous-like phase (SiₓNᵧH) was formed for samples milled in ammonia, but no such phase was found for the nitrogen milling case. Furthermore, the high nitrogen content in the as-milled powder only occurs after milling in ammonia and is always accompanied by significant iron contamination in the powder. The differences between milling in ammonia and nitrogen gas suggest that hydrogen may play a
significant role in the ultimate formation of the amorphous phase. Iron silicide was found in the case of milling 3 g of silicon, but not in the case of milling 1 g of silicon. Thus, when sufficient nitrogen is present, a silicide does not form. The question then arises as to what are the precise roles of nitrogen, hydrogen and iron during milling? This issue will be discussed later, after the results of initial annealing experiments are presented.

### 3.4 Initial Annealing Studies

#### 3.4.1 Formation of Si$_3$N$_4$

Fig. 3.5 shows XRD patterns of the as-milled 1 g silicon samples (in ammonia) after ramp annealing in argon (in the TGA apparatus) at 1100 °C. Crystalline $\alpha$-Si$_3$N$_4$ was found for samples milled for 48h or longer, together with peaks indicating the presence of Fe$_3$Si. The amount of Fe$_3$Si increases with milling time. Free silicon still remains in the annealed samples milled for shorter times (48h and less).

![XRD patterns of Fig. 3.4 samples annealed at 1100 °C in Ar.](image)

Fig. 3.5 XRD patterns of Fig. 3.4 samples annealed at 1100 °C in Ar.
3.4.2 Composition and Phase Changes during Annealing

To study the thermal behavior of the powder milled for 168h (1g silicon) in ammonia, composition analysis, DTA, TGA, XRD and Mössbauer were carried out. Table 3.3 gives the composition of the as-milled powder during annealing at different temperatures. Fig. 3.6 shows the normalized TGA and DTA traces of the sample heated at a rate of 20 °C /min in argon atmosphere. The structural changes during annealing are shown in Fig. 3.7. The room temperature Mössbauer spectra of the samples after milling and annealing are shown in Fig. 3.8.

3.4.2.1 From room temperature to 770 °C

As described previously, there is a slight excess of nitrogen with respect to stoichiometric Si$_3$N$_4$ formation and a large amount of residual hydrogen in the as-milled sample. The XRD suggests that at least some nitrogen may be in solution in iron (i.e. Fe(N)) giving rise to broadened α-Fe and γ-Fe peaks. The TGA curve in Fig. 3.6 shows there is initially a small weight loss at temperatures less than 300 °C, which is consistent with loss of hydrogen and a small amount of nitrogen as indicated in Table 3.3. Some of the nitrogen and hydrogen may be in the form of residual, undissociated ammonia. A further substantial weight loss (8.5 wt%) is observed up to 750 °C on the TGA curve. This weight loss may relate to nitrogen loss from Fe(N). A broad endothermic peak is also observed in

<table>
<thead>
<tr>
<th>Annealing Temperature (°C)</th>
<th>N (at%)</th>
<th>H (at%)</th>
<th>Si (at%)</th>
<th>Fe (at%)</th>
<th>Cr (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As- milled</td>
<td>43</td>
<td>17</td>
<td>29</td>
<td>9</td>
<td>2</td>
</tr>
<tr>
<td>660</td>
<td>47</td>
<td>---</td>
<td>38</td>
<td>13</td>
<td>2</td>
</tr>
<tr>
<td>770</td>
<td>48</td>
<td>---</td>
<td>38</td>
<td>13</td>
<td>2</td>
</tr>
<tr>
<td>810</td>
<td>46</td>
<td>---</td>
<td>39</td>
<td>13</td>
<td>2</td>
</tr>
<tr>
<td>900</td>
<td>45</td>
<td>---</td>
<td>40</td>
<td>13</td>
<td>2</td>
</tr>
<tr>
<td>1100</td>
<td>42</td>
<td>---</td>
<td>42</td>
<td>14</td>
<td>2</td>
</tr>
</tbody>
</table>
Chapter 3 Formation of Si$_3$N$_4$ by Ball Milling of Silicon in Nitrogen Containing Gases

Fig. 3.6 DTA & TGA curves of 1 g Si milled in NH$_3$ for 168h

Fig. 3.7 XRD patterns of (1g Si) samples annealed at different temperatures
Chapter 3 Formation of Si₃N₄ by Ball Milling of Silicon in Nitrogen Containing Gases

Fig. 3.8 Mössbauer spectra of the samples after milling and annealing at different temperatures
Chapter 3 Formation of Si$_3$N$_4$ by Ball Milling of Silicon in Nitrogen Containing Gases

the temperature range 250-750 °C on the DTA curve, which correlates with the weight loss from TGA. The heat of this endothermic peak is 630 J/g. If the weight loss is a result of the decomposition of Fe(N), this may suggest that the nitrogen has been strongly bonded to iron. The XRD analysis appears to confirm this prediction. For example, the as-milled sample presents a broadened, highly diffuse background with the almost complete disappearance of silicon diffraction peaks. Both γ-Fe and α-Fe (with broadened or shifted peaks) were also observed. After annealing up to 770 °C, a sharp, well defined α-Fe peak appears and the Si:N ratio is close to Si$_3$N$_4$. In this case, there is ~12 at% iron and a small amount of chromium. There is no evidence for a change in the silicon structure up to this temperature. The room temperature Mössbauer spectra show a dominant double line in the center after milling which is believed to be γ-Fe. A distorted α-Fe six line feature is also visible but this becomes well defined after annealing up to 770 °C. The γ-Fe also exhibits no significant change up to this temperature. A similar result has been previously reported by Calka for milling of iron in ammonia. A concentrated solid solution of Fe(N) or iron nitride was formed after milling for 500h, which was unstable at 400-700 °C and decomposed into nitrogen and iron. In the present case, iron contamination from the milling media has been introduced to powders during milling. This also allows Fe(N) to form during milling but decomposition may occur upon annealing up to 770 °C.

3.4.2.2 From 770 to 900 °C

The nitrogen content exhibits a further slight decrease in this temperature range as indicated in Table 3. 3 and the TGA curve of Fig. 3.6. A sharp exothermic peak at 831 °C on the DTA curve was also observed. The α-Si$_3$N$_4$ phase is clearly observed on the XRD pattern of Fig. 3.7 after annealing at a temperature just above where the exothermic peak appears. This observation suggests that the formation of α-Si$_3$N$_4$ is strongly related to the exothermic peak on the DTA curve. The α-Fe and γ-Fe peaks show no significant changes as indicated by XRD and Mössbauer spectra.
3.4.2.3 From 900 to 1100 °C

After α-Si₃N₄ formation, there is a further nitrogen loss, which continues to 1100 °C. XRD indicates that Fe₃Si phase formation occurs during this temperature range, which coexists with α-Si₃N₄. The further nitrogen loss at temperatures above 900 °C probably results from γ-Fe reacting with residual silicon or α-Si₃N₄, to form Fe₃Si. The disappearance of γ-Fe and the appearance of a new dominant phase in the Mössbauer spectrum are believed to be a result of Fe₃Si formation. The Mössbauer spectrum is therefore quite consistent with XRD analysis. Both the composition and XRD analysis suggests the following phases after annealing at 1100 °C: Si₃N₄ (75% Si) with Fe₃Si (7% Si) and FeSi₂ (18% Si). Here, the assumption is that all the nitrogen is contained in Si₃N₄ and the remaining silicon has reacted with iron to form a mixture of Fe₃Si and FeSi₂.

3.4.3 Summary of Initial Annealing Studies

From the above study, excess nitrogen and residual hydrogen are released from the powder during annealing up to 770 °C, together with a large amount of heat absorption. The nitrogen loss is believed to result from unstable Fe(N), Fig. 3.7 and Fig. 3.8. The formation of crystalline α-Si₃N₄ is clearly related to the exothermic peak on the DTA curve. The following question may now be raised: how is the α-Si₃N₄ formed? Is it the crystallization of amorphous SiₙNₙ or the reaction between an intimately mixed amorphous silicon and nitrogen? The above results cannot answer this question. A more detailed study follows.

3.5 More Detailed Studies

3.5.1 Effect of Milling Conditions

It has been found that the end products and their properties strongly depend on the milling conditions, such as milling energy, milling times, atmosphere, and milling temperature. Therefore, the aim of this part of the study was to examine the effect of milling conditions on a specific solid-gas reaction, i.e. milling of silicon in ammonia, and
hence to improve the understanding of the mechanism of solid-gas reactions during ball milling.

3.5.1.1 Milling of silicon in ammonia at different temperatures

The ambient milling temperature might be expected to be an important parameter in solid-gas reactions induced by ball milling. The adsorption and decomposition processes, defect relaxation, atomic motion and grain growth are all expected to be influenced by milling at different temperatures and hence may affect the end products. The present experiments were carried out by milling 1 g of silicon in ammonia at room temperature and 100 °C.

The room temperature milling and subsequent annealing effects were shown in sections 3.3.2 and 3.4. Here, the concentration is on milling at 100 °C. The composition analysis of the samples (1g Si) milled at 100 °C is shown in Table 3.4. The nitrogen content varies in a complex way, whereby it rapidly increases during the first 24h of milling, then decreases slightly after 48h of milling, whereas the hydrogen content remains essentially constant. (In the case of room temperature milling, the nitrogen content tends to increase and hydrogen content decreases with increasing milling time). At 100 °C iron contamination is again observed to increase with milling time, and the rate of the increase is much faster at early milling stage compared with room temperature milling (Table 3.2).

Table 3.4 Composition of as-milled sample (100°C)

<table>
<thead>
<tr>
<th>Milling time(h)</th>
<th>N at%</th>
<th>H at%</th>
<th>Si at%</th>
<th>Fe at%</th>
<th>Cr at%</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>36</td>
<td>25</td>
<td>32</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>34</td>
<td>37</td>
<td>23</td>
<td>34</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>48</td>
<td>38</td>
<td>26</td>
<td>28</td>
<td>7</td>
<td>1</td>
</tr>
<tr>
<td>72</td>
<td>34</td>
<td>28</td>
<td>29</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td>116</td>
<td>29</td>
<td>28</td>
<td>34</td>
<td>7</td>
<td>2</td>
</tr>
</tbody>
</table>
Fig. 3.9 XRD patterns of Ig samples milled at 100 °C

Fig. 3.10 XRD patterns of the Ig samples annealed at 1100 °C in Ar. (a) room temperature, (b) 100 °C
Fig. 3.9 shows the structural development of the sample (1 g of silicon milled at 100 °C) as a function of milling time. The silicon diffraction peaks rapidly decrease and disappear after 48h milling, which is much faster than for milling at room temperature (168h). A high background peak in the range $2\theta = 20-40^\circ$ was observed for 100 °C milling, even after just 24h, which is a similar structural feature to the room temperature milling case. It again suggests that an amorphous-like phase (Si$_x$N$_y$H) is formed after milling at 100 °C, and this amorphization process is greatly enhanced by milling at the higher temperature.

After milling for 168h at room temperature and 48h at 100 °C, the samples have the same XRD structure. After annealing, these samples also show similar phase transformations. Fig. 3.10 shows the XRD pattern of these as-milled samples annealed at 1100 °C in argon. The $\alpha$-Si$_3$N$_4$ and Fe$_3$Si phases are the main annealing products in both cases.

![Fig. 3.11 DTA curves of samples milled at room temperature. (heating rate: 20 °C/min, in Ar)](image_url)
Chapter 3 Formation of $\text{Si}_3\text{N}_4$ by Ball Milling of Silicon in Nitrogen Containing Gases

DTA experiments were carried out at a heating rate of 20 °C/min in an argon atmosphere. Fig. 3.11 shows the normalized DTA curves of samples milled for 48h and 168h at room temperature. In the present case the exothermic peak temperature decreases for increasing milling times. Fig. 3.12 shows the DTA curves of samples milled at 100 °C for 48h and 116h. More extensive data (not shown) shows that the exothermic peak temperatures are observed at 800, 790, 773, 798 and 822 °C for milling times of 24, 34, 48, 72 and 116h, respectively. This temperature decreases up to 48h milling then increases.

Taken together, the samples milled at room temperature and 100 °C end up in with the same microstructure: an amorphous-like $\text{Si}_x\text{N}_y\text{H}$ phase, which transforms to $\alpha$-$\text{Si}_3\text{N}_4$ upon annealing. However, the formation of the amorphous-like $\text{Si}_x\text{N}_y\text{H}$ phase induced by ball milling is greatly enhanced by milling at 100 °C. The formation temperature of $\alpha$-$\text{Si}_3\text{N}_4$ during annealing decreases or increases in a complex way with increased milling time depending on milling temperature.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Fig_3.12_DTA_curves_of_samples_milled_at_100_C}
\caption{DTA curves of samples milled at 100 °C}
\end{figure}
3.5.1.2 Milling energy

Ball milling experiments were carried out at two different milling energy modes: low energy shearing force and high energy impact force (Chapter 2.1). As mentioned before, all the results presented to date have used a low energy shearing force and a low rotating speed (110 rpm). Here a high energy impact mode was used and the rotating speed is 160 rpm. 3 g of silicon was milled in ammonia for 118h and 190h for low energy (shearing) and high energy (impact) modes, respectively. The effect of milling energy is shown in Fig. 3.13 and Fig. 3.14, for as-milled and annealed samples, respectively. In the case of shearing force, the silicon diffraction peaks are replaced by a broad, diffuse background, indicative of an amorphous-like structure, together with well defined iron peaks. There is some evidence for FeSi₂ formation during milling. In the case of impact

![XRD patterns of samples milled at different intensity](image)

*: FeSi
#: Si

Fig. 3.13 XRD patterns of samples milled at different intensity
Fig 3.14 XRD patterns of annealed samples in Fig. 3.13.

Two Theta

Intensity (a.u.)

mode, strong FeSi and non-reacted silicon diffraction peaks are observed and no evidence for an amorphous-like phase is found after milling. Fig. 3.14 shows the XRD patterns of above samples annealed in argon at a temperature of 1100 °C. Crystalline α-Si₃N₄ is found for the sample milled under shearing mode, together with peaks indicating the presence of both iron and FeSi₂. For the sample milled under impact mode, no clear evidence for the α-Si₃N₄ is found upon annealing. Non-reacted silicon and FeSi are the only products of annealing in this case.

It has been pointed out previously² that higher energy ball milling introduces higher levels of iron contamination. Under higher energy ball impacts, the iron has more reactivity with silicon, more easily forming iron silicide. It appears that the iron and formation of iron silicide affect the formation of amorphous Si₃N₄H during milling. A more detailed study of this effect and further discussion will be given later in this chapter.
3.5.2 Role of Hydrogen, Iron and Oxygen

In previous sections, it has been mentioned that hydrogen and iron may play important roles for formation of crystalline α-Si₃N₄ during milling and subsequent annealing. For instance, the formation of an amorphous-like phase (SiₓNᵧH) and a corresponding significant iron contamination only occur in the case of milling in ammonia, but not in nitrogen gas. There is some evidence to suggest that there is a relationship between hydrogen, iron and the formation of an amorphous-like (SiₓNᵧH) phase during milling. What is this relationship? In addition, oxygen is always present during the experiments. Does the amount of oxygen affect the final product of milling?

3.5.2.1 Effects of hydrogen

For investigation of the effect of hydrogen during milling, further experiments were carried out. The milling conditions are shown in Table 3.5. The milling processes for case 1 and case 2 were described previously. The milling processes in cases 3 and 4 were disturbed after every two or three days milling, respectively, to replenish the ammonia gas to the chamber, and milling was then continued for different total times. The amounts of hydrogen adsorbed by the final powders for the various cases are very different: 35 at% and 27 at% for cases 3 and 4, respectively. For case 1 in Section 3.3.1, the hydrogen content is 13 at%. This means that more frequent replenishing of ammonia during milling results in

<table>
<thead>
<tr>
<th>Case 1 (3.3.1)</th>
<th>3 g of Si continue milling in NH₃ for 118h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 2 (3.3.1)</td>
<td>3 g of Si continue milling in N₂ for 168h</td>
</tr>
<tr>
<td>Case 3</td>
<td>3 g of Si milling in NH₃, replenish NH₃ gas every Two days</td>
</tr>
<tr>
<td>Case 4</td>
<td>3 g of Si milling in NH₃, replenish NH₃ gas every Three days</td>
</tr>
</tbody>
</table>
suppression of hydrogen loss from the powders and consequential reduction in hydrogen gas in the chamber. It is observed that the release of hydrogen from the powder and the amount and time of hydrogen gas remaining in the chamber significantly affect the iron content (from balls and chamber) in the final powders. For example, Fig. 3.15 plots the Fe content as a function of milling time for the four different cases. Case 1 corresponds to maximum hydrogen release from the powder and the longest time that hydrogen is available in the chamber. In this case, the iron content rises much faster in comparison with the others. Case 2 has almost no iron after 168h of milling (for milling in nitrogen gas) and case 3 (replenishing ammonia every 2 days) has a relatively low level of iron content. Thus, it appears that the higher the hydrogen release from the powder and the longer the hydrogen gas remains in the chamber during milling, the higher is the iron content. This suggests that the presence of hydrogen enhances the removal of the iron from the milling media to contaminate the silicon powder.
In attempting to explain the role of hydrogen or hydrogen gas in introducing iron, it should be pointed out that neither silicon nor iron hydride was found. However, ball impacts are known to cause disorder, micro-cracks, fragmentation and particle size reduction to powders, as has been reported previously. There may also be defects and micro-cracks on the surface of balls and the cell wall. This suggests that ammonia is decomposed (releasing hydrogen) on powder, ball and chamber surfaces during milling in ammonia. Under ball impacts, hydrogen can penetrate the ball and cell surfaces through defects and cracks, and hence cause embrittlement and lead to enhanced fragmentation of iron from the surfaces and consequential contamination of the silicon powder. Such a process is consistent with the results from the experiments, where the iron content in the powder increases with the amount of hydrogen released and the time of milling in a hydrogen gas environment. Moreover, the silicon powder particles may also be influenced by hydrogen, causing embrittlement to create new surfaces and/or enhancing the "amorphization" of silicon. As is discussed later, hydrogen does not play a direct role in silicon nitridation, but rather allows (through dissociation of ammonia) the availability of atomic nitrogen and also the introduction of iron, which seem to play a more direct role.

