CHARACTERIZATION OF AMORPHOUS SILICON CARBIDE AND SILICON CARBONITRIDE THIN FILMS SYNTHESIZED BY POLYMER-SOURCE CHEMICAL VAPOR DEPOSITION

Mechanical Structural and Metal-Interface Properties

by

YOUSEF ODEH AWAD

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CARCTÉRISATION DE COUCHE MINCES DE CARBURE DE SILICIUM ET DE CARBONITRURE DE SILICIUM DÉPOSER PAR UN PROCESSUS CHIMIQUE DE POLYMÈRE EN PHASE GAZEUSE

les propriétés mécaniques de la structure et les propriétés du métal au niveau de l’interface

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Mechanical Structural and Metal-Interface Properties

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Yousef AWAD

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YOUSEF ODEH AWAD

Approved:

Advisor

Date

Committee Member

Date

Committee Member

Date

Committee Member

Date

Committee Member

Date
ABSTRACT

Amorphous silicon carbide (a-SiC) and silicon carbonitride thin films have been deposited onto a variety of substrates by Polymer-Source Chemical Vapor Deposition (PS-CVD). The interfacial interaction between the a-SiC films and several substrates including silicon, SiO$_2$, Si$_3$N$_4$, Cr, Ti and refractory metal-coated silicon has been studied. The effect of thermal annealing on the structural and mechanical properties of the prepared films has been discussed in detail. The composition and bonding states are uniquely characterized with respect to the nitrogen atomic percentage introduced into the a-SiCN:H films. Capacitance-voltage (C-V) measurements were systematically used to evaluate the impurity level of the deposited a-SiC films. The chemical bonding of the films was systematically examined by means of Fourier transform infrared spectroscopy (FTIR). In addition, elastic recoil detection (ERD) and X-ray photoelectron spectroscopy (XPS) techniques were used to determine the elemental composition of the films and of their interface with substrates, while X-ray reflectivity measurements (XRR) were used to account for the film density. Spectral deconvolution was used to extract the individual components of the FTIR and XPS spectra. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were also employed to characterize the surface morphology of the films. In addition, their mechanical properties [(hardness ($H$) and Young’s modulus ($E$))] were investigated by using the nanoindentation technique.
The impurity levels of the a-SiC films were found to be clearly correlated with the nature of the underlying substrates. The Pt-Rh and TiN-coated Si substrates were shown to lead to the lowest impurity level (\(\sim 1 \times 10^{13} \text{ cm}^{-3}\)) in the PS-CVD grown a-SiC films, while Cr and Ti-coated Si substrates induced much higher impurity concentrations. Such high impurity levels were shown to be a consequence of a strong metallic diffusion of the metallic species (Cr or Ti). In contrast, no diffusion was observed at the interface of a-SiC with either Pt-Rh or TiN. Our results pinpointed TiN-coated Si as the electrode material of choice that satisfied best all criteria required for the integration of a-SiC into opto-electronic devices. FTIR measurements revealed that not only the intensity of a-SiC absorption band linearly increased, but also its position is found to shift to a higher wave number as a result of annealing. In addition, the bond density of Si–C is found to increase from \((101.6-224.5) \times 10^{21} \text{ bond cm}^{-3}\) accompanied by a decrease of Si–H bond density from \((2.58-0.46) \times 10^{21} \text{ bond cm}^{-3}\) as a result of increasing the annealing temperature \(T_a\) from 750 to 1200 °C. Annealing-induced film densification is confirmed by the XRR measurements, as the a-SiC film density is found to increase from 2.36 to \(\sim 2.75 \text{ g/cm}^3\) when \(T_a\) is raised from 750 to 1200 °C. In addition, as annealing temperature \(T_a\) is increased from 750 to 1200 °C, both hardness and Young’s modulus are found to increase from 15.5 to 17.6 GPa and 155 to 178 GPa, respectively. On the microstructural level, the increase incorporation of N in the a-SiCN:H films is found not only to lead to C atoms substitution by N atoms in the local Si–C–N environment but also to the formation of a complex structure between Si, C and N. For instance, the FTIR spectra show a remarkable drop in the intensity of Si–C vibration accompanied by the formation of
further bonds including Si–N, C–N, C=N, C≡N and N–H with increasing NH₃/Ar ratio. Moreover, the XPS spectra showed the existence of different chemical bonds in the a-SiCN:H films such as Si–C, Si–N, C–N, C≡N and C=C. Both FTIR and XPS data demonstrate that the chemical bonding in the amorphous matrix is more complicated than a collection of single Si–C, Si–N, or Si–H bonds. Furthermore, the increase incorporation of N in the a-SiCN:H films resulted in an increase of the average Rₘₐₜ surface roughness from 4 to 12 nm. Moreover, the films became porous with pore size and density increase as a result of increasing N at.%. Ultimately, both H and E of the a-SiCN:H films were found to be sensitive to their N content, as they decreased (from ~17 GPa and 160 GPa to ~13 GPa and 136 GPa, respectively) when the N content was increased from 0 to 27 at.%. The formation of Si–N, Si–H, and N–H bonds at the detriment of the more stiffer Si–C bonds are thought to account for the observed lowering of the mechanical properties of the a-SiCN:H films such as their N content increased. Our results confirmed the previously-established constant-plus-linear correlation between the mechanical properties of the a-SiC films and their bond densities.
La technique de déposition chimique en phase vapeur utilisant un polymère comme source, a été utilisée pour déposer des couches minces de carbure de silicium (a-SiC) et de carbonitrure de silicium sur différents types de substrats. Ceci a permis d'étudier les interactions, au niveau de l'interface, du carbure de silicium et des différents matériaux utilisés comme substrat tels que le silicium (Si), l’oxyde de silicium (SiO₂), le nitrure de silicium (Si₃N₄), le chrome (Cr), le titane (Ti) et d'autres matériaux réfractaire qui étaient déposés sur le silicium. L’effet du recuit thermique sur les propriétés mécaniques et la structure des couches déposées, a été étudié en détail. Une attention particulière a été accordée à la caractérisation de la composition et des liaisons atomiques de ces couches, en fonction du pourcentage d’atomes d’azote introduit dans le a-SiCN:H. Des mesures expérimentales capacité-voltage ont été utilisées systématiquement pour évaluer le niveau d’impureté des couches du a-SiC déposées. Les liens atomiques chimiques de ces dernières ont été examinés à l’aide de la spectroscopie infrarouge à transformée Fourier (FTIR). En plus, les techniques de détection de la relaxation élastique (ERD) et la spectroscopie des photoélectrons de rayons X (XPS) ont été utilisées pour déterminer la composition élémentaire des couches et de l’interface couche-substrat, alors que la réfraction de rayons X (XRR) a été utilisée pour déterminer la densité des couches. L’interprétation spectrale a été utilisée pour déterminer les différents composants du
matériau à partir des données du FTIR et XPS. Un microscope électronique à balayage (SEM) et un microscope à force atomique (AFM) ont aussi été utilisés pour caractériser la morphologie de la surface des couches. D’un autre côté, leurs propriétés mécaniques (dureté (H) et module de Young (E)) ont été étudiées en utilisant la technique de nanoindentation.