3.5.2.2 Effects of iron

In order to further clarify the role of iron in the nitridation process during milling and annealing, a further series of experiments was carried out. Firstly, pure silicon and iron were milled separately in ammonia under the same milling conditions for 48 h, and then mixed prior to annealing. This sample was then annealed up to 1100 °C in the TGA apparatus. As expected from the data of section 3.3.1 (Fig. 3.2), the silicon-only sample shows only the diffraction peaks of silicon after annealing, with no clear evidence for the formation of α-Si₃N₄, see Fig. 3.16. However, there is strong evidence of formation of α-Si₃N₄ for annealing of the milled, then mixed, silicon and iron powder. The short milling time of 48h was chosen since the silicon-only sample did not contain appreciable iron.
Chapter 3 Formation of Si$_3$N$_4$ by Ball Milling of Silicon in Nitrogen Containing Gases

Fig. 3.16 XRD patterns of the samples annealed at 1100 °C in Ar. (a): as-milled Si only sample, (b): mixture of the separately milled Si and Fe.

Table 3.6 Composition of starting materials

<table>
<thead>
<tr>
<th>Starting Materials</th>
<th>Composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>1% Fe + 99% Si</td>
</tr>
<tr>
<td>(ii)</td>
<td>3% Fe + 97% Si</td>
</tr>
<tr>
<td>(iii)</td>
<td>20% Fe + 80% Si</td>
</tr>
<tr>
<td>(iv)</td>
<td>25% Fe + 75% Si</td>
</tr>
<tr>
<td>(v)</td>
<td>40% Fe + 60% Si</td>
</tr>
<tr>
<td>(vi)</td>
<td>50% Fe + 50% Si</td>
</tr>
</tbody>
</table>

contamination from the mill. This clearly suggests that the presence of iron can enhance the ability of silicon to react with nitrogen during annealing.

To further understand the role of iron, different iron contents were added to the starting silicon wafer prior to milling as shown in Table 3.6. In order to minimize the amount of additional iron from the milling media, the milling time for all samples was kept...
short (48h). After milling and subsequent annealing, several trends were clearly observed. Firstly, the nitrogen content in the as-milled powder increased with increasing iron content, confirming that the presence of iron is important for ammonia adsorption, dissociation and incorporation of nitrogen into milled silicon powder. After annealing, the amount of $\alpha$-Si$_3$N$_4$ formed also increased with iron content, as expected. For high iron content (~40 wt%), high nitrogen content (32 at%) was obtained, and very strong $\alpha$-Si$_3$N$_4$ diffraction peaks were observed after annealing, see Fig. 3.17. Compared with the silicon-only milling in ammonia for 48h, less nitrogen (25 at%, Table 3.1) was found in the as-milled sample, and no $\alpha$-Si$_3$N$_4$ was obtained after annealing, see Fig. 3.16 (a). It was also noticed that the temperature at which the exothermic peak was observed in the DTA trace of milled powders also decreased with increasing iron content. Thus, the main conclusions from these results are that iron has a marked (catalytic) effect on enhancing the nitrogen content of the

![XRD pattern of sample with 40 wt% starting Fe annealed at 1100 °C in Ar.](image)
Chapter 3 Formation of Si$_3$N$_4$ by Ball Milling of Silicon in Nitrogen Containing Gases

Two Theta

Fig. 3.18 XRD pattern of a typical sample after leaching

milled powder during milling and also appears to enhance α-Si$_3$N$_4$ formation during subsequent annealing. After annealing, we have attempted to remove iron from the α-Si$_3$N$_4$ powder with some success. For example, for 1 g of silicon (Section 3.3.2) milled in ammonia for 168h and annealed up to 1100 °C in nitrogen gas, then leaching in 50% HCl at 90 °C for 1h resulted in removal of most of the iron. Fig. 3.18 shows the XRD pattern of the sample after leaching. Strong α-Si$_3$N$_4$ diffraction peaks are observed and iron diffraction peaks are almost non-existent. Chemical analysis shows that the iron content is less than 2 at%.

3.5.2.3 Effect of oxygen

3 g of silicon milled in ammonia under 500 kPa pressure has been studied. The milling process was disturbed after 48h milling, to replenish the ammonia gas to the chamber, and milling continued for 72h. When recharging with ammonia, two different processes are employed. First, the gas tube connected to the milling cell space (which was
sealed by a valve) was not well-evacuated prior opening the valve. Second, to minimize the introduction of oxygen into the system, the gas tube connected to the cell was repeatedly evacuated and purged with ammonia before opening the valve.

Fig. 3.19 shows the XRD patterns of the above samples after milling and annealing. With the high vacuum sample, the amorphous-like phase formed after milling and the formation of crystalline α-Si₃N₄ occurred after annealing. In contrast, no amorphous phase and α-Si₃N₄ are observed after milling and subsequent annealing for the poor vacuum case. Fig. 3.20 shows the RBS spectrum of the above samples. About 5 and 29 at% oxygen is found in the samples at high and low vacuum cases by RUMP simulation, respectively. This indicates that the poor vacuum introduces appreciable oxygen into the milling system, to presumably “poison” the surface of silicon by forming a thin layer of silicon dioxide. Because of the thermodynamic stability of silicon dioxide, it may provide a barrier to gas adsorption and further reaction. This protective barrier against extensive ammonia adsorption during milling may inhibit the formation of an amorphous-like phase.

3.5.3 Microstructure and Phase Changes during Milling and Annealing

Fig. 3.21(a)-(d) gives SEM observations of the samples ball milled in ammonia (3 g of silicon) and annealed at 1100 °C in argon. Both particle size and morphology changes are observed. For the sample milled for a short time (48h), the particle size is about 150-300 nm. The particles appear to be welded together, and the shape is irregular. The particle surfaces are rather rough. For the sample milled for a longer time (118h), the particle size decreases to the range of 100-150 nm. The shape of the particles tends towards a spherical shape with a smooth surface. SEM observation (Fig. 3.21 (b)) shows that the particle size is about 300-500 nm after annealing of the short time milled sample, indicating that silicon grain growth and deformation recovers upon annealing, which is consistent with the XRD study. For the longer-time milled sample, the particle size slightly decreases to less than 100 nm, and the shape of particles becomes more irregular. This is probably a result of
Chapter 3 Formation of Si₃N₄ by Ball Milling of Silicon in Nitrogen Containing Gases

Fig. 3.19 XRD patterns of samples affected by oxygen.

Fig. 3.20 RBS spectra of samples effected by oxygen.
phase transformations (to $\alpha\text{-Si}_3\text{N}_4$ and Fe$_4$Si) during heating.

Transmission electron microscopy observations have been carried out. Fig. 3.22 shows the TEM micrograph of a typical as-milled sample. A quite featureless structure is revealed. The SAD pattern presents an amorphous halo pattern, indicating that an amorphous phase is formed after silicon is milled in ammonia for 168h. This suggests that the amorphous phase is Si$_x$N$_y$H, according to earlier chemical composition and XRD analyses. The few diffraction spots observed were indexed as crystalline $\alpha\text{-Fe}$ contamination. High resolution TEM clearly shows that an amorphous Si$_x$N$_y$H phase formed after ball milling of silicon in ammonia, as shown in Fig. 3.23. HRTEM also shows crystalline $\alpha\text{-Fe}$ precipitates with a diameter of 60-160 Å within an amorphous Si$_x$N$_y$H matrix in as-milled powder. The insert diffraction patterns show the iron (100) diffraction spot, consistent with the XRD data. Fig. 3.24 presents the HRTEM micrograph of the above
Chapter 3 Formation of Si$_3$N$_4$ by Ball Milling of Silicon in Nitrogen Containing Gases

Fig. 3.22 TEM micrograph and diffraction pattern (insert) of 1 g Si milled in NH$_3$ for 168h.

It is also of interest to notice that Fe$_3$Si is excluded from the α-Si$_3$N$_4$ structure during annealing, appearing as separate crystallites. Taken together all of the above results confirm an amorphous phase (Si$_x$N$_y$H) after milling, and strongly support mechanochemical reaction during milling and subsequent crystallization to α-Si$_3$N$_4$ during annealing. It is also instructive to examine the Fe$_x$Si$_y$ phases formed as a function of milling and annealing conditions. We note that some evidence for FeSi$_2$ was found in a 3g Si sample continuously milled for 118h in ammonia (Section 3.3.1), where insufficient nitrogen was in the as-milled powder, see Fig. 3.25 (a). However, no evidence for this phase was found in a
sample milled for 230h but with the chamber replenished with ammonia gas every three days during milling (Section 3.5.2), see Fig. 3.25 (b). When samples corresponding to curves a) and b) in Fig. 3.25 were annealed up to 1100 °C in argon, different iron silicide phases (FeSi₂ and Fe₃Si) were formed in each case, see Fig. 3.25 (c) and (d), respectively.

The form of iron silicide depends on the ratio of nitrogen and silicon but also on the amount of iron in the sample. With a low ratio of N : Si, say ~0.77, it tends to form a Si-rich silicide such as FeSi₂, Fig. 3.25 (c). With a higher ratio of N : Si, say ~0.88 as in b), it tends to form an iron-rich silicide, such as Fe₃Si, at high temperature, see Fig. 3.25 (d). However, when sample (b) is heated to 1100 °C in nitrogen gas, such that N >> Si, elemental iron results and all the silicon is converted to α-Si₃N₄, Fig. 3.25 (e). Fig. 3.26 shows DTA
Fig. 3.24 HRTEM micrographs of the sample in Fig. 3.23 annealed at 1100 °C in Ar.
Chapter 3 Formation of Si$_3$N$_4$ by Ball Milling of Silicon in Nitrogen Containing Gases

Fig. 3.25 XRD patterns of the Fe$_x$Si$_y$ phase formation as a function of milling and annealing conditions.

analysis of the above (b) sample heated in nitrogen gas or argon. The first sharp exothermic peak at 1020 °C is a result of the crystallization of α-Si$_3$N$_4$ (see section 3.4.2). The second broad exothermic peak (heating in argon) probably relates to the formation of Fe$_3$Si. For heating in nitrogen gas, excess nitrogen is available for any unreacted silicon, to form Si$_3$N$_4$ and elemental iron. When heating in argon, the iron reacts with excess silicon to form Fe$_3$Si. Thus, it is considered that, in the Si-N-Fe system, reaction between silicon and nitrogen is favored if there is sufficient nitrogen, since the product (Si$_3$N$_4$) has a lower free energy than the silicide phases: $\Delta G_{Si_3N_4} = -153.6$ kcal/mol, $\Delta G_{Fe_3N_y} = -17.6 \sim -22.6$ kcal/mol. Thus, the reaction between silicon and iron will be inhibited when there is sufficient nitrogen existing in the system. These observations on silicide formation are consistent with above model of α-Si$_3$N$_4$ formation under various milling and annealing conditions.
3.6 Reaction Mechanisms during Milling and Annealing

In attempting to determine the reaction sequence for the formation of $\alpha$-Si$_3$N$_4$ during milling and annealing, there are several issues, which emerge from the current study. Firstly, nitrogen is not readily adsorbed into silicon powders when silicon is milled in nitrogen gas and silicon nitride is not formed during annealing. With milling in ammonia, both hydrogen and iron play important roles in the incorporation of nitrogen into silicon during milling and ultimate formation of $\alpha$-Si$_3$N$_4$. Hydrogen appears to play an indirect role in facilitating the incorporation of iron into the powder: it is iron which appears to be crucial in catalyzing nitrogen adsorption and nitride formation.

3.6.1 Amorphous Phase Formation during Ball Milling.

Ball milling creates enormous mechanical damage to nanoscale powders, producing
fracture and new surfaces, work hardening, plastic flow, grain boundaries and, on an atomic scale, defects such as dislocations. Ball milling also introduces iron contamination from the milling media. In the present study of silicon milled in ammonia at room temperature, ammonia is first adsorbed and then decomposed on new surfaces of silicon (and iron as well) under ball impact. The creation of fresh surfaces and defects allows chemisorption of atomic nitrogen and hydrogen, which, together with the increasing free energy of the nanocrystalline silicon powders may result in the formation of an amorphous Si$_x$N$_y$(H) phase. As the level of iron contamination increases with increasing milling time, the formation of an Fe(N) solid solution and γ-Fe can occur. It has previously been suggested that the amount of adsorbed gas is an important factor for the amorphization of Ti$_{50}$Zr$_{50}$ by ball milling. Other studies have also shown the enhancements of amorphization by ball milling. However the previous study (Section 3.3.1) showed that no fully amorphous Si(N) structure was obtained after milling silicon in nitrogen gas for 168h, whereas an amorphous Si$_x$N$_y$(H) phase readily forms during milling in ammonia under the same milling conditions. Hence absorbed N(H) is an important factor in the formation of an amorphous phase.

There is a competition between adsorption and desorption, strain-energy increase and relaxation during ball milling in an active gas. The rate of chemisorption will increase with milling temperature, consistent with a chemical reaction, whereas desorption of physically absorbed species increases with temperature. It is also noted that iron contamination increases more rapidly for the sample milled at 100 °C than for room temperature. As suggested before, the iron appears to catalyze the adsorption and/or dissociation of ammonia on the silicon powders. Furthermore, diffusion of nitrogen and hydrogen increase with temperature. All these factors accelerate atomic mixing and chemisorption of nitrogen (and hydrogen) and, with increasing free energy of mechanically damaged powder grains, may favor the formation of the amorphous structure Si$_x$N$_y$H at a higher milling temperature. Thus, completely amorphous Si$_x$N$_y$H is formed after 48h milling at 100 °C compared with 168h for milling at room temperature. At this stage,
chemisorption and increasing free energy through mechanical damage dominate the milling process.

Koch et al. suggested that the mechanism of amorphization of an intermetallic compound might be a response to severe plastic deformation provided by ball milling which generates lattice defects which, in turn, cause the free energy of the crystalline phase to rise above that of the amorphous phase, thus resulting in the formation of an amorphous phase. In addition to the build-up of internal strain resulting from ball milling, in the case of solid-gas reactions induced by ball milling, adsorbed gas is also an important factor. The newly exposed surfaces created by ball milling are highly reactive to an active atmosphere (ammonia). The ammonia gas adheres to the fresh surface, dissociates under ball impacts, and subsequently is incorporated into the silicon matrix. Rawers et al. showed that the nitrogen concentration, during mechanical treatment of iron in nitrogen gas, increased with decreasing particle size and prolonged milling. They suggested that the nitrogen concentrated in the outer regions of each grain in the early stage of milling. Ball milling greatly decreases the size of crystalline grains and the diffusion distance required for adsorbates such as nitrogen to reach the interior of grains, thus giving an intimately mixed powder. In the case of milling of silicon in ammonia, the amount of adsorbed nitrogen and hydrogen and their intimate mixing appears to be a crucial factor in determining a crystalline to amorphous transition and stabilization of an amorphous Si$_x$N$_y$H phase. Free energy considerations of this process are considered later in Section 3.6.3.

### 3.6.2 Processes during Annealing

During annealing, as has been suggested in section 3.4.2, un-dissociated ammonia is released from as-milled powder at low temperature (room temperature to 400 °C). The Fe(N) solid solution is also unstable at temperatures above 400 °C and results in a significant weight loss on the TGA curve as it dissociates, and this is accompanied with a broad endothermic peak on the DTA curve. The amorphous structure (Si$_x$N$_y$H) crystallizes at a higher temperature (750-1000 °C), and forms α-Si$_3$N$_4$ and ultimately Fe$_3$Si forms when
the temperature reaches 1100 °C. The crystallization temperature of amorphous Si$_x$N$_y$H is strongly affected by milling conditions, such as milling time (and corresponding level of iron contamination), starting amount of silicon and milling temperature. In the case of milling at room temperature, longer milling time results in a decrease in the crystallization temperature, (presumably as a result of increasing iron), and a larger amount of starting silicon leads the crystallization shifting to a higher temperature. For example, exothermic peaks (characteristic of crystallization) occur at 994 and 831 °C for samples milled at 48 and 168h (1 g of silicon), respectively. 938 °C is the exothermic peak temperature for 3 g of silicon milled for 118h. This effect could be due to a lower Fe : Si ratio in the 3 g case compared to the 1 g case. It is of significance to notice that the crystallization temperature is strongly related to iron content from Tables 3.1 and 3.2. As suggested before, the iron appears to catalyze the formation of α-Si$_3$N$_4$ from an amorphous structure. However, the iron is not the only factor which affects the crystallization temperature. For instance, prolonged milling at 100 °C leads to a subsequent increase in the crystallization temperature, which is difficult to explain in view of the fact that Fe contamination is still increasing with milling time. However, it has been noted that the nitrogen content also appears to decrease slightly for the longest milling time at 100 °C (Table 3.4). It may be that some structural relaxation occurs in the powders during prolonged milling at 100 °C and that this influences the composition of the amorphous phase and subsequent crystallization.

3.6.3 Thermodynamic Considerations

Using the schematic free energy diagram in Fig. 3.27, the following extremities of behavior for the ball milled Si-N-Fe system are suggested. The curves labeled a) and b) represent the situation for conventional formation of α-Si$_3$N$_4$ from silicon powder heated with ammonia, both without an iron catalyst and with iron, respectively$^{15}$. The presence of iron presumably lowers the activation energy for nitride formation (from $E^a_1$ and $E^b_1$ in fig 3.27). In the case of ball milling, two possibilities could lead to α-Si$_3$N$_4$ formation. Curve c) and d) are possible cases for ball milling. The free energy increases during ball
Fig. 3.27 Possible differences in free energy for alternate reaction pathways for conventional formation of Si₃N₄, (a) without iron; (b) with iron; and for milled samples, (c) mixing of N with Si and Fe; (d) Si nitridation takes place during ball milling and crystallization occurs upon annealing.

milling as a result of mechanical damage, grain size reduction and defect formation. Adsorbed nitrogen and hydrogen are mixed with the disordered silicon crystalline structure. Thus the strain energy of the system is envisaged to increase with milling time. Once the free energy of this disordered system is greater than the amorphous phase, the amorphous phase (SiₓNᵧH) then represents the energetically favored state and will preferentially form. For curve c) we have assumed that nitrogen does not react during ball milling (i.e. is physically adsorbed and unbonded to silicon) but reaction takes place during annealing to form α-Si₃N₄ crystallites. For example, in this situation the exothermic peak in the DTA trace (Figs. 3.6 and 3.25) would correspond to a nitridation reaction during annealing (with
activation energy $E^{d}_{a_2}$ in Fig. 2.27). In case d), this is considered to be in better agreement with our observations. It is assumed that the intimate mixing of atomic nitrogen with silicon, the increase in strain energy and the breaking of silicon bonds during mechanical action, will provide a strong driving force for a mechanochemical reaction during milling to form amorphous $Si_xN_yH$ with a stoichiometry close to $Si_3N_4$ (to saturate all silicon bonds). In this case, the energy required to overcome the activation barrier for amorphous $Si_xN_yH$ (i.e. $E^{d}_{a_1}$) is provided athermally by mechanical action and build up of strain energy. Limited diffusion of N (and H) at room temperature is overcome by the intimate mixing which occurs during milling. This situation may be similar to the amorphous $Si_xN_y$ phase which is formed during low energy $N^+$ ion bombardment of silicon\(^{16}\). In the case of ion implantation, the ion beam generates both the disorder (rise in free energy) and the intimate mixing, as described more fully in Chapter 5. During annealing, thermal energy is needed to overcome the activation barrier to crystallization ($E^{d}_{a_2}$). Therefore, during annealing of case d), the exothermic peak in the DTA (Fig. 3.6) would correspond to crystallization of amorphous $Si_3N_4$ to $\alpha$-$Si_3N_4$ crystallites. Hence, the activation energy of crystallization is 280 kJ/mol for the sample milled 168h at room temperature. Again, somewhat analogous crystallization behavior (for amorphous $Si_xN_y$) is observed in the ion implanted case referred to above\(^{37}\). This may suggest that the ball milling behavior for $\alpha$-$Si_xN_y$ formation may have striking similarities to the ion implantation case. In chapter 5, ion implantation is explored for comparison to provide insight into the ball milling process.

### 3.7 Conclusions

Ball milling of silicon in ammonia at room temperature induces gas chemisorption and the formation of an amorphous $Si_xN_y(H)$ phase on prolonged milling. For milling at 100 °C the amorphization reaction is enhanced (i.e. is completed at shorter milling times) and it is suggested that this occurs because the chemisorption rate is increased. The formation of the amorphous phase is due to mechanical damage and defect accumulation during ball
impacts (and associated increase in strain energy) together with intimate mixing of nitrogen and hydrogen into the silicon matrix. This amorphous phase recrystallizes to α-Si₃N₄ upon annealing and residual silicon reacts with iron to form Fe₃Si.

Both hydrogen and iron are found to have a strong influence on the ability to form α-Si₃N₄ by ball milling of silicon in ammonia gas followed by annealing. The presence of hydrogen (for milling in ammonia) embrittles the surfaces of balls and the cell wall and hence progressively introduces iron into the silicon powder. Iron may catalyze the reaction between silicon and nitrogen (by, for example, the provision of atomic nitrogen), thus enhancing silicon nitridation. When iron, silicon and nitrogen are present during annealing, the reaction of silicon and nitrogen is always favored when sufficient nitrogen exists in the system: excess silicon then reacts to form a silicide. Finally, the behavior in α-Si₃N₄ formation by ball milling appears to have analogies with α-Si₃N₄ formation during ion implantation, an aspect that is explored in more detail in Chapter 5.
References

Chapter 4 Preparation of Nanocomposite of Si₃N₄-SiC by Ball Milling

4.1. Introduction

As described in Chapter 1, development of a nanocomposite such as Si₃N₄-SiC significantly increases the toughness of monolithic Si₃N₄. However, conventional methods to synthesize this composite are often complex and/or costly. Ball milling (mechanochemistry) may have significant advantages for its synthesis, but it has not been used previously. Therefore, this chapter investigates ball milling as a possible novel method to prepare a Si₃N₄-SiC nanocomposite powder at room temperature. The ball milling experiments were carried out in a nitrogen atmosphere with a mixture of silicon and carbon powders with different compositions and phases, used as starting materials. The experiments show that formation of an amorphous phase (Si-C-N) is very sensitive to the starting carbon content and phases, and also the nature of iron contamination introduced during milling. This study is concentrated on the understanding of the mechano-chemical reactions occurring between silicon, carbon, nitrogen and iron. The roles of carbon and iron are particularly considered.

4.2 Experimental Procedures

Pure silicon semiconductor wafer (99.99%), activated carbon and iron (98%), were used as starting solid materials. Different ratios of Si:C were used to investigate the effects of carbon during ball milling. Also, pure silicon carbide, mixtures of silicon carbide and silicon, silicon carbide and iron silicide were used as starting materials to study the effects of nitrogen adsorption and phase formation on the starting phases. The various milling experiments and sample starting compositions are shown in Table 4.1. The starting materials were sealed in a stainless steel cell under vacuum or with high purity nitrogen (99%) gas at a certain pressure. The limited series of millings were also carried out in
### Table 4.1 Compositions and milling conditions used in this study.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Starting phases</th>
<th>Starting Composition Si:C</th>
<th>Milling atmosphere</th>
<th>milling pressure kPa</th>
<th>milling time hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC-1</td>
<td>Si, C</td>
<td>50:50</td>
<td>vacuum</td>
<td>-</td>
<td>73</td>
</tr>
<tr>
<td>SiC-2</td>
<td>Si, C</td>
<td>50:50</td>
<td>vacuum</td>
<td>-</td>
<td>96</td>
</tr>
<tr>
<td>SiC-3</td>
<td>Si, C</td>
<td>50:50</td>
<td>vacuum</td>
<td>-</td>
<td>170</td>
</tr>
<tr>
<td>SiCN1-1</td>
<td>Si, C</td>
<td>50:50</td>
<td>N₂</td>
<td>400</td>
<td>41</td>
</tr>
<tr>
<td>SiCN1-2</td>
<td>Si, C</td>
<td>50:50</td>
<td>N₂</td>
<td>400</td>
<td>96</td>
</tr>
<tr>
<td>SiCN1-3</td>
<td>Si, C</td>
<td>50:50</td>
<td>N₂</td>
<td>400</td>
<td>168</td>
</tr>
<tr>
<td>SiCN1-4</td>
<td>Si, C</td>
<td>50:50</td>
<td>N₂</td>
<td>400</td>
<td>263</td>
</tr>
<tr>
<td>SiCN1-5</td>
<td>Si, C</td>
<td>50:50</td>
<td>N₂</td>
<td>400</td>
<td>307</td>
</tr>
<tr>
<td>SiCN2-1</td>
<td>Si, C</td>
<td>57:43</td>
<td>N₂</td>
<td>400</td>
<td>263</td>
</tr>
<tr>
<td>SiCN2-2</td>
<td>Si, C</td>
<td>57:43</td>
<td>NH₃</td>
<td>400</td>
<td>263</td>
</tr>
<tr>
<td>SiCN3-1</td>
<td>Si, C</td>
<td>62:38</td>
<td>N₂</td>
<td>400</td>
<td>263</td>
</tr>
<tr>
<td>SiCN3-2</td>
<td>Si, C</td>
<td>62:38</td>
<td>N₂</td>
<td>200</td>
<td>263</td>
</tr>
<tr>
<td>SiCN4-1</td>
<td>Si, C</td>
<td>68:32</td>
<td>N₂</td>
<td>400</td>
<td>263</td>
</tr>
<tr>
<td>SiCN4-2</td>
<td>Si, C</td>
<td>68:32</td>
<td>N₂</td>
<td>200</td>
<td>263</td>
</tr>
<tr>
<td>SiCN5</td>
<td>Si, C</td>
<td>72:28</td>
<td>N₂</td>
<td>400</td>
<td>263</td>
</tr>
<tr>
<td>SiCN6</td>
<td>SiC, Fe₃Si</td>
<td>57:43</td>
<td>N₂</td>
<td>400</td>
<td>118</td>
</tr>
<tr>
<td>SiCN7</td>
<td>SiC</td>
<td>50:50</td>
<td>N₂</td>
<td>400</td>
<td>118</td>
</tr>
<tr>
<td>SiCN8</td>
<td>SiC, Si</td>
<td>62:38</td>
<td>N₂</td>
<td>400</td>
<td>118</td>
</tr>
</tbody>
</table>

ammonia gas. The pressure of the cell during ball milling was monitored by an attached pressure gauge. The milling was carried out in a home-built milling device as described in Chapter 2. An external magnet was placed near the milling cell at 45° to provide a relatively high impact force compared with the conditions used in the previous Chapter 3. The composition analysis was performed by combustion analysis (Carlo Erba 1106) and energy-dispersive X-ray analysis (EDXA) on a Cambridge S360 scanning electron microscope and a VG601UX STEM. The structural development was studied after milling and following various annealing treatment using a Philips X-ray diffractometer equipped
with Co $K\alpha$ radiation. The thermal properties were investigated with a Shimadzu differential thermal analyzer (DTA-50), as previously.

4.3 Results

There were a wide range of experiments carried out to form and understand $Si_3N_4$-SiC composite formation. The results are mostly organized in this section starting from the least complicated, to show the overall effects, and then test various possibilities with more complicated experiments.

4.3.1 Silicon and Carbon (1:1) Milled in Vacuum

A mixture of pure silicon and carbon with a ratio of 1:1 was milled in vacuum for different times. The structural development as a function of milling time is presented by XRD spectra in Fig. 4.1. Broad SiC diffraction peaks, together with residual silicon and iron contamination are observed after 73h milling. This indicates that a silicon and carbon

![Fig. 4.1 XRD Spectra showing the formation of SiC during milling in vacuum of Si and C powders (1:1).](image)
solid state reaction takes place during milling and the SiC crystallites induced by ball milling are nanostructure as we discuss below. The silicon diffraction peaks disappear, and only SiC is revealed after about 96h milling. Simultaneously, Fe$_5$Si$_3$ was clearly observed after this time. The intensity of SiC diffraction peaks increases with prolonged milling. Based on the X-ray line broadening, the average sizes of SiC crystallites are estimated to be 3.7, 4.2, and 5.0 nm, and the internal strains are 3.2, 2.8, and 2.4 % for samples milled for 73, 96, and 170h, respectively. It should be pointed out that, when there are defects and strains in very small crystallites, the interpretation of average grain size and strain is complicated, especially if there is some amorphous phase or solid solution existing in the sample (see section 2.3). Here, we have assumed that no amorphous or solid solution phases exist in the sample. The SiC grain size increases and the internal strain decreases with milling time. This suggests that, following nucleation of SiC, some grain growth may be induced by ball milling, simultaneously with a reduction in internal strain.

![XRD spectra showing the annealing at 1000 °C in DTA of samples in Fig. 4.1.](image)

*Fig. 4.2 XRD spectra showing the annealing at 1000 °C in DTA of samples in Fig. 4.1.*
Chapter 4 Preparation of Nanocomposite of Si₃N₄-SiC by Ball Milling

Fig. 4.2 shows the X-ray diffraction patterns of the above samples after annealing at 1100 °C in argon. Sharp SiC and Fe₃Si₃ diffraction peaks are observed after annealing, indicating substantial grain growth upon annealing. SiO₂ appears in the sample ball milled for 170h followed by subsequent annealing. This suggests that the sample milled for a longer time is more sensitive to oxidation, as discussed later.

The thermal behavior of as-milled powders is shown in Fig. 4.3. An exothermic peak is observed on the DTA curve at 778, 727, and 589 °C for milling at 73, 96, and 170h, respectively. The peak temperatures and intensities decrease as milling time increases. Detailed XRD analysis was taken for the sample milled for 73h as a function of annealing temperature. For annealing the sample at temperatures just below and just above the exothermic peak, XRD spectra showed that residual silicon exists below the peak, but disappears above it. This suggests that the exothermic peak may correspond to the formation of SiC (i.e. the solid state reaction Si + C = SiC). In this case, the reaction may not have been completed during milling. For longer milling times (96 and 170h), XRD analysis did not show a significant change for annealing temperatures below and above the

![Fig. 4.3 DTA curves of samples from Fig. 4.1.](image-url)
Chapter 4 Preparation of Nanocomposite of Si$_3$N$_4$-SiC by Ball Milling

exothermic peak. This may suggest much more complete reaction of silicon with carbon during milling for longer milling times and hence the less intense exothermic peak in these cases. However, the nature of the as-milled materials (i.e. fraction of an amorphous Si-C phase, amount of oxygen, the homogeneity of mixing of carbon with silicon and the fraction of nanocrystalline SiC) is not well known without more extensive composition and microstructural (TEM) analysis. An interpretation and discussion of these results will be given later after further results are presented.

In summary, SiC can be directly synthesized by ball milling a mixture of silicon and carbon powder in vacuum.

### 4.3.2 Silicon and Carbon (1:1) Milled in Nitrogen Gas

A mixture of pure silicon and activated carbon powders with the ratio of Si:C=1:1 was milled in nitrogen gas.

#### 4.3.2.1 Composition analysis

The ball milling experiment was performed for various times in nitrogen gas at a starting pressure of 400 kPa. The pressure change during milling is shown in Fig. 4.4. The nitrogen pressure gradually decreases during milling, indicating that nitrogen has been adsorbed by the milled Si-C mixture. The composition of the as-milled powder is presented in Table 4.2.

<table>
<thead>
<tr>
<th>sample name</th>
<th>milling time(h)</th>
<th>Si at%</th>
<th>C at%</th>
<th>N at%</th>
<th>Fe at%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiCN1-1</td>
<td>41</td>
<td>46</td>
<td>46</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>SiCN1-2</td>
<td>96</td>
<td>42</td>
<td>42</td>
<td>14</td>
<td>2</td>
</tr>
<tr>
<td>SiCN1-3</td>
<td>168</td>
<td>33</td>
<td>33</td>
<td>29</td>
<td>5</td>
</tr>
<tr>
<td>SiCN1-4</td>
<td>263</td>
<td>32</td>
<td>32</td>
<td>29</td>
<td>7</td>
</tr>
<tr>
<td>SiCN1-5</td>
<td>307</td>
<td>30</td>
<td>30</td>
<td>33</td>
<td>7</td>
</tr>
</tbody>
</table>
in Table 4.2. Some nitrogen is observed in the sample ball milled for 41h and the nitrogen content increases with milling time, which is consistent with the pressure measurements. After 307h milling, the nitrogen content reaches 33 at %, close to the Si$_3$N$_4$ stoichiometry for the available silicon in the sample. Iron contamination was detected in all the as-milled powders, and this again increases with milling time.

### 4.3.2.2 XRD analysis

The structural development as a function of milling time is shown at Fig. 4.5. A silicon and carbon solid state reaction takes place at an early stage of milling, as shown by the SiC diffraction peaks observed after 41h milling. This reaction continues, as indicated by the increasing intensity of SiC peaks and decrease in silicon peaks. This is consistent with the previous case of silicon and carbon milled under vacuum. The silicon diffraction peaks disappear after 96h milling. With continuous milling, SiC diffraction peaks gradually broaden, indicating the adsorption of nitrogen by as-milled powder. There is no evidence from XRD of any crystalline $\alpha$-Si$_3$N$_4$ formed during milling. After prolonged milling the
Fig. 4.5 XRD spectra of Si:C=1:1 powders milled at different times in N₂ gas at a starting pressure of 380 kPa.

Fig. 4.6 XRD spectra of samples of Fig. 4.5 after annealing at 1100 °C.
SiC diffraction peaks almost disappear with a high background (307h). As in Chapter 3, this suggests that an amorphous (Si-C-N) phase, with a small amount of residual nanocrystalline SiC, may result after prolonged milling. The iron contamination diffraction peaks were revealed in the form of α-Fe and γ-Fe. There is no evidence for any iron silicides formed during ball milling. Fig. 4.6 shows the XRD patterns of the above samples annealing up to 1100 °C in DTA. For short milling times (19-96h) only SiC and Fe₅Si₃ were found, with no evidence for α-Si₃N₄. For longer times, it is clear that an Si₃N₄-SiC composite is formed after annealing, together with Fe₅Si₃. The diffraction intensity of SiC decreases with prolonged milling. After 307h milling, only α-Si₃N₄ is observed. This suggests, as discussed later, that a higher nitrogen content favors Si₃N₄ formation.

4.3.2.3 Microstructural analysis

A bright field TEM micrograph and selected area diffraction pattern of a sample

![TEM micrograph and SAED pattern](image)

*Fig. 4.7 Bright field micrograph and selected area diffraction pattern (insert) for Si:C=1:1 powders milled in N₂ gas for 263h.*
Chapter 4 Preparation of Nanocomposite of $\text{Si}_x\text{N}_y\text{SiC}$ by Ball Milling

milled for 263h (sample SiCN1-4) is shown in Fig. 4.7. A background amorphous halo is observed after milling on the selected area diffraction pattern (insert), indicating that an amorphous phase is formed. Considering the composition analysis of this sample (Table 4.2), this amorphous phase is expected to be an Si-C-N mixture. A narrower diffraction ring is also observed on the selected area diffraction pattern and, when indexed, this corresponds to nano-crystalline SiC. Diffraction patterns from other regions of the sample show a well defined $\alpha$-Fe diffraction ring (not show here), indicating large $\alpha$-Fe crystallites in some regions. The microstructure of sample SiCN1-4 after milling is further shown using STEM in Fig. 4.8. The average particle/grain size is about 3-6 nm and the structure within grains is featureless as expected for an amorphous phase, consistent with the observation in Fig.4.7. 

Fig 4.9 is a STEM image of selected grains from the above sample from which EDS analysis was taken at selected points. The spots 1-6 (in Fig. 4.9(a)) were taken across one particle (area 1), and spots 7-9 (in Fig. 4.9(b)) were taken from a different particle (area 2). The distribution of elements is shown in Table 4.3, where the composition is very different from the average composition in Table 4.2. The C content is much higher than it

Table 4.3 Elemental distribution across particles of as-milled sample SiCN1-4.