Les niveaux d’impuretés des couches du a-SiC ont paru clairement corrélés avec la nature du substrat utilisé. Les substrats constitués de Pt-Rh et de TiN déposés sur le Si démontrent le plus bas niveau d’impuretés $1 \times 10^{13}$ cm$^{-3}$, alors que ceux obtenus par du Cr et du Ti déposés sur le Si donnent des concentrations d’impuretés beaucoup plus grandes. Ceci s’explique par la forte diffusion des éléments métalliques (Cr ou Ti), ce qui n’est pas le cas du Pt-Rh ou TiN. Ainsi, nos résultats démontrent que ces matériaux constituent la solution de choix qui satisferait le mieux les critères d’utilisation du a-SiC pour les composants optoélectroniques. Les mesures FTIR ont révélé que le recuit n’augmente pas seulement l’intensité de la bande d’absorption du a-SiC linéairement, mais aussi il déplace sa position spectrale vers un ordre plus grand. En plus, en augmentant la température du recuit ($T_a$) de 750 à 1200 °C, la densité des liaisons Si–C augmente de $101.6 \times 10^{21}$ à $224.5 \times 10^{21}$ bond·cm$^{-3}$ et la densité des liaisons Si–H diminue de $2.58 \times 10^{21}$ à $0.46 \times 10^{21}$ bond·cm$^{-3}$. La densification des couches résultante du recuit a été confirmée par les mesures XRR qui ont montré que la densité du a-SiC a augmenté de $2.36$ à $2.75$ g/cm$^3$ lorsque la température ($T_a$) a été augmentée de 750 à 1200 °C. D’un autre côté, cette augmentation de température résulte en une augmentation de la dureté et du module de Young de 15.5 à 17.6 GPa et de 155 à 178 GPa respectivement. Au niveau
microstructure, l'augmentation de la quantité d'azote incorporée dans la couche du a-SiCN:H n'a pas seulement permis la substitution des atomes C par des atomes N dans l'environnement immédiat du Si–C–N, mais aussi la formation d'une structure complexe entre Si, C et N. Pour l'instant, les spectres FTIR démontrent une chute remarquable de l'intensité de vibration du Si–C accompagnée par d'autres liaisons telles que Si–N, C–N, C=N, C≡N et N–H avec une augmentation du rapport NH₃/Ar. En plus, les spectres du XPS montrent l'existence de différentes liaisons chimiques dans les couches du a-SiCN:H telles que Si–C, Si–N, C–N, C=N et C≡C. Les données obtenues par la FTIR et la XPS démontrent que les liaisons chimiques dans la matrice amorphe sont plus compliquées qu'une collection de liaisons simples Si–C, Si–N ou Si–H. D'un autre côté, l'augmentation de la quantité d'azote incorporée dans les couches du a-SiCN:H provoque une augmentation de la rugosité moyenne de la surface (Rₘₚ) de 4 à 12 nm. Aussi, les couches deviennent poreuses avec des ports de plus en plus grands et de plus en plus denses. En somme, les paramètres H et E des couches du a-SiCN:H paraissent sensitifs à la quantité d'azote puisqu'ils diminuent de 17 ou 160 GPa à 13 ou 136 GPa respectivement, quand la quantité d'azote est augmentée de 0 à 27 at.%. La formation des liaisons Si–N, Si–H et N–H ay détriment de plus fortes liaisons Si–C semble intervenir dans la diminution des propriétés mécaniques des couches du a-SiCN:H suite à une augmentation de la quantité d'azote. Nos résultats confirment la corrélation constante et linéaire, déjà établie, entre les propriétés mécaniques des couches du a-SiC et leurs densités de liaisons.
PUBLICATIONS ARISING FROM THIS THESIS