<table>
<thead>
<tr>
<th>Spot taken</th>
<th>Si at%</th>
<th>C at%</th>
<th>N at%</th>
<th>Fe at%</th>
<th>O at%</th>
</tr>
</thead>
<tbody>
<tr>
<td>area 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>17</td>
<td>58</td>
<td>12</td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>21</td>
<td>52</td>
<td>13</td>
<td>5</td>
<td>9</td>
</tr>
<tr>
<td>3</td>
<td>25</td>
<td>55</td>
<td>10</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>53</td>
<td>11</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>5</td>
<td>27</td>
<td>49</td>
<td>12</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>6</td>
<td>13</td>
<td>54</td>
<td>15</td>
<td>7</td>
<td>11</td>
</tr>
<tr>
<td>area 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>33</td>
<td>47</td>
<td>8</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>24</td>
<td>50</td>
<td>6</td>
<td>1</td>
<td>9</td>
</tr>
<tr>
<td>9</td>
<td>36</td>
<td>51</td>
<td>4</td>
<td>2</td>
<td>7</td>
</tr>
</tbody>
</table>
Chapter 4 Preparation of Nanocomposite of Si₃N₄-SiC by Ball Milling

Fig. 4.8 STEM micrograph of Si:C=1:1 powder particles after milling in N₂ for 263h.

Fig. 4.9 STEM image showing spots where EDS data were taken for sample in Fig. 4.8 (area 1), and another area (area 2).
should be, noting that the starting powders are Si:C=1:1. The extra carbon is most likely from the sample holder (carbon grids) which were described in Chapter 2. Thus, only the trends in the content of other elements relative to carbon are examined here. The nitrogen content also appears slightly higher for outer-region than the inner-region of the particle in area 1. This is consistent with the finding of reference\(^1\), where they studied iron milling in a nitrogen atmosphere and found that the outer-region of particles had a higher nitrogen content. It is noticed that oxygen is also relatively high in this analysis, noting that the composition analysis in Table 4.2 was not sensitive to oxygen. In addition, oxygen is highest (~10 at\%) near the particle surfaces whereas it is closer to 5 at\% in the interior of the particle. Much of this oxygen content may arise from oxidation of nano-particles after removal from the mill and during the sample preparation for TEM. It is also interesting to notice that area 1 has a higher iron contamination than area 2 and the nitrogen content is also higher in area 1 than area 2. Consistent with Chapter 3, this suggests that the nitrogen adsorption may depend on the local level of iron contamination.

4.3.2.4 DTA analysis

The DTA experiments were carried out at a heating rate of 20 °C/min in an argon atmosphere. The thermal behavior of samples with a starting ratio of Si:C=50:50 and milling for various times is shown in Fig. 4.10. An exothermic peak is observed on the DTA curves in the temperature ranges of 750-850 °C and 900-1100 °C for short milling (19 and 41h) and longer milling (168-307h), respectively. No clear exothermic peak is revealed for the 96h milled sample. As before, detailed XRD analysis was made after annealing the samples at temperatures just below and just above the exothermic peaks. The results show that the exothermic peak for the short milling times corresponds to the formation of SiC as described in section 4.3.1. For the exothermic peak in the temperature
range of 900-1100 °C, XRD results clearly indicate that the peak is related to the formation of α-Si$_3$N$_4$, similar to the behavior in Chapter 3. Thus, this high temperature exothermic peak would appear to correspond to crystallization of α-Si$_3$N$_4$ from amorphous Si-C-N.

As a summary of the above results, nitrogen adsorption and dissociation occur during ball milling of a mixture of silicon and carbon in a nitrogen atmosphere. An amorphous phase Si-C-N and some free iron (α-Fe and γ-Fe) from contamination results after extended milling. This amorphous phase appears to crystallize to a composite of Si$_3$N$_4$-SiC and iron silicide upon annealing up to 1100 °C. The previous study in Chapter 3 shows that there is no nitrogen adsorption and dissociation during milling of pure silicon in a nitrogen atmosphere, but adsorption does occur in the case of silicon and a carbon mixture. This indicates that carbon may play an important role for nitrogen adsorption during milling. Iron contamination was shown to catalyze nitrogen adsorption during milling in ammonia (Chapter 3). In the present case, the question arises as to what are the precise roles of carbon and iron in formation of the Si$_3$N$_4$-SiC composite during milling and subsequent annealing?
4.3.3 Varying the Carbon Content

In order to study the effects of carbon, different carbon content in the starting material was examined. The ball milling experiments were performed for 263h under nitrogen atmosphere. The starting ratio of silicon and carbon, and the compositions of as-milled powder are shown in Table 4.4. It is shown that the nitrogen content first increases slightly with decreasing carbon content from 29 at% nitrogen at Si:C=50:50 to 35 at% nitrogen at 38 at% carbon. The nitrogen content then decreases again when carbon is 32 at%, and when the carbon content is 28 at%, the nitrogen content is only 6 at%. This suggests that the nitrogen adsorption is strongly dependent on the carbon content, and a carbon threshold (32 at%) may exist for nitrogen adsorption during milling. The pressure measurements show that the nitrogen pressure gradually decreases during the milling as shown in Fig. 4.4, when the carbon content is higher than the threshold. When the carbon content is lower than the threshold, the nitrogen pressure exhibits no significant decrease (not show here), which is consistent with the composition analysis.

The structural study confirms the existence of a carbon threshold for nitrogen adsorption. Fig. 4.11 presents the XRD patterns of as-milled powders with different starting carbon content. Broadened SiC diffraction peaks are observed after milling for the samples with higher starting carbon content(≥ 32 at%), indicating the formation of the amorphous phase Si-C-N, together with α-Fe and γ-Fe contamination. The diffraction intensity of α-Fe and γ-Fe increases with decreasing carbon. When the carbon content is 28 at%, much

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Si:C</th>
<th>Si at%</th>
<th>C at%</th>
<th>N at%</th>
<th>Fe at%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiCN1-4</td>
<td>50:50</td>
<td>32</td>
<td>32</td>
<td>29</td>
<td>7</td>
</tr>
<tr>
<td>SiCN2-1</td>
<td>57:43</td>
<td>35</td>
<td>27</td>
<td>32</td>
<td>6</td>
</tr>
<tr>
<td>SiCN3-1</td>
<td>62:38</td>
<td>36</td>
<td>22</td>
<td>35</td>
<td>7</td>
</tr>
<tr>
<td>SiCN4-1</td>
<td>68:32</td>
<td>43</td>
<td>20</td>
<td>31</td>
<td>6</td>
</tr>
<tr>
<td>SiCN5</td>
<td>72:28</td>
<td>66</td>
<td>25</td>
<td>6</td>
<td>3</td>
</tr>
</tbody>
</table>
Chapter 4 Preparation of Nanocomposite of Si$_3$N$_x$-SiC by Ball Milling

**Fig. 4.11** XRD patterns of milled samples (263h) with different C content in N$_2$ gas

**Fig. 4.12** XRD patterns of annealed samples with different C content from Fig. 4.11
stronger SiC diffraction peaks are observed compared with the higher carbon content case. In this latter case, iron silicide (FeSi2) is found in the sample rather than free α-Fe and γ-Fe. This suggests that a silicon and iron solid state reaction occurs during milling when the starting composition is far from SiC stoichiometry. Fig. 4.12 presents the XRD patterns of the above samples after annealing at 1100 °C in argon. For the samples with higher carbon content, the Si3N4-SiC composite and Fe5Si3 are formed after annealing. For the sample below the carbon content threshold, SiC, Si and FeSi2 are the annealing products. No Si3N4-SiC composite is observed in this case.

Fig. 4.13 shows the DTA curves of the above samples. The crystallization temperature of Si-C-N is also affected by the starting carbon content. The exothermic peaks on the DTA curve are 1081, 1021, 963, and 1058 °C for samples with 50, 43, 38, 32 at% carbon content, respectively. Except the sample with 32 at% carbon, the exothermic peaks decrease as the carbon content decreases. Compared with the composition analysis in Table 4.4, the lower exothermic peak correlates with the higher nitrogen content. This suggests

![Fig. 4.13 DTA curves of samples with different starting C content milled for 263h in N2.](image-url)
Chapter 4 Preparation of Nanocomposite of Si₃N₄-SiC by Ball Milling

that the closer the composition to Si₃N₄ stoichiometry, the lower the crystallization peak temperature.

Taken together, the above results suggest that the carbon starting content strongly affects the nitrogen adsorption during milling and therefore, strongly determines the final milling products. The formation of an amorphous (Si-C-N) phase during milling only occurs when the carbon content is above the 32 at% carbon threshold. No such phase can be formed when carbon starting content is below this threshold. It is also interesting to notice that the final iron contamination phases are affected by the starting carbon content. Free α-Fe and γ-Fe are always found in the cases when the nitrogen-containing amorphous phase (Si-C-N) is formed (Fig. 4.5 and Fig. 4.11). Alternatively, nitrogen adsorption only occurs during milling in cases where the samples contain free α-Fe and γ-Fe (i.e. in high carbon content samples). No nitrogen adsorption and subsequent formation of the amorphous (Si-C-N) phase was found when an iron silicide formed during milling (Fig. 4.11). This indicates that nitrogen adsorption during milling strongly depends on both the amount of carbon content and also the iron phases formed during milling.

4.3.4 Silicon Carbide Milled in Nitrogen

It is clear that nitrogen is adsorbed when silicon and carbon are milled in a nitrogen atmosphere. A question here is: does carbon play a similar role to iron in catalyzing nitrogen adsorption? (Note that iron played a key role in ammonia adsorption and formation of an amorphous SiₓNᵧ phase in Chapter 3). However, if carbon is initially bonded to silicon in the starting powders (i.e. milling of silicon carbide rather than a mixture of silicon and carbon powder), is nitrogen still adsorbed by the powder? To answer this question, pure SiC was milled in nitrogen at a pressure of 400 kPa for 118h.

Fig. 4.14 shows the structural evolution of the above as-milled and annealed samples. Substantially broadened SiC diffraction peaks are observed in the XRD patterns of the as-milled powder, together with a high background, which suggests the formation of an amorphous (Si-C-N) phase (section 3.4.2). The α-Fe and γ-Fe peaks are also revealed in the
Chapter 4 Preparation of Nanocomposite of Si$_3$N$_4$-SiC by Ball Milling

Fig. 4.14 XRD spectra for milled SiC in N$_2$ and subsequent annealing at 1100 °C

Fig. 4.15 XRD spectra of SiC and Si powders (Si:C = 62:38) milled for 118h in N$_2$ gas and subsequent annealing at 1100 °C.
as-milled powder. No iron silicide was found in this case. The Si$_3$N$_4$-SiC composite and Fe$_5$Si$_3$ are formed upon annealing. Now, if extra silicon is added to pure silicon carbide before milling, it might be expected to enhance the fraction of Si$_3$N$_4$ as was found previously for Si + C powders. So, in an additional experiment, a mixture of silicon and silicon carbide (composition: 62 at% Si, 38 at% C) is milled in nitrogen atmosphere under the same milling conditions as above. The XRD patterns of the as-milled and annealed sample are shown in Fig. 4.15. Instead of the expected broadened SiC diffraction peaks, only sharp SiC and strong Fe$_5$Si$_3$ diffraction peaks are revealed in the as-milled powder. Composition analysis shows that the as-milled powder has very low nitrogen content. The pressure measurement also shows that there is no significant pressure decrease during milling. All these facts suggest that no nitrogen adsorption and formation of amorphous Si-C-N occurs in the case of milling a mixture of silicon carbide and silicon in nitrogen gas. At first sight, in light of the opposite effect for silicon and carbon powders of the same Si:C ratio (section 4.3.3), this is a very surprising result. On closer inspection, the difference

![Fig. 4.16 XRD spectrum of Fe$_5$Si and SiC powders milled for 118h in N$_2$ gas.](image-url)
between these two cases is that different iron contamination phases result during milling. Milling of silicon and carbon powders contains free iron, whereas milling of silicon carbide and silicon powders contains iron silicide. This indicates that the excess silicon (in the case of SiC + Si) reacts with iron from the mill forming silicide. Thus, it seems that iron silicide inhibits nitrogen adsorption whereas free iron (as found in Chapter 3) aids nitrogen adsorption. To test this further, a mixture of Fe₃Si and SiC powder was milled in nitrogen to confirm this behavior.

The XRD patterns of the above sample are shown in Fig. 4.16. No significant structural changes are observed after 118h milling except for another iron silicide phase (Fe₅Si₃) forming. The pressure measurement did not show any pressure drop, and there was no evidence for an amorphous phase forming during milling. This behavior is discussed more fully in section 4.4 but suggests that only free iron aids nitrogen adsorption during milling, but iron silicides do not.

### 4.3.5 Effect of Milling Atmosphere and Pressure

#### 4.3.5.1 Milling pressure

As described before, there is a carbon threshold for formation of amorphous Si-C-N during milling. The following experiments show that this threshold is affected by milling pressure. Two groups of experiments were carried out, with the starting carbon content either 38 or 32 at%. These compositions were then milled at different nitrogen pressures, 400 and 200 kPa. The compositions of the as-milled samples are shown in Table 4.5.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Starting Composition Si:C</th>
<th>Pressure kPa</th>
<th>Si (at%)</th>
<th>C (at%)</th>
<th>N (at%)</th>
<th>Fe (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiCN3-2</td>
<td>62:38</td>
<td>200</td>
<td>39</td>
<td>26</td>
<td>22</td>
<td>11</td>
</tr>
<tr>
<td>SiCN4-2</td>
<td>68:32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiCN3-1</td>
<td>62:38</td>
<td>400</td>
<td>36</td>
<td>22</td>
<td>35</td>
<td>7</td>
</tr>
<tr>
<td>SiCN4-1</td>
<td>68:32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Chapter 4 Preparation of Nanocomposite of $\text{Si}_3\text{N}_4$-$\text{SiC}$ by Ball Milling

Fig. 4.17 XRD patterns showing the effects of pressure for two different starting C content of Si:C milled in $\text{N}_2$ gas.

![XRD patterns showing the effects of pressure for two different starting C content of Si:C milled in $\text{N}_2$ gas.](image)

Fig. 4.18 XRD patterns showing the effect of pressure for two different starting C content in Si:C milled in $\text{N}_2$ after annealing at 1100 °C in Ar.

![XRD patterns showing the effect of pressure for two different starting C content in Si:C milled in $\text{N}_2$ after annealing at 1100 °C in Ar.](image)
nitrogen contents are low for both samples milled at 200 kPa compared with those milled at 400 kPa, especially for the 32 at% carbon sample, where only 8 at% nitrogen is detected, which is far from Si$_3$N$_4$ stoichiometry. This indicates that nitrogen adsorption during milling strongly depends on the milling pressure: lower milling pressure results in lower nitrogen content in the final milling product.

Fig. 4.17 shows the X-ray diffraction patterns of the above samples. As described before, milling in nitrogen under a pressure of 400 kPa with a starting C content at or above threshold (32 at%) results in the formation of amorphous Si-C-N. When milling is carried out under a pressure of 200 kPa, different results are observed. For the 38 at% carbon sample, amorphous Si-C-N and free iron are formed after milling. For the 32 at% carbon sample, strong SiC diffraction peaks are observed, together with the formation of Fe$_5$Si$_3$ during milling. No strong evidence exists for an amorphous (Si-C-N) phase formed during milling, which is consistent with the composition analysis. This indicates that the carbon threshold depends on the nitrogen milling pressure. In other words, there is a balance

![Fig. 4.19 DTA curves for 38 at% C in Si:C powders milled at two different pressures.](image)
between the silicon, carbon, and nitrogen content in determining the threshold for nitrogen adsorption. A higher nitrogen pressure needs a lower carbon content. Fig. 4.18 shows the XRD traces of the above samples after annealing at 1100 °C in argon. The Si$_3$N$_4$-SiC composite is not observed in the 32 at% carbon sample milled at 200 kPa.

Fig. 4.19 shows the DTA curves of samples with 38 at% starting carbon milled under pressures of 400 and 200 kPa for 263h. The exothermic peak temperature (representative of crystallization of α-Si$_3$N$_4$) increases as the nitrogen pressure decreases. As discussed before, the crystallization temperature of amorphous Si-C-N strongly depends on the nitrogen content. Higher nitrogen content is obtained in the sample milled at 400 kPa than that at 200 kPa. Therefore, the lower crystallization temperature is obtained for the sample milled at 400 kPa, as expected.

4.3.5.2 Milling in ammonia

Silicon and carbon powders with a ratio of 57:43 were milled in ammonia under a pressure of 400 kPa for 263h. The structural evolution after milling and annealing (at 1100

![Fig. 4.20 XRD spectra for Si and C powders (57:43) milled in NH$_3$ for 263h before and after annealing at 1100 °C.](image-url)
Chapter 4 Preparation of Nanocomposite of Si$_3$N$_4$-SiC by Ball Milling

°C in Ar) is shown by X-ray diffraction patterns in Fig. 4. 20. Broadened silicon diffraction peaks together with α-Fe and FeSi$_2$ are observed after milling. There is no strong evidence for SiC and/or amorphous Si-C-N formed after milling in ammonia. By careful analysis of the XRD pattern with ABFfit, a slight shift in silicon peaks to large angles was found. Combustion analysis shows 14 wt% nitrogen, 1 wt% hydrogen and 5 wt% carbon in the as-milled sample. Considering the composition analysis, it is most likely that a solid solution of nitrogen and carbon in silicon, was formed after milling in ammonia. It is also clear that the carbon content is very much lower than the starting content, which may be because the following reaction takes place during milling:

$$\text{Si} + \text{C} + \text{NH}_3 \rightarrow \text{Si} + \text{C} + \text{CH}_x \text{ (gas)} + \text{residual} \ (\text{Si} + \text{C}).$$

Here, the formation of CH$_x$ gas during milling reduces the carbon content in the final powder. A Si$_3$N$_4$-SiC composite and iron silicides are formed after annealing up to 1100 °C, together with some free silicon. It seems that the solid solution and/or amorphous Si(C, N, H) phase converted to Si$_3$N$_4$-SiC during annealing. No strong exothermic peak was found in DTA analysis, which may indirectly indicate that a different mechanism of formation of the composite Si$_3$N$_4$-SiC is obtained after milling in ammonia. A more detailed study would be needed to clarify this behavior.

In summary, the composite Si$_3$N$_4$-SiC can be formed by ball milling a mixture of silicon and carbon in nitrogen and ammonia atmospheres, following subsequent annealing in argon. However, the composite can be formed more easily by milling in nitrogen gas, where the presence of free iron aids nitrogen adsorption but the milling time needs to be carefully controlled to achieve the desired composition of the composite.

4.4 Discussion

4.4.1 SiC Formation

It was shown that crystalline silicon carbide directly forms after milling silicon and carbon in vacuum at room temperature. Furthermore, the SiC nanocrystallite grains grow
Chapter 4 Preparation of Nanocomposite of Si₃N₄-SiC by Ball Milling

up to 5 nm with increasing milling time. The question raised here is what is the mechanism of SiC formation induced by mechanochemical reaction? In particular, where does the reaction take place and how does the grain growth occur? There are two possible ways. First, silicon and carbon powder particles are reduced in size and intimately mixed during milling. The nucleation of SiC may then occur by local mechanochemical reaction at the site of a ball and powder collision. Silicon and carbon are continuously brought to the SiC nuclei and, when further impact occurs, the solid state reaction may continue at the surfaces of SiC grains. Second, the nucleation of SiC may alternatively take place at surfaces of silicon particles during ball-powder impacts and grain growth may occur towards the inner region of the silicon particle during subsequent impacts. In this case, carbon atoms need to be continuously injected into the small silicon carbide grain under ball impact and interstitial carbon diffuse into the silicon. If this occurs, it would require a very large enhancement in carbon diffusivity in silicon at room temperature. However, under ball impacts involving damage and strain induced in nanosize particles such diffusion may be possible. For example, carbon diffusion has been observed in silicon at room temperature by Lalita et al. Their results show that, when damage induced by ion implantation is present in silicon, carbon in the form of interstitial carbon is mobile. At this stage, it is difficult to determine the exact model responsible for silicon carbide grain growth under ball milling. A more detailed microstructure and grain composition analysis would need to be carried out.

As shown in Chapter 3 and also in this chapter, milling can result in an amorphous phase or at least partial amorphization. Thus, is any amorphous SiC formed during milling? None of the data in section 4.3.1 can unequivocally answer this question, since partially amorphous SiC induced by ball milling may not be easily observed by XRD, although the high background to XRD spectra could indicate some amorphous phase. However, Fig. 4.15 in 4.3.4 shows the XRD spectra after the milling of a mixture of pure SiC and silicon in nitrogen gas. Since iron silicide is formed, very low nitrogen content was detected and no broadened SiC diffraction peaks are observed in the powder, which may suggest that
pure SiC is difficult to amorphize if nitrogen is absent in the phase. If this is the case and no amorphous SiC formation results, the exothermic peak on the DTA curve (Fig. 4.3) would most likely correspond to the chemical reaction between silicon and carbon. The decrease of the DTA peak temperature and intensity with prolonged milling suggests that the reaction between silicon and carbon is more complete during milling and little reaction takes place upon annealing.

4.4.2 Composite and Si₃N₄ Formation

As described previously, an amorphous (Si-C-N) phase, together with free iron contamination, can be formed after milling a mixture of silicon and carbon, or pure silicon carbide, in a nitrogen atmosphere. To obtain the amorphous phase, the nitrogen adsorption is a key. The nitrogen adsorption and subsequent formation of the Si-C-N amorphous phase strongly depend on both the carbon content and the presence of free iron contamination in the form of α-Fe and γ-Fe. There is a carbon threshold for each nitrogen pressure: above the threshold nitrogen adsorption takes place and the amorphous phase forms during milling. When the carbon content is far from SiC stoichiometry (below the threshold), nitrogen adsorption is difficult and no subsequent amorphous phase formation occurs. This is no surprise since pure silicon does not adsorb nitrogen when milled in a nitrogen atmosphere (section 3.3.1). The question may raise here as to what are the precise roles of carbon and iron in this process? Before addressing this issue, the processes during milling are examined in more detail.

When silicon and carbon are milled in nitrogen, silicon carbide forms at an early milling stage (section 4.3.2 and 4.3.3). The crystallites of silicon carbide may initially contain carbon vacancies, depending on the carbon content, particularly if SiC formation requires carbon diffusion into silicon particles. The concentration of vacancies may also increase as carbon content decreases. It is obvious that carbon vacancies would favor nitrogen incorporation into silicon during milling. Furthermore, the nitrogen adsorption increases as carbon content decreases and presumably as the vacancy concentration
increases. This trend is noticeable in the samples with 43 and 38 at% carbon content. However, when the carbon content decreases below about 32 at%, the nitrogen adsorption starts to decrease. For example, when the carbon content decreases to 28 at%, a nitrogen content of only 6 at% is observed in the as-milled powder and iron silicide is present after milling. There are two possible processes occurring in this case during milling. First, assuming the available carbon still converts the silicon fully to silicon carbide, this phase may be unstable since the vacancy excess existing in the structure will be very large. Thus, it may easily react with subsequent iron contamination forming iron silicide (Fig. 4.11). Second, some free silicon may be left after the carbon reacts to form silicon carbide during milling. This free silicon reacts with iron forming iron silicide. As is discussed more fully later, either possibility will result in the loss of free iron and the inhibition of nitrogen adsorption.

Whereas pure silicon carbide is very difficult to amorphize during milling, the increasing nitrogen adsorption and mixing with the silicon carbide, under ball impacts in nitrogen gas, readily leads to an amorphous nitride phase. From a thermodynamic point of view, amorphous phase formation may reduce the free energy of the Si-C-N system when both defects and nitrogen are introduced into the SiC lattice. Further support for this process and insight into the driving forces present may be obtained from ion implantation studies. Ion implantation, as discussed in the next chapter, is a non-equilibrium process for injecting ions of elements into a matrix at room temperature, such as N⁺ into SiC in references 3-5. In the ion implantation case, crystalline SiC is rendered amorphous (as SiCₓNᵧ) by the incorporation of nitrogen. In ref. 3, after a high dose (1E10¹⁸/cm²) of nitrogen is implanted into silicon carbide, the atomic concentrations of silicon and carbon decrease as that of nitrogen increases. The reduction of carbon concentration in the region of implanted nitrogen is remarkable and suggests the migration of carbon through defects induced by ion implantation. In ref. 4, the implanted nitrogen is shown to bond to silicon selectively, substituting for carbon atoms in the silicon carbide lattice, resulting in an amorphous carbonitride composite layer and free carbon. An ion-induced carbon transport
is also observed, which appears to result both from a chemically-induced atomic redistribution, required by preferred Si-N bonding and local stoichiometry, and space-filling limitations in an amorphous network. The ball milling of silicon and carbon powders, or silicon carbide, in a nitrogen atmosphere shows similar behavior to these ion implanted cases and may derive from similar mechanisms. Both ball milling and ion implantation introduce large concentrations of defects into SiC while nitrogen is mixed with the lattice. These defects and nitrogen introduced by ball milling lead to an unstable defective silicon carbide structure and the formation of an amorphous (Si-C-N) phase is thermodynamic favored (see Chapter 3 for analogies with amorphous Si-N formation).

During annealing, the amorphous (Si-C-N) phase crystallizes to an Si$_3$N$_4$-SiC composites together with formation of Fe$_5$Si$_3$. In the case when the adsorbed nitrogen content is high and close to the Si$_3$N$_4$ stoichiometry for the available silicon in the sample, only Si$_3$N$_4$ and free carbon are formed (Fig. 4.6). This again strongly suggests that silicon prefers to bond with nitrogen, consistent with previous work$^4$ and the fact that α-Si$_3$N$_4$ has
Chapter 4 Preparation of Nanocomposite of \( \text{Si}_3\text{N}_4-\text{SiC} \) by Ball Milling

A lower free energy than SiC. The crystallization temperature also strongly depends on the carbon content (section 4.3.3) and the carbon content determines how much nitrogen is ultimately adsorbed and how close the composition is to \( \text{Si}_3\text{N}_4 \) stoichiometry. The carbon then has to be kicked out from amorphous Si-C-N before or during \( \alpha-\text{Si}_3\text{N}_4 \) formation. The closer the nitrogen content is to \( \text{Si}_3\text{N}_4 \) stoichiometry, the fewer the number of carbon atoms that need to move from Si-C-N, and hence the lower the temperature that is needed for complete carbon out-diffusion. A further experiment, whereby an annealed sample is heated in the TGA in air, confirms that the carbon is kicked out from \( \text{Si}_3\text{N}_4 \) during annealing. A large weight loss occurs in the temperature range of 300-500 °C as shown in Fig. 4.21. It is believed that the reaction: \( \text{C} + \text{O}_2 = \text{CO}_2 \) takes place during heating.

Fig. 4.22 gives a summary of the steps to formation of the composite and \( \text{Si}_3\text{N}_4 \) after milling and annealing. In the upper part of Fig. 4.22, the steps in the phase evolution of short and long term milling of silicon and carbon powders in nitrogen gas are shown. For short time milling, the nitrogen content is considerably less than 1:1 with silicon. After milling, crystallites of SiC are observed together with some amorphous Si-C-N and \( \alpha \) or \( \gamma \) iron. Upon annealing, an \( \text{Si}_3\text{N}_4-\text{SiC} \) crystalline composite is formed, together with iron silicide and some free carbon, possibly at grain boundaries. For long time milling, the nitrogen content is close to \( \text{Si}_3\text{N}_4 \) stoichiometry and an amorphous Si-C-N phase and free iron are obtained. Upon annealing, \( \alpha-\text{Si}_3\text{N}_4 \) crystallizes, iron silicide is observed by reaction of free iron with any excess silicon and amorphous carbon is most probably segregated to the \( \alpha-\text{Si}_3\text{N}_4 \) grain boundaries.

The various stages of reaction and phase transformations during long time milling and annealing are illustrated schematically on a system free energy diagram in the lower half of Fig. 4.22. Initially, mechanical energy is the driving force for overcoming the energy barrier for SiC formation by inducing defect formation and carbon mixing and/or migration into silicon. As the milling time increases, nitrogen (and iron) are increasingly accumulated and mixed. Along with defect accumulation in SiC (and remaining free silicon) this leads to a continual increase in free energy. It becomes energetically favorable.
Chapter 4 Preparation of Nanocomposite of Si$_3$N$_4$-SiC by Ball Milling

Short time milling (Si+C)

- Low nitrogen content accumulated
- Annealing in Ar
- SiC + amorphous Si-C-N + free Fe

$\text{Si}_3\text{N}_4$-SiC + Fe silicide + free C (little)

Long time milling (Si+C)

- High nitrogen content accumulated
- Annealing in Ar
- Amorphous Si-C-N + free Fe

$\text{Si}_3\text{N}_4$ + Fe silicide + free C

---

**Fig. 4.22** Schematic free energy diagram of formation of composite of $\text{Si}_3\text{N}_4$-SiC and $\text{Si}_3\text{N}_4$ after milling and annealing.

- milling
- disorder, nitrogen, Fe accumulation
- heating 1000 °C

- activation barrier for SiC formation
- Si+C powders
- SiC nanocrystals (small N/Fe)

- crystallization + silicide formation activation barriers
- amorphous Si-C-N + α/γ-Fe

- heavily disordered (unstable) SiC mixed with N
- $\alpha$-$\text{Si}_3\text{N}_4$
- Fe silicide free C

Free energy of system

Time
for an Si-C-N amorphous phase to form together with free iron (as α-Fe and γ-Fe). Nitrogen can be adsorbed to high concentrations with extended milling, up to α-Si$_3$N$_4$ stoichiometry. Heating to 1100 °C allows the system to overcome the activation barriers to α-Si$_3$N$_4$ and iron silicide formation, permitting the system to achieve its lowest free energy structure at that temperature. In the next section the roles of iron and carbon in the process of nitrogen adsorption and reaction are examined in more detail.

4.4.3 The Role of Carbon and Iron in Nitrogen Adsorption

In attempting to explain the role of iron on nitrogen adsorption during milling, a brief review of the ball milling of iron powder in nitrogen is given as below. Cook et al. have studied the microstructural development of iron powder during milling in nitrogen gas by Mössbauer spectroscopy. They found that milling for times up to 50h produced a highly strained nanocrystalline structure (α-Fe). During this time, the nitrogen concentration in the iron far exceeded the solubility limit but did not affect the microstructure. With increasing mechanical processing, the α-Fe became unstable. The local environment favored the local redistribution of iron and nitrogen atoms into a lower energy configuration, an Fe$_x$N$_y$ structure, in which the phase depended on nitrogen content. Chen et al. have claimed that up to 14 at% nitrogen is adsorbed by α-Fe forming an Fe(N) solid solution during the milling of iron in nitrogen atmosphere for 528h. It is clear that iron has a high affinity for absorbing nitrogen during milling in a nitrogen atmosphere. The atomic nitrogen in the solid solution Fe(N) has a much higher reactivity than that of a nitrogen molecule. In the present study, the nitrogen molecule is most likely to be first adsorbed by the free iron contamination revealed as broadened α-Fe and γ-Fe diffraction peaks (Fig. 4.5 and Fig. 4.11). Si$_3$N$_4$ has a more negative formation enthalpy than SiC and Fe(N), indicating that Si-N bonding should be preferred when atomic nitrogen in the Fe(N) coexists with SiC or a mixture of Si+C during milling. It is suggested that a transfer of atomic nitrogen from iron to small SiC crystallites occurs during milling, resulting in the formation of a Si-N-C mixture containing free iron. Thus, iron is a catalyst for nitrogen adsorption, conversion to
atomic nitrogen, continuous transfer to SiC and the ultimate formation of an amorphous Si-C-N phase when the nitrogen content is high enough. The results of this chapter suggest that iron silicide has no such catalytic function as free iron, whereby the formation of iron silicides results in no significant nitrogen adsorption during milling.

A further question is: why is the nitrogen adsorption strongly affected by carbon content and phase? There are two possible reactions for silicon during the early stages of milling: Si + C = SiC or Si + Fe = Fe₅Si₇. From thermodynamic data: $\Delta G_{\text{SiC}} = -14 - 15$ kcal/mol, $\Delta G_{\text{Fe₅Si₇}} = -14 - 22.6$ kcal/mol; hence they have a similar reaction tendency. During the early stages of milling, iron contamination is low and the carbon reaction with silicon to form SiC dominates. When the carbon content is above the threshold (32 at%), silicon fully forms SiC, although there may be some carbon vacancies in the structure. Little free silicon is then left to react with iron to form iron silicide, as iron is gradually accumulated during milling. Thus, the carbon acts as a barrier to the reaction of silicon with iron: hence the availability of free iron leads to nitrogen adsorption and the development of the amorphous Si-C-N phase. When the carbon content is below the threshold (or there is no carbon present as in Chapter 3) enough free silicon is available after SiC formation to react with iron, forming iron silicide. Hence, the absence of free iron inhibits nitrogen adsorption.

To summarize, free iron is essential for nitrogen absorption during milling of silicon. Without the presence of sufficient carbon, silicon will react with accumulating iron from the mill to form silicide and no nitrogen adsorption will result. The presence of carbon allows SiC to form before the iron contamination content is appreciable. Hence this removes free silicon and allows free iron to accumulate, thus providing the mechanism for nitrogen adsorption. This description is consistent with the results of all ball milling experiments presented in this chapter.

4.5. Conclusions

Nanocomposite Si₃N₄-SiC can be formed by ball milling a mixture of silicon and
carbon under both nitrogen and ammonia atmospheres in a stainless steel milling cell and subsequent annealing of the milling product in argon. Nitrogen adsorption, which is essential for formation of a composite, is strongly affected by the starting carbon content and the iron contamination phases formed during milling. Free iron from the mill acts as a catalyst for adsorption of nitrogen molecules from the atmosphere and permits the transfer of atomic nitrogen into silicon carbide during milling. When this occurs it leads to a Si-C-N amorphous phase during milling, which crystallizes on annealing. If iron silicide forms during milling it results in a loss of free iron and nitrogen adsorption is inhibited. Carbon is also crucial for nitrogen adsorption and the formation of an amorphous Si-C-N. Above a threshold carbon content, silicon fully reacts with carbon, nitrogen is adsorbed and an amorphous phase of Si-C-N forms after milling. Below this threshold carbon content, no nitrogen adsorption occurs during milling. The carbon threshold is affected by milling pressure, whereby a higher milling pressure results in a lower threshold. The role of carbon is to provide a barrier to the reaction between silicon and iron contamination (by allowing SiC to form) and hence free iron is available to catalyze nitrogen adsorption.

The formation of an Si$_3$N$_4$-SiC composite or $\alpha$-Si$_3$N$_4$ and free carbon after annealing depends on the nitrogen content in the powder, which is controlled by the milling time. If the nitrogen content is close the Si$_3$N$_4$ stoichiometry for the available silicon, only $\alpha$-Si$_3$N$_4$ and free carbon can be obtained.
Chapter 4 Preparation of Nanocomposite of Si$_3$N$_4$-SiC by Ball Milling

References:

Chapter 5 Ion Implantation and Comparison with Ball Milling

5.1 Introduction and Background

The motivation for the present ion implantation study arose from previous reports of the synthesis of silicon nitride by nitrogen ion bombardment and the opportunity for comparing this cleaner nitridation process with the nitridation behavior of mechanochemistry (chapter 3 and 4). Previous chapters have shown that an amorphous Si-N phase is formed after milling silicon in ammonia and that crystallization appears to occur on annealing beyond about 800 °C. However, the role of contamination in the amorphization and crystallization processes is not clear. Thus, there is a clear need to establish the phase evolution after milling and subsequent annealing. Hence, a comparative study with the cleaner ion implantation process may provide further insight into mechanochemistry.

For ion implantation, it has also been shown that nitrogen bombardment of silicon forms α-Si$_3$N$_4$ after subsequent high temperature annealing (≥ 1200 °C). Such nitride layers are normally buried below the surface of silicon as a result of deep penetration of nitrogen ions. The fabrication of such a silicon nitride layer on a single crystal silicon, a so called silicon-on-insulator (SOI) structure, is important for the semiconductor industry. For example, it is capable of supporting metal oxide semiconductor (MOS) transistor action and has the advantage of low leakage current. It was found that an amorphous (nitride) layer forms during ion implantation in most cases but the microstructure of this layer is dependent on the implantation conditions, such as dose and implantation temperature. For example in ref. 4, after implantation at 500 °C with 200 keV N$^+$ ions and subsequent annealing at 1200 °C, for a low dose sample (0.25E18 cm$^{-2}$), a buried discontinuous polycrystalline α-Si$_3$N$_4$ layer was observed. For a medium dose sample (0.75E18 cm$^{-2}$), there was a buried continuous polycrystalline α-Si$_3$N$_4$ layer containing small silicon
islands. For a higher dose sample (1.4E18 cm^-2), there was a buried multilayer structure consisting of bubbles within an amorphous Si-N layer. If the amorphous silicon nitride layer extends to the surface and is exposed to oxygen during annealing, it is readily oxidized and is very difficult to crystallize on annealing. However, it is difficult to compare these implantation results with the behavior of nitrides formed by mechanochemistry, particularly in terms of the role of contamination, such as oxygen and iron, in stabilizing an amorphous phase and influencing the crystallization temperature. For example, no study of the role of iron on silicon nitride formation has been made using ion implantation.

In this chapter, nitrogen ions were implanted into silicon under different ion implantation conditions: with the nitrogen concentration above and below that required for

![Diagram](image-url)
Si₃N₄ stoichiometry. The implanted and annealed samples (up to 1000 °C in argon) were studied by RBS, TEM and XRD. Also, some samples were implanted with iron ions to better compare with the ball milling results.

5.2 Experimental Procedures

Two types of nitrogen implantation experiments were carried out as follows: Firstly, ion implantation of positive nitrogen ions into Si (100) wafers was carried out using the Mk4 implanter at Harwell. This arrangement allowed the nitrogen concentration to exceed that in Si₃N₄ (above stoichiometry) for doses greater than about 4×10¹⁷ cm⁻². The implanted area was 6.25 cm². 15-40 keV N⁺ (also N₂⁺) ions were implanted into a Si wafer with doses from 1E16 cm⁻² to 1E18 cm⁻² at different beam currents between 50 and 550 µA. The beam currents determine the implantation time. Another effect of beam current is that the average temperature of the wafer during implantation increases when the beam power increases, see Fig 5.1. From Fig 5.1, which is taken from the work of Chivers et al. for the Harwell Mk4 implanter, wafer temperatures during implantation are estimated to be about 150, 350, and 600 °C for beam currents of 50, 200 and 550 µA, respectively. A wafer glowing dull red was observed when the current was 550 µA, indicating that the temperature is at least 520 °C.

Table 5.1 Possible the depth of implanted ions at different energy estimated by TRIM

<table>
<thead>
<tr>
<th>Ion</th>
<th>Energy (keV)</th>
<th>Projected Range (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>70</td>
<td>1019</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>1167</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>1851</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>4597</td>
</tr>
<tr>
<td>N</td>
<td>15</td>
<td>400</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>1027</td>
</tr>
<tr>
<td>Fe</td>
<td>45</td>
<td>392</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>967</td>
</tr>
</tbody>
</table>
Some of the Si wafers were previously amorphized with Si ions to a depth of several thousand Angstroms in order to examine differences between amorphous and crystalline substrates. The amorphization of silicon was carried out by $3 \times 10^{15}$ cm$^{-2}$ Si ions implanted into a silicon wafer at two energies, 300 and 70 keV, at liquid nitrogen temperature. To simulate the ball milling cases, Fe$^-$ (45 keV, $5 \times 10^{16}$ cm$^{-2}$, room temperature) was also implanted at ANU into the samples after nitrogen implantation. The projected range of the implanted ions at the different energies was calculated by TRIM and shown in Table 5.1.

Secondly, SiN$^-$ molecular ions were used as a nitrogen source. In this case, a $1 \times 10^{18}$ cm$^{-2}$ dose of 120 keV ions was implanted into silicon at liquid nitrogen temperature at ANU. The implantation area was $1 \times 2$ cm$^2$. Implantation of SiN$^-$ molecules meant that the nitrogen concentration was always below Si$_3$N$_4$ stoichiometry (nitrogen deficient) for all doses. When 120 keV SiN$^-$-ions reach the surface of silicon, the molecule breaks up into silicon and nitrogen atoms with energies of 80 and 40 keV, respectively. These projected ranges of silicon and nitrogen ions (in silicon) are also shown in Table 5.1. Prior to SiN$^-$ implantation, the silicon was amorphized by implanting a $3 \times 10^{15}$ cm$^{-2}$ dose of Si$^+$ at 125 keV into a silicon wafer at liquid nitrogen temperature. Fe$^-$-ions were also implanted with an energy of 125 keV to a dose of $3.75 \times 10^{16}$ cm$^{-2}$ into half of this amorphized area ($1 \times 1$ cm$^2$) at room temperature. The reason for the very different choices of ion species were that the ion implanters at ANU are negative ion source machines. Here, N$_2^+$ ions are impossible and SiN$^-$ ions are the only feasible nitrogen-containing molecular ions for high dose cases. It was because of the difficulty in implanting nitrogen on the ANU machines that the Harwell ion implanter was used. Although this allowed many implants to be done in a short time, as a result of the high N$_2^+$ beam currents used, there were problems such as temperature rise during implantation as indicated above. As the results will demonstrate, the use of both types of implanter and different implantation conditions used was quite fortuitous and allowed some interesting comparisons to be made with nitrides formed by ball milling.
Chapter 5 Ion Implantation and Comparison with Ball Milling

The implanted samples were annealed in a quartz tube furnace. Before annealing, the samples were cleaned with acetone and methanol. The annealing were carried out under an argon flow with 2h purging time prior to the annealing. RBS or RBS-C was used to analyze the composition, stoichiometry and damage (channeling), and depth profiles for as-implanted and annealed samples. The microstructure and phases were observed by XTEM on a Philips EM430 instrument operated at 300 keV. The standard XRD technique is not sensitive enough for most of the thin layer implanted samples used, and attempts at using glancing angle XRD gave results which were difficult to interpret. However, the thicker implanted layers, for example the SiN⁺ implanted samples, were able to be analyzed by standard XRD.

5.3 Results and Discussion

5.3.1 N⁺ as Nitrogen Source

5.3.1.1 Formation of a silicon nitride layer

Fig. 5.2 shows RBS spectra for the case of 30 keV N₂⁺ implantation of silicon to a dose of 10¹⁸ cm⁻² at a temperature (see Fig. 5.1) of about 350 °C. The sample was previously amorphized with Si⁺ ions to a depth of 4500 Å (from TRIM). Both the random and channeling spectra are shown for the as-implanted sample and these spectra were collected in the same geometry as indicated in the insert. The random spectrum clearly shows evidence for a SiₙNᵧ film on silicon, where the signal from silicon is low in the near surface and a clear nitrogen signal is observed as labeled. The channeling spectrum also shows the nitride layer, which exhibits no channeling effect. Also, the silicon signal remains at the random level until about channel 100, where it drops below the random level due to channeling in the underlying crystalline silicon. This suggests an amorphous silicon layer underneath the SiₙNᵧ layer as shown in the schematic insert. RUMP simulations¹⁰,¹¹ were used to estimate the stoichiometry and thickness of the SiₙNᵧ and amorphous silicon layers.
Chapter 5 Ion Implantation and Comparison with Ball Milling

Fig. 5.2 RBS-C spectra from a Si implanted with 30 keV N$_2^+$ to a dose of $1\times10^{18}$ cm$^{-2}$.

The thickness of the Si$_x$N$_y$ layer was found by using the normal density ($1.036\times10^23$ atoms/cm$^3$) of Si$_3$N$_4$. The RUMP fit shows the nitrogen-rich Si$_x$N$_y$ layer to be about 440 Å in thickness, where $y>2x$, for all depths up to the surface. Thus, the implanted layer is considerably richer in nitrogen than Si$_3$N$_4$, as illustrated more clearly later. It is impossible from the spectrum to determine if oxygen is in the nitride layer but the sensitivity of RBS suggests it to be below about 10-15%.

Fig. 5.3(a) shows an XTEM micrograph of the sample where nitrogen was implanted into amorphous silicon. The residual amorphous (originally 4500 Å) and crystalline silicon regions are clearly observed. An unusual dark contrast is observed apparently within an amorphous layer. The cause of this different contrast in this region is
Fig. 5.3 XTEM micrograph of the Si implanted with 30 keV $N_2^+$ to a dose of $1 \times 10^{18}$ cm$^{-2}$ (a) and subsequent annealing at 1000°C.
unknown. It probably is due to an effect of recrystallization of part of the amorphous layer during the N\textsuperscript{2+} implantation, or a result of the incomplete amorphization of the original layer to the surfaces. However, the original amorphous silicon layer has not completely crystallized during the N\textsuperscript{2+} implantation, supporting an implantation temperature of below about 500 °C. Changes in implantation temperature may be important in determining the final structure and this is explored in the following sections. XTEM in Fig. 5.3.(a) also shows that the nitrogen implanted layer has a very porous (bubble-like) structure and is about 600 Å in thickness, which is larger than the RBS simulated result of 440 Å. The difference in the two techniques is most likely due to the fact that, for the RBS simulation, it was assumed that the silicon nitride layer density is that of normal Si\textsubscript{3}N\textsubscript{4} and this density is not applicable for porous Si\textsubscript{3}N\textsubscript{y} as determined by TEM above. The size of the “bubbles” decreases towards the interface with the silicon substrate. This porous structure is believed to be due to the low diffusivity of nitrogen in nitrogen-rich silicon after high dose implantation, whereby the excess nitrogen not used in Si\textsubscript{3}N\textsubscript{4} formation is segregated into nitrogen bubbles\textsuperscript{4-12, 13}. This is consistent with the RBS result of a stoichiometry of Si\textsubscript{x}N\textsubscript{y} with \( y > 2x \). Electron diffraction did not reveal any diffraction spots related to polycrystalline Si\textsubscript{3}N\textsubscript{4} formation. Liliental et al.\textsuperscript{14} have also reported a porous as-implanted nitride structure. It contains two phases, small needlelike particles of a polycrystalline phase in an amorphous matrix for a 2.6E18 cm\textsuperscript{-2} nitrogen implantation dose. Chang et al.\textsuperscript{5} suggested that the porous layer is basically amorphous since only a few needlelike features are observed in the porous region when lower dose (1.4E18 cm\textsuperscript{-2}) nitrogen was implanted at a temperature of 450 °C. In the present study, for a dose of 1E18 cm\textsuperscript{-2} at an implant temperature about 350 °C, the porous structure is observed to be amorphous, as determined from a diffraction pattern with broad halos (not shown). This behavior is illustrated more clearly later.

After annealing at 1000 °C for 1h in argon atmosphere, the RBS-C spectrum (Fig. 5.2) shows that oxygen appears on the sample surface and the amorphous Si underlying the
silicon nitride has crystallized since the silicon signal is much reduced from the random. No channeling was observed for the nitride layer since this layer either remains amorphous or is polycrystalline. The stoichiometry of the nitride region and composition-thickness profiles remain unchanged, indicating that no nitrogen migration is observed. This suggests that most nitrogen atoms are most likely chemically bonded with silicon, and that an amorphous silicon nitride layer is formed after implantation. An XTEM weak beam image of an annealed sample is shown in Fig. 5.3b. It shows that the interface between the nitride layer and the silicon substrate exhibits a strong "mottled" structure. The underlying amorphous silicon has also recrystallized and dislocation loops exist at the original amorphous-crystalline interface, consistent with the RBS-C data (see Fig. 5.2). A different contrast in the underlying silicon is also observed after silicon crystallization. The bright contrast is probably caused by some polycrystalline silicon, which is formed during annealing. No evidence is shown for a significant change in the porous nitride structure, and a selected area diffraction pattern from the nitride layer does not give rise to any diffraction spots of crystalline $\alpha$-$\text{Si}_3\text{N}_4$, indicating that it is probably still amorphous after this annealing temperature (1000 °C). Similar behavior was reported by Chang et al. (ref. 5), where, after a 1.4E18 cm$^{-2}$ dose of nitrogen implantation and annealing at 1200 °C for 2h, polycrystalline $\alpha$-$\text{Si}_3\text{N}_4$ only formed in parts of the nitrogen implanted layer which did not contain a porous structure. However, no polycrystalline $\alpha$-$\text{Si}_3\text{N}_4$ was found in the porous structure region by selected area diffraction, suggesting that the porous structure is difficult to crystallize, even at 1200 °C. Another possible reason for no polycrystalline $\alpha$-$\text{Si}_3\text{N}_4$ formation in our case is described in section 5.1 (and also ref.7), where it is suggested that an oxidation reaction may occur during annealing, thus suppressing crystallization of amorphous silicon nitride.

Attempts were made to examine if the above implantation results are reproducible. A different sample with the same nominal implantation conditions as the previous sample was studied. The RBS-C spectrum of this sample is shown by the solid curve in Fig. 5.4.
Again, a silicon nitride layer on top of silicon is observed, but it is a surprise that the amorphous silicon underlying the silicon nitride layer has crystallized during nitrogen implantation. A careful check of the implantation conditions revealed that this sample was tilted off from the implantation holder and heated up to a higher temperature during implantation. This temperature is estimated to be above 550 °C, as amorphous silicon crystallizes at 550 °C. In order to see if the bubbles or porous structure were affected by subsequent implantation and injection of extra silicon into the structure, the near-surface nitride was subsequently implanted at liquid nitrogen temperature with 30 keV Si⁺ ions (to doses ≥ 10¹⁶ cm⁻²). The composition and damage of the re-implanted layer is given by RBS-C by the dashed curve in Fig. 5.4. Damage (amorphization) to the underlying silicon substrate is observed. The nitrogen concentration through the nitride region slightly

![Fig. 5.4 RBS-C spectra of a Si implanted with 30 keV N₂⁺ to dose of 1x10¹⁸ cm⁻² (solid line) and subsequent re-implanted with 30 keV Si⁻ to dose of 1x10¹⁶ cm⁻².](image-url)
Fig. 5.5 XTEM micrograph of the re-implanted sample before (a) and after (b) annealing
decreases since more silicon is now injected into this layer, but the nitride thickness remains unchanged. This suggests that the amorphous silicon nitride formed after implantation is very stable, although it contains excess nitrogen.

A bright field micrograph of the re-bombarded sample is shown in Fig. 5.5(a). A porous structure is still observed but the thickness (compared with Fig. 5.3a) has decreased to about 310 Å. The original amorphous silicon thickness is indicated by the double arrows (i.e. prior to nitrogen bombardment). The micrograph is overexposed to show the porous structure but clearly the original amorphous silicon layer has crystallized (during nitrogen bombardment), consistent with RBS. After re-bombardment with silicon, the new amorphous-crystalline interface is at 1000 Å (shown by the single arrow).

After annealing at 1000 °C for 1h in argon, the micrograph of the sample of Fig. 5.5a) is shown in Fig. 5.5(b). The thickness of the porous structure and size of the “bubbles” are now similar to that in Fig. 5.3. This suggests that re-injected Si ions may change the local nitrogen content, by redistributing the nitrogen into smaller bubbles, with an apparent reduction in the thickness of the porous structure. During heating, nitrogen migrates towards the middle of the nitride layer, re-forming large bubbles there and extending the porous structure again.

The question still remains as to what is the nature of the porous structure and how it forms? What is occurring during annealing? Before addressing these points, it is instructive to study the nitride layer formation as function of implantation parameters.

5.3.1.2 Implantation parameters: effect on nitride layer

For investigation of the effects of implantation parameters on the nitride layer, a series of implantation experiments were carried out with 30 keV N$_2^+$ implanted into crystalline or pre-amorphous silicon with different doses at different beam current (temperature). The stoichiometry and depth profiles of the nitrogen implanted layer of the samples, as obtained from RBS spectra were simulated by RUMP. Fig. 5.6 shows a RBS
random spectrum for one of the samples with a RUMP simulation. The position arrowed with the label Si$_3$N$_4$ indicates the height for a stoichiometry of Si$_3$N$_4$. The arrows with labels of Si, O and N indicate the elemental energy channel for scattering from the surface. The solid line is the RUMP simulation. It was assumed that most of the oxygen is concentrated at the surface of the silicon nitride layer. Thus, two nitrogen-containing layers were used for the simulation: one with oxygen contamination of silicon nitride at the near-surface, one without oxygen contamination between the oxygen contaminated layer and the silicon substrate. Table 5.2 shows the simulation results for stoichiometry and thickness of the nitride layer for different implantation conditions. It is found that the stoichiometry and depth of the implanted layer are not sensitive to the starting state (crystal or amorphous), but are strongly affected by the implanted dose and moderately affected by temperature.

![RBS spectrum](image)

Fig. 5.6 RBS spectrum of one implanted sample with a RUMP simulation.
Table 5.2 $N^+$ implanted into crystal and amorphous silicon: (measured stoichiometry and thickness of the implanted $Si_xN_y$ layer.

<table>
<thead>
<tr>
<th></th>
<th>Current $\mu$A</th>
<th>Temperature ($^\circ$C)</th>
<th>1st layer stoichiometry</th>
<th>1st layer thickness (Å)</th>
<th>2nd layer stoichiometry</th>
<th>2nd layer thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Crystalline</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>silicon, low dose</td>
<td>50</td>
<td>150</td>
<td>$Si_3N_{1.4}$</td>
<td>340</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(1E16 cm$^{-2}$)</td>
<td>200</td>
<td>350</td>
<td>$Si_3N_{1.2}$</td>
<td>350</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>high dose, low dose</td>
<td>50</td>
<td>150</td>
<td>$Si_3N_{6}O_{1.5}$</td>
<td>100</td>
<td>$Si_3N_{7.5}$</td>
<td>410</td>
</tr>
<tr>
<td>(1E18 cm$^{-2}$)</td>
<td>200</td>
<td>350</td>
<td>$Si_3N_{4.4}O_{0.6}$</td>
<td>70</td>
<td>$Si_3N_{5.3}$</td>
<td>430</td>
</tr>
<tr>
<td>high dose, high dose</td>
<td>500</td>
<td>600</td>
<td>$Si_3N_{4.5}O_{0.8}$</td>
<td>80</td>
<td>$Si_3N_{5.6}$</td>
<td>270</td>
</tr>
<tr>
<td><strong>Amorphous</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>silicon, low dose</td>
<td>50</td>
<td>150</td>
<td>$Si_3N_{1.1}$</td>
<td>380</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(1E16 cm$^{-2}$)</td>
<td>200</td>
<td>350</td>
<td>$Si_3N_{1.2}$</td>
<td>300</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>high dose</td>
<td>50</td>
<td>150</td>
<td>$Si_3N_{5}O_{0.5}$</td>
<td>50</td>
<td>$Si_3N_{6.5}$</td>
<td>400</td>
</tr>
<tr>
<td>(1E18 cm$^{-2}$)</td>
<td>200</td>
<td>350</td>
<td>$Si_3N_{4.5}O_{0.6}$</td>
<td>70</td>
<td>$Si_3N_{5.8}$</td>
<td>370</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>600</td>
<td>$Si_3N_{4.5}O_{1.2}$</td>
<td>200</td>
<td>$Si_3N_{2}O_{1}$</td>
<td>180</td>
</tr>
</tbody>
</table>
Chapter 5 Ion Implantation and Comparison with Ball Milling

Basically, a lower dose results in a thinner amorphous nitrogen-containing layer and low nitrogen content. For example, at 1E16 cm\(^{-2}\), the stoichiometry and depth of the implanted layer are almost independent of the beam current, implantation temperature and starting state (amorphous or crystalline) of the silicon. The layers exhibit low nitrogen content (less than 35 at\%) and a thin implanted layer (300–380 Å). It is clear that a 1E16 cm\(^{-2}\) dose results in insufficient nitrogen for stoichiometric \(\text{Si}_3\text{N}_4\) to form.

When a higher dose of 1E18 cm\(^{-2}\) was used, a thicker nitrogen layer was observed (380-500 Å). The thickness of this layer depends on the implantation temperature. A higher temperature results in a thinner nitride layer. A similar result was reported by Petruzzello et al.\(^6\), where a buried porous structure with a thickness of 1400 or 1000 Å was observed after implantation (150 keV, 1.6E18 cm\(^{-2}\)) at a temperature below 200 °C or above 800 °C, respectively. The nitrogen content is also slightly affected by implantation temperature. The Table 5.2 N\(^+\) implanted into crystal and amorphous silicon: measured stoichiometry and thickness of the implanted \(\text{Si}_x\text{N}_y\) layer. The higher the temperature, the lower the nitrogen content. This is probably due to the fact that nitrogen has more mobility in silicon or amorphous \(\text{Si}_x\text{N}_y\) at higher temperatures during implantation. Thus, in the high temperature case, nitrogen has more chance to "escape" from the nitride layer to the chamber. However, all of the samples are considerably more nitrogen-rich than is required for \(\text{Si}_3\text{N}_4\). There is also 7-14 at\% oxygen found in the higher dose cases. Oxygen content is very sensitive to implantation parameters, such as chamber vacuum and implant current. In general, a higher temperature or a longer implantation time lead to more oxygen introduced into the implanted nitrogen layer. Results seem to suggest that oxygen content does not greatly influence nitrogen content but that the implantation temperature is the more important factor for nitrogen content. For example, in the low implantation current case, higher oxygen content results in a higher nitrogen content and a thicker nitride layer. However, in the high current case, a much higher oxygen content leads to an opposite result, where low nitrogen and a thin layer are observed. The different oxygen contents probably result from
differences in the chamber vacuum, implant temperature and duration of implant. The effect of oxygen on crystallization of amorphous silicon nitride has been reported by other researchers\textsuperscript{15,16}. In a study of crystallization behavior, Edelman \textit{et al} (ref.15) found that oxygen suppresses the crystallization of stoichiometric silicon nitride. They suggested that oxygen disordered the nitride and separated the nitride from the substrate, thus preventing the orientation effect whereby crystal growth is seeded from the crystalline silicon. Olofsson \textit{et al} (ref.16) further found that the presence of oxygen in the nitride, and diffusion of oxygen to the buried interface, prevents crystallization of silicon nitride on annealing. In the present study, crystalline $\alpha$-Si$_3$N$_4$ is not found after annealing (see Fig. 5.3b), which is consistent with these reports.

\textbf{5.3.1.3 Post-implantation with Fe$^+$}

A further sample nominally implanted under the same conditions as that in Fig. 5.2 (pre-amorphized to a depth of 5000 Å and then 1E18 cm$^{-2}$ of 15 keV N$^+$ implanted at 220 μ A) was subsequently implanted with Fe$^+$ ions. In this case, 5E16 cm$^{-2}$ Fe$^+$-ions at 45 keV were implanted into the amorphous (porous) silicon nitride layer at room temperature. TEM and RBS analysis before and after annealing at 1000 °C were carried out.

Fig. 5.7 (crosses) shows RBS results of the sample after implantation. The nitrogen content and its distribution is reasonably similar to that in Fig. 5.2 shown earlier. The iron profile is a Gaussian shape and, in light of the almost unchanged nitrogen profile, sputtering of the nitride layer by the iron has not been excessive.

Fig. 5.8a shows the TEM micrograph after iron implantation. There are several interesting features: i) Partial recrystallization of amorphous silicon during nitrogen bombardment means that the implantation temperature was probably around 450 °C. ii) The surface is considerably smoother than the previous samples (Fig. 5.3a and Fig. 5.5a) and the number of bubbles seems to be smaller. This result is probably due to either the fact that
Chapter 5 Ion Implantation and Comparison with Ball Milling

Fig. 5.7 RBS spectra of the sample, previously implanted with $N^+$ and subsequently implanted with $Fe^+$ ions, before and after annealing at 1000 °C.

conditions of nitrogen bombardment gave a more uniform layer (not very porous) or that iron did cause some (sputter) modification of the nitrogen-rich layer. It is difficult to distinguish between these two possibilities at this stage without further temperature-dependent studies. iii) It is found that only a small band of bubbles is observed in the middle of the nitride layer, which is even lower than that for the rebombarded $Si^+$ case in Fig. 5.5a. This might indicate that there is some interaction between nitrogen bubbles and implanted iron, such as $N_2 + Fe \rightarrow Fe(N)$, which may take place, resulting in a reduced concentration of nitrogen bubbles.

After annealing at 1000 °C for 1h in argon, the RBS spectrum shows (Fig. 5.7 broken line) that the iron concentration mostly moves to the near-surface, with a slightly increased concentration at the interface with the silicon substrate. This suggests that most of the iron is rejected from the silicon nitride structure during annealing. The migration of iron
Fig. 5.8 XTEM micrograph of the sample, previously implanted with $N^+$ ions and subsequently implanted with $Fe^+$ ions, before (a) and after (b) annealing.
suggests that the implanted iron is only weakly bonded with the silicon nitride after implantation (as Fe(N), Fe_xN_y). The nitrogen content appears to be reduced at the near surface and this is accompanied by a significant oxygen concentration appearing at the surface of the nitride layer. This suggests that an oxidation reaction may have taken place at the surface.

The bright field micrograph of the sample annealed at 1000 °C is shown in Fig. 5.8b. There are some quite large precipitates on the surface and underneath is a well-defined amorphous layer. Below this layer is a band of defects in silicon crystal. The porous structure observed previously is not clear in this magnification. A higher magnification micrograph is shown in Fig. 5.9. A fine porous structure (single arrow), together with precipitates (possibly nitrogen bubbles) in the middle of the nitride layer, is observed. This shows that the surface precipitates (double arrow) lie above the nitride layer. Detailed microdiffraction analysis (see Fig. 5.10) shows the presence of two different iron oxides (Fe_3O_4 and Fe_2O_3) at the surface. This is consistent with the RBS data which indicated

![surface](image)

**Fig. 5.9 Higher magnification of XTEM micrograph of the sample in Fig.5.8(b).**
Chapter 5 Ion Implantation and Comparison with Ball Milling

Fig. 5.10 XTEM micrograph showing that the precipitates lie on the surface and micro diffraction pattern of surface precipitates (a) Fe$_2$O$_3$, (b) Fe$_3$O$_4$. 
layer inhibited the crystallization of amorphous silicon nitride. In the latter case, the formation of silicon-nitride-oxide during annealing also inhibited crystallization. The present results are entirely consistent with these reports.

5.3.2 SiN\textsuperscript{+} Implantation as Nitrogen Source

120 keV SiN\textsuperscript{+}-ions were implanted into silicon at liquid nitrogen temperature. The sample was previously amorphized with 125 keV Si\textsuperscript{+} ions, as indicated previously, and then Fe\textsuperscript{+}-ions were implanted at an energy of 125 keV to a dose of 5E16 cm\textsuperscript{-2} into half of the amorphized area at room temperature.

The SiN\textsuperscript{+} implanted sample without iron was analyzed by RBS after implantation using both channeling and random spectra as shown in Fig. 5.11(a). The channeling spectrum shows that the silicon signal remains at the random level beyond the silicon nitride layer until about channel 220, indicating that an amorphous silicon layer sits underneath the silicon nitride layer. The RUMP simulation shows that this amorphous silicon layer is about 3200 Å. Furthermore, the nitrogen content is slightly less than Si\textsubscript{3}N\textsubscript{4} stoichiometry (e.g. Si\textsubscript{3}N\textsubscript{3.4}), which is not a surprise since every nitrogen atom implanted is accompanied by one silicon atom at the same time. The nitrogen implant layer is about 1700 Å (based on an Si\textsubscript{3}N\textsubscript{4} density of 1.036E23 atoms·cm\textsuperscript{-3}). Comparing with the sample implanted with 40 keV N\textsuperscript{+}, to a dose of 1E18 cm\textsuperscript{-2} at a temperature of about 350 °C at Harwell, the nitride layer is 1100 Å by RUMP simulation (not shown). Although the energy is the same (40keV equivalent) in both cases, the difference in the depth of the nitride layer is a result of the following. When SiN\textsuperscript{+} is implanted, both silicon and nitrogen atoms are injected. The extra silicon atoms accumulate (since the sputtering coefficient is considerably less than 1\textsuperscript{17}) and the nitride layer is effectively thickened in comparison with the 40 keV N\textsuperscript{+} case, where only nitrogen atoms are accumulated.

For the SiN\textsuperscript{+} implantation into the sample with iron, the nitrogen and iron distributions after implantation are shown by the RBS spectra in Fig. 5.12a) (solid line). Nitrogen appears to be uniformly distributed throughout the nitride layer, very similar to
Fig. 5.11 RBS spectra of SiN implanted sample (without iron) before (a) and after (b) annealing.
Chapter 5 Ion implantation and Comparison with Ball Milling

Fig. 5.12 RBS spectra of SiN implanted sample (with iron) before (a) and after (b) annealing
Chapter 5 Ion Implantation and Comparison with Ball Milling

the case without iron. However, the iron distribution exhibits a double peak in this case where SiN' was implanted after the Fe' ions. This is to be compared with Fig. 5.7, where Fe' was implanted into an already formed silicon nitride layer and the iron distribution is Gaussian shaped. This indicates that, in the case of SiN' implantation, iron is segregated both towards the surface and the interface during SiN' implantation. Only a small amount of iron remains in the (presumably) amorphous silicon nitride layer. This suggests that the "solubility" of iron in silicon nitride is low, consistent with the results of the previous sections. The channeled spectrum (dashed line) in fig. 5.12a shows damage (an amorphous silicon layer) underneath the nitride layer. This results mainly from the pre-amorphizing 125 keV Si' implant. The total thickness of the Si,N, and a-Si is about 3000 Å using RUMP simulations (not shown).

Fig. 5.13 shows the XTEM micrograph of the above sample (with Fe') before annealing. The original amorphous-crystal interface is indicated by the double arrows at the thickness of about 3250 Å (dark contrast). The top part of this dark contrast is implanted with SiN' (and Fe'). It is not possible by this TEM micrograph to determine where is the

Fig. 5.13 XTEM micrograph of SiN' implanted sample (with iron).
nitrogen containing layer. From RBS, it is most likely that the rejected iron segregates into the amorphous silicon at the amorphous nitride-amorphous silicon interface. There is no evidence for c-Fe in the TEM micrograph and the iron is probably incorporated into the amorphous structure. No porous surface structure is observed in this micrograph. This indicates that the excess nitrogen, shown previously during implantation of N\textsuperscript{2+}, presumably results in nitrogen bubbles, and this is the cause of the porous structure.

Annealing of samples with and without iron was carried out at 1000 °C for 1h in argon. Fig. 5.11b shows the RBS spectrum of the nitrogen-only sample (pre amorphous case). The crystallization of the amorphous silicon under the silicon nitride layer is observed in the channeling spectrum. No significant change in the silicon nitride layer is observed. The RBS spectra for the sample with iron (after annealing) are shown in Fig. 5.12b (broken line). Again there is no change in the nitrogen signal after annealing. However, the deeper iron peak is sharper indicating that the iron is slightly segregated towards the nitride layer at the crystallizing interface of the underlying amorphous silicon. After annealing iron remains at the Si-Si\textsubscript{x}N\textsubscript{y} interface in the sample.

XRD analysis was carried out on the annealed samples (with and without iron), since the depth of nitride implanted layer (1700 Å) was expected to be large enough to provide some phase information. The XRD data is shown in Fig. 5.14. In the sample without iron, only a trace indication of some polycrystalline silicon is observed. There is no evidence that polycrystalline \textalpha-Si\textsubscript{3}N\textsubscript{4} is formed at this temperature (1000 °C/1h). This is consistent with the Si\textsubscript{x}N\textsubscript{y} region remaining amorphous after the 1000 °C anneal. However, in the case with iron, polycrystalline \textalpha-Si\textsubscript{3}N\textsubscript{4} is clearly observed. There is again some evidence for polycrystalline silicon as well but, there is no evidence for iron silicide formation. This suggests (as discussed later) that iron is a catalyst for crystallization of amorphous silicon nitride, consistent with the case of ball milling.

Fig. 5.15a shows a bright field XTEM micrograph of the annealed sample with iron. A uniform crystallized (polycrystalline) layer with a thickness of about 2600 Å is observed. As indicated in the corresponding RBS spectrum (Fig. 5.12b), the iron migrates towards the
annealed 1000 °C/1h

Fig. 5.14 XRD of SiN⁺ implanted samples with and without iron after annealing at 1000 °C

The nitride layer during annealing, as the underlying a-Si layer epitaxially crystallizes. An XTEM sample was also prepared and examined. A selected area diffraction pattern taken from the nitride layer is shown in Fig. 5.15c. Fig. 5.15c shows two important features. Firstly, the arcs corresponding to the α-Si₃N₄ reflections clearly indicate the presence of polycrystalline α-Si₃N₄. Secondly, the sharp rings corresponding to silicon spacings arising from the presence of polycrystalline silicon. The presence of polycrystalline silicon is expected as the nitrogen content is lower than is required for stoichiometric Si₃N₄. A dark field image selecting diffraction arising from a silicon nitride spot (101) was recorded and is shown in Fig. 5.15b. In this figure, we note the presence of moiré fringes arising from α-Si₃N₄ polycrystalline within 1700 Å of the near surface region. Part of the underlying a-Si layer has crystallized epitaxially and a transition region, containing silicon twins and other defects (dark band), has recrystallized poorly. A EDX analysis taken at a precipitate near the nitride layer-silicon interface shows a strong iron peak, see Fig. 5.16, indicating the precipitate is iron or iron silicide which is consistent with RBS analysis. However, the
Fig. 5.15 XTEM micrographs of SiN$^+$ implanted into Si (Fe) and subsequent annealing annealing at 1000 °C, (a) BFI and (b) DFI.
Chapter 5 Ion Implantation and Comparison with Ball Milling

Fig. 5.15c SADP of Si\textsuperscript{+} implanted sample (with iron) after annealing at 1000 °C shows the polycrystalline a-Si\textsubscript{3}N\textsubscript{4} and Si.

selected area diffraction pattern did not reveal any diffraction related to an iron or iron silicide phase. More detailed TEM observation needs to be carried out.

This ion implantation study has established interesting similarities both in the formation of the amorphous Si-N phase and the crystallization behavior between the two diverse non-equilibrium process, namely mechanochemical reaction and ion implantation, both at room temperature. Detailed comparison is given as following.
5.3.3 Comparison between Ion Implantation and Ball Milling

Ball milling and ion implantation are both non-equilibrium processes. Previous studies show crystalline $\alpha$-$\text{Si}_3\text{N}_4$ can be obtained by both processes and subsequent annealing. Comparison of ball milling and ion implantation similarities and differences are shown in Table 5.3. For example, an initial amorphous silicon nitride phase forms after both processes. In ball milling, the amorphous silicon nitride contains hydrogen and iron, contamination from the milling atmosphere ($\text{NH}_3$) and milling media (stainless steel), respectively. The nitrogen content in the amorphous nitride phase increases up to $\text{Si}_3\text{N}_4$ stoichiometry as the milling process progresses. The nitrogen adsorption during milling is enhanced as the temperature is increased. In the case of ion implantation, the amorphous silicon nitride contains a porous structure since excess nitrogen can not diffuse out of the amorphous $\text{Si}_x\text{N}_y$ and forms nitrogen bubbles. The thickness and nitrogen content of the porous nitride layer decrease as implantation temperature increases. Annealing the amorphous nitride obtained by both ball milling and ion implantation up to 1000 °C, result in crystallization of the amorphous nitride only when iron is present and oxygen is absent in
### Table 5.3 Comparison of ball milling and ion implantation

<table>
<thead>
<tr>
<th></th>
<th>Ball Milling</th>
<th>Ion Implantation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Phase(s) Formed</td>
<td>amorphous Si$_x$N$_y$H$_z$(Fe)</td>
<td>amorphous/porous Si$_x$N$_y$</td>
</tr>
<tr>
<td>Nitrogen Content</td>
<td>up to Si$_3$N$_4$ stoichiometry, Fe present</td>
<td>Can exceed Si$_3$N$_4$ nitrogen content</td>
</tr>
<tr>
<td>Milling/Implantation</td>
<td>fast nitrogen adsorption as temperature increases, but</td>
<td>thinner nitride layer and less nitrogen content in the</td>
</tr>
<tr>
<td>Temperature</td>
<td>nitrogen content never greater than Si$_3$N$_4$</td>
<td>implanted layer as temperature increases</td>
</tr>
<tr>
<td>Annealing</td>
<td>amorphous Si$_3$N$_4$ crystallizes to $\alpha$-Si$_3$N$_4$ at 800-1000 °C (Fe present)</td>
<td>amorphous Si$_3$N$_4$ crystallizes to $\alpha$-Si$_3$N$_4$ at 1000 °C/1h (Fe present)</td>
</tr>
<tr>
<td>Role of Iron</td>
<td>Iron enhances nitrogen adsorption during milling and the crystallization during annealing</td>
<td>Iron enhances the crystallization during annealing</td>
</tr>
<tr>
<td>Role of Oxygen</td>
<td>Oxygen inhibits nitrogen adsorption during milling and crystallization during annealing</td>
<td>Oxygen inhibits crystallization during annealing</td>
</tr>
</tbody>
</table>

The role of iron in ball milling was previously suggested to be the following. Free iron is a catalyst for nitrogen adsorption during milling and also for crystallization of the amorphous silicon nitride during annealing. In a typical example, for 1 g of silicon milled in ammonia for 168h, about 9 at% free iron ($\alpha$-Fe, $\gamma$-Fe) was found after milling. High resolution TEM observation showed small iron precipitates were distributed in the amorphous Si$_x$N$_y$H$_z$ matrix (Fig. 3.23). After subsequent annealing up to 1100 °C in argon, crystalline $\alpha$-Si$_3$N$_4$ and iron silicide Fe$_3$Si phases were observed by XRD. A typical RBS spectrum of a ball milled sample after annealing to form $\alpha$-Si$_3$N$_4$ and iron silicide (Fe$_3$Si) is shown in Fig. 5.17a. This is a case of 1 g silicon milled in ammonia for 168h and then annealed at 1000 °C. Note the small oxygen signal (less than 5 at%) but the strong iron.
Fig. 5.17 RBS spectra of a typical ball milled (a) and ion implanted (b) samples after annealing at 1000 °C.
Chapter 5 Ion Implantation and Comparison with Ball Milling

signal. HRTEM observations show that well-defined crystalline $\alpha$-Si$_3$N$_4$ structures and iron silicide (Fe$_3$Si) precipitates exist in different areas (Fig. 3.24). In the case of implantation, polycrystalline $\alpha$-Si$_3$N$_4$ is only observed in a sample containing iron after annealing to 1000 °C: no polycrystalline $\alpha$-Si$_3$N$_4$ is found in the sample without iron as described previously (Figs. 5.14 and Fig. 5.15). This strongly supports the suggestion in the ball milling case that the iron plays a catalytic role in the crystallization of amorphous silicon nitride. The iron is also rejected from silicon nitride and segregated at the interface (to presumably form FeSi$_2$) between a silicon nitride layer and the silicon substrate as shown by the RBS spectrum in Fig. 5.17(b) and TEM observation in Fig. 5.15. This iron segregation is consistent with the ball milling case.

The role of oxygen in ball milling is described in a previous Chapter (3.5.2.3). Crystalline $\alpha$-Si$_3$N$_4$ formation occurs after annealing up to 1000 °C in argon, but not in air. This suggests that oxygen inhibits the crystallization of amorphous silicon nitride during annealing. Another example of the effect of oxygen contamination is that of silicon milled in an ammonia atmosphere which contained some air due to insufficient purging of the mill. The composition by RBS is shown in Fig. 5.18(a). About 28 at% oxygen and only about 3 at% nitrogen are found in this sample. No amorphous silicon nitride phase was found after milling by previous XRD analysis (Fig. 3.19). It was suggested that the existence of oxygen in the milling atmosphere may 'poison' the surface of silicon and result in no nitrogen adsorption. Without nitrogen it seemed that the formation of an amorphous phase was difficult. In the case of ion implantation, a porous amorphous silicon nitride layer is obtained at the surface of silicon for some of the samples, for example, the sample shown in Fig. 5.3. As described before, this porous structure is easily contaminated with oxygen during implantation and annealing. Fig. 5.18b shows the RBS spectrum of such a sample after annealing. A strong oxygen peak is observed in this sample. XTEM observation shows that no polycrystalline $\alpha$-Si$_3$N$_4$ is found even if iron is presents as a catalyst. This suggests that the presence of oxygen in the sample inhibits formation of a uniform amorphous silicon nitride layer during implantation and suppresses crystallization during annealing.
Fig. 5.18 RBS spectra of the typical ball milled (a) and ion implanted samples show the effects of Oxygen.
This is very consistent with the ball milling case.

Taken together, both ball milling and ion implantation have very similar behavior for the formation of silicon nitride. First, an amorphous silicon nitride is formed in both cases, which crystallizes upon annealing. Second, iron is a catalyst for crystallization of amorphous silicon nitride, as observed in both cases. Third, the presence of oxygen inhibits formation of amorphous silicon nitride and also suppresses its crystallization upon annealing.

5.3.4 Thermodynamics of Ball Milling and Ion Implantation

Fig. 5.19 shows a schematic illustration of possible free energy changes during ball milling and ion implantation and how the free energy further changes on annealing. The left side of the diagram is a further development of the diagram present in Fig. 3.27. It was assumed that mechanical damage introduces enormous damage (defects and strain) and new surfaces, which increase the free energy of the milling system as shown in Fig. 5.19. The adsorption of hydrogen and nitrogen, as well as the intimate mixing of atomic nitrogen and hydrogen with silicon lead a further increase in strain energy. This continual increase in free energy of the system eventually provides a strong driving force for a mechanochemical reaction during milling to form a lower free energy amorphous silicon nitride ($\text{Si}_3\text{N}_4\text{H}_x$) phase with a stoichiometry close to $\text{Si}_3\text{N}_4$. This amorphous silicon nitride crystallizes to $\alpha$-$\text{Si}_3\text{N}_4$ upon heating beyond 850 °C when iron is present. The right side of Fig. 5.19 shows the free energy change during implantation and annealing. The structural damage to silicon resulting from nitrogen implantation also leads to an increase in the free energy and finally the formation of an amorphous silicon nitride phase. The crystallization of the amorphous silicon nitride also takes place during annealing up to 1000 °C when iron is a catalyst.

Comparing the formation of silicon nitride induced by ball milling and ion implantation, both techniques are non-equilibrium processes. However, the nitrogen accumulation processes are different in both cases. In the case of ion implantation, nitrogen ions are injected to a certain depth in silicon and the nitrogen content in the nitride layer...
Chapter 5: Ion Implantation and Comparison with Ball Milling

Fig. 5.19. Schematic diagram of the free energy comparison between ball milling and ion implantation.
depends on the implantation dose. However, excess nitrogen can result in the formation of nitrogen bubbles in the silicon nitride layer, due to the low diffusivity of nitrogen in the nitrogen-rich (amorphous) silicon. During ball milling, nitrogen adsorption is strongly dependent on the surface area and available silicon bonds, the state (molecular or atomic) of nitrogen. Iron would appear to play a role in decomposition of ammonia to give atomic nitrogen for bonding to free silicon at surfaces. It is known that the chemisorption only can take place when the surface of an adsorbent has unsaturated valence forces\textsuperscript{18}. That is, when all silicon bonds are saturated with atomic nitrogen, there is no longer a driving force for nitrogen adsorption. Thus, when silicon and nitrogen are intimately mixed to give Si\textsubscript{3}N\textsubscript{4}, all silicon bonds are saturated and no further nitrogen adsorption occurs. Therefore no excess nitrogen occurs in the ball milling case. Finally, incorporation of nitrogen into a silicon structure either by ball milling or ion implantation results in the formation of amorphous silicon nitride. For ion implantation, amorphous silicon is first created by ion irradiation of nitrogen and nitrogen accumulated in this phase with continued bombardment. For ball milling, silicon is only amorphized when the nitrogen content exceeds a critical value: nitrogen appears to stabilize an amorphous phase in this case.

5.4. Conclusions

By combining RBS, XTEM and XRD characterization, the formation of a silicon nitride layer by ion implantation has been studied. The results show that the structure of the silicon nitride layer is strongly affected by implantation conditions and subsequent annealing, such as implant dose, temperature and target chamber vacuum. For example, excess nitrogen implantation results in a porous nitride layer, which contains a large amount of excess nitrogen in the form of gas bubbles. Implantation at a high temperature results in a thinner silicon nitride layer. Lower chamber vacuum leads to more oxygen contamination in the sample. It is also found that oxygen and iron play very important roles in formation of polycrystalline $\alpha$-Si\textsubscript{3}N\textsubscript{4}, during implantation and subsequent annealing. The presence of oxygen during implantation and annealing inhibits the formation of a uniform
amorphous silicon nitride layer and suppresses its crystallization upon annealing. Iron is a catalyst for crystallization of amorphous silicon nitride during annealing.

Comparing the behavior of formation of silicon nitride induced by ball milling and ion implantation, it is found that these non-equilibrium processes are remarkably similar. For instance, an amorphous silicon nitride phase is formed in both cases and the amorphous phase crystallizes at temperatures up to 1000 °C only when iron is present in the sample. The presence of oxygen inhibits the ultimate formation of crystalline silicon nitride in both cases. Therefore, the study of ion implantation has been very useful for helping to understand the ball milling processes.
References

Chapter 6 Conclusions

6.1 Summary and Conclusions

In this study, the synthesis of both $\alpha$-Si$_3$N$_4$ and the composites of Si$_3$N$_4$-SiC by mechanochemistry and subsequent annealing have been demonstrated and the mechanisms for their formation studied in some detail. The most significant outcomes of this thesis are:

1) the ball milling and annealing conditions for optimum formation of $\alpha$-Si$_3$N$_4$ and Si$_3$N$_4$-SiC composite have been established for the first time; and
2) the complex mechanochemical and annealing processes associated with $\alpha$-Si$_3$N$_4$ and Si$_3$N$_4$-SiC composites have been characterized in detail, also for the first time. In particular, amorphous Si-N and Si-C-N phases have been identified after milling and the crystallization processes examined during annealing. Considerable insight has been obtained into the various roles of hydrogen, oxygen and especially iron in catalyzing, enhancing or, alternatively, inhibiting $\alpha$-Si$_3$N$_4$ or composite formation. Furthermore, the similarities (and differences) between two diverse, non-equilibrium processes for low temperature compound formation, namely ball milling and ion implantation, have been determined. Specific findings of this thesis are summarized below.

For Si-NH$_3$ and Si-$N_2$ systems, the adsorption of nitrogen and formation of an amorphous silicon nitride phase occur during milling in ammonia, but not in nitrogen gas. Detailed investigations show that the formation of amorphous silicon nitride is strongly affected by hydrogen and iron contamination and milling conditions. For instance, hydrogen (dissociated from NH$_3$) plays a significant role in the milling processes: it appears to enhance fragmentation of iron from the surfaces of milling media (cell wall and balls), presumably by embrittlement. Hydrogen may also embrittle the silicon particles to enhance
fracturing and the creation of new surfaces: a crucial factor for nitrogen adsorption and ultimately silicon amorphization. The results also show that iron contamination plays an important catalytic role during both milling and annealing. It enhances nitrogen adsorption, dissociation into atomic nitrogen and formation of amorphous silicon nitride during milling. It also catalyses crystallization of amorphous silicon nitride during annealing. The effect of oxygen during milling is also crucial: it may "poison" the surfaces of silicon particles and create a barrier to nitrogen gas adsorption and further reaction, if sufficient oxygen is present during milling. Moreover, the effects of milling conditions, such as temperature (room temperature and 100 °C) and energy (shearing and impact), were studied. The formation of amorphous silicon nitride is greatly enhanced by milling at 100 °C compared with room temperature. In terms of milling energy, it was found that only a shearing force (low energy milling mode) was efficient in producing amorphous silicon nitride during milling.

For the Si-C-N$_2$ system, the following mechanochemical reactions appear to take place during milling:

\[ \text{Si} + \text{C} \rightarrow \text{SiC}, \text{ during the early stages of milling, and} \]

\[ \text{SiC} + \text{N} \rightarrow \text{amorphous Si-C-N}, \text{ as high nitrogen content is incorporated during the latter stages of milling.} \]

The amorphous Si-C-N phase crystallizes to a composite of Si$_3$N$_4$-SiC after heating up to 1000 °C. The results show that nitrogen adsorption is a key factor for formation of the amorphous (Si-C-N) phase. Moreover, nitrogen adsorption is strongly influenced by iron contamination and iron phases formed during milling (free iron: α-Fe and γ-Fe, or iron silicide: Fe$_x$Si$_y$). The free iron appears to act as a catalyst for adsorption and dissociation of nitrogen gas into atomic nitrogen. This allows nitrogen to be incorporated into silicon
Chapter 6 Conclusions

carbide leading to the formation of an amorphous (Si-C-N) phase. For example, the formation of an amorphous (S-N-C) phase after milling and Si₃N₄-SiC composite formation after annealing only occur when free iron is present in the as-milled powder. However, no such phases are observed after the loss of free iron, when iron silicide is formed. Detailed investigations reveal that the iron phases formed during milling relate to the starting carbon content and the availability of free silicon. A role of carbon is to inhibit the reaction between free silicon and iron contamination by the formation of SiC, which therefore, restrains the formation of iron silicide. A threshold carbon content is observed, above which nitrogen adsorption and formation of amorphous Si-C-N occur during milling. Below the threshold, free iron reacts with excess silicon forming iron silicide, which, in turn, inhibits nitrogen adsorption. The starting carbon phases are also critical in determining the end result of milling. For instance, when SiC and free silicon are milled in nitrogen gas, there is no nitrogen adsorption during milling even though the carbon content is higher than threshold. This result can be interpreted in terms of the fact that carbon in the SiC does not prevent the reaction between free silicon and iron contamination.

The results of ion implantation of nitrogen into silicon gave considerable insight into the ball milling process. When nitrogen was implanted in excess of the Si₃N₄ stoichiometry, an amorphous, porous structure was observed which did not crystallize during annealing at 1000 °C. Even when iron was implanted into this porous structure, it did not crystallize at 1000 °C. However, there was a high oxygen content in the amorphous phase and it was assumed that oxygen inhibited crystallization. In contrast, when nitrogen was implanted such that its concentration was less than that for stoichiometric Si₃N₄, a smooth, amorphous Si-N layer was obtained. When Fe⁺ ions were also implanted into this amorphous silicon nitride layer, polycrystalline α-Si₃N₄ was obtained after annealing at
1000 °C. However, without iron, the Si-N amorphous layer did not crystallize at 1000 °C, consistent with previous work.

Comparing the results of ball milling and ion implantation, there are great similarities between these two non-equilibrium processes. An amorphous silicon nitride phase is formed after both ball milling and ion implantation. Iron is a catalyst for crystallization of amorphous silicon nitride and reduces the crystallization temperature during annealing. The contamination of both ball milled Si-N phases and ion implanted Si-N layers with oxygen inhibits crystallization of the amorphous phase during annealing. The main difference between ball milling and ion implantation for silicon nitride formation relates to the way nitrogen is introduced into silicon. The former process is limited by nitrogen adsorption and dissociation, and the presence of iron was an essential catalyst for the process. Ultimately the amount of nitrogen in the amorphous Si-N phase never exceeded Si$_3$N$_4$ stoichiometry, presumably as a result of saturation of silicon dangling bonds. However, the implantation of nitrogen to form amorphous Si-N did not require the presence of iron, and nitrogen could be accommodated in excess of Si$_3$N$_4$ stoichiometry, resulting in gas bubbles and a porous structure.

Overall, this study provided a great deal of insight not only into mechanochemical processing for the formation of silicon nitride, silicon carbide and their composites, but also into general processes of compound formation occurring during ball milling of elemental powders with gases. For example, species and conditions, which enhance or inhibit gas adsorption and chemical reaction have been identified. Comparing ball milling and ion implantation has uncovered important similarities between both non-equilibrium processes for the formation of amorphous silicon nitride and its crystallization during annealing. In particular, this comparison has confirmed the role of iron in lowering the crystallization temperature for ball milled powders.
6.2 Future Work

Based on the findings of this thesis, further research in the following areas may prove fruitful.

1) It was impossible to eliminate iron contamination from our milling arrangement. The use of ceramic mills could eliminate this problem and allow the milling of silicon in ammonia to be studied with and without iron as a catalyst. Without iron it may not be possible to adsorb ammonia and form atomic nitrogen and thus “clean” milling experiments would clarify this issue. In addition, other possible catalysts could be examined such as transition metals, titanium and chromium.

2) There is an opportunity to further examine the formation of iron silicides during milling and annealing. This could best be achieved by milling iron and silicon powders (in vacuum) for a range of compositions, followed by annealing. Such studies may add the interpretation of the phase transformations that iron undergoes when milling silicon in ammonia or silicon and carbon powders in nitrogen gas.

3) Ion implantation could also be used to form SiC and Si$_3$N$_4$-SiC composites for comparison with ball milling. For example, formation of the nanocrystalline SiC phase under ball milling (and its annealing behavior) could be compared with SiC phases (amorphous or crystalline) formed by implantation at a range of temperatures. “Cold” ball milling (at liquid nitrogen temperature, for example) may lead to amorphous SiC or, alternatively, limit SiC formation. Such experiments may provide further insight into the ball milling process.

4) Preliminary leaching experiments in this thesis indicated that it may be possible to remove iron completely from α-Si$_3$N$_4$ powders after milling and annealing. Further work needs to be done in this area to establish the “purity” of α-Si$_3$N$_4$ powders that can be
Chapter 6 Conclusions

5) From a practical point of view, it would be important to study the consolidation of ball milled Si$_3$N$_4$ powders into bulk material. Thus, a range of pressing and sintering or hot pressing experiments would be needed to establish the consolidation conditions and then the properties of the bulk Si$_3$N$_4$ measured. Because the grain size (and particle size) of ball milled and annealed powders is in the nanometer scale, it may be that lower sintering or hot pressing conditions are required for ball milled powders compared with $\alpha$-Si$_3$N$_4$ powders obtained from more conventional preparation methods.