**Paper I:** Thermally induced interfacial reactions between various metal substrates and a-SiC thin films deposited by a polymer-source chemical vapor deposition

Submitted to Journal of Materials Chemistry and Physics (Feb. 2006).

**Paper II:** Effect of thermal annealing on the structural and mechanical properties of amorphous silicon carbide films prepared by polymer-source chemical vapor deposition


**Paper III:** Structural and mechanical properties of amorphous silicon carbonitride films prepared by polymer-source chemical vapor deposition


**Paper IV:** Silicon carbon nitride films prepared by polymer-source chemical vapor deposition technique

(To be submitted to Journal of Applied Physics)
CONFERENCE PRESENTATIONS


2. **Y. Awad** "Investigation of interaction and adhesion between metallic substrates and a-SiC thin films deposited by polymeric-source chemical vapor deposition". An oral presentation at Symposium Annuel de Chimie Inorganique au Quebec (SACIQ), Lennoxville, Quebec, Canada (August 9-11, 2005).


STATEMENT OF ORIGINAL AUTHORSHIP

I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, the work in this thesis contains no material previously published or written by another person nor material which to a substantial extent has been accepted for the award of any other degree or diploma, except where due acknowledgement has been made in the text. I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all sources of information and literature used are indicated in the thesis.

Signature of candidate:

Name: Yousef AWAD

Date:

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LIST OF ABBREVIATIONS AND SYMBOLS

1. AFM: Atomic Force Microscopy
2. C-V: Capacitance-Voltage
3. CVD: Chemical Vapor Deposition
4. ECR-CVD: Electron Cyclotron Resonance Chemical Vapour Deposition
5. ERD: Elastic Recoil Detection
6. HBT: Heterojunction Bipolar Transistor
7. I-V: Current-Voltage
8. IR: Infrared
9. FTIR: Fourier Transform Infrared Spectroscopy
10. LED: Light Emitting Diodes
11. LPCVD: Low Pressure Chemical Vapour Deposition
12. MEMS: Micro Electro Mechanical Systems
13. MIM: Metal Insulator Metal
14. PA-CVD: Plasma Assisted-Chemical Vapor Deposition
15. PDMS: Poly(dimethylsilane)
16. PECVD: Plasma Enhanced Chemical Vapor Deposition
17. PID: Proportional Integral Derivative
18. PLD: Pulsed Laser Deposition
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<td>19.</td>
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<td>RF: Radio Frequency</td>
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<td>21.</td>
<td>$R_{\text{rms}}$: Root Mean Square Roughness</td>
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<td>22.</td>
<td>SEM: Scanning Electron Microscopy</td>
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<td>23.</td>
<td>UHP: Ultra High Purity</td>
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<td>24.</td>
<td>XPS: X-Ray Photoelectron Spectroscopy</td>
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<tr>
<td>25.</td>
<td>XRR: X-Ray Reflectivity</td>
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<td>26.</td>
<td>$\Phi_B$: Schottky Barrier Height</td>
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CHAPTER 1

INTRODUCTION

Amorphous silicon carbide (a-SiC) thin films continue to attract considerable attention because they are highly promising materials for a variety of applications, spanning from passive coatings for very harsh environments to active opto-electronic devices. The wide range of applications of a-SiC is due to the unique combination of excellent properties, such as the wide band gap,\(^1\) high breakdown electric field,\(^2\) unprecedented mechanical properties\(^3\) and chemical inertness (due to the covalent Si–C bonding energies). Indeed, a-SiC films have been extensively investigated for applications such as optoelectronics devices,\(^4\) solar cells,\(^5\) photo transistors,\(^6\) light emitting diodes,\(^7\) color sensors,\(^8\) photo modulator devices\(^9\) and flat-screen full color displays.\(^9\)

1.1. Description of the Research Problem Investigated

The objective of the work presented in this thesis is to assess the a-SiC thin films produced by the newly developed polymer source chemical vapor deposition (PS-CVD) technique.\(^10\) The developed technique is expected to be a potential substitution to the highly toxic conventional chemical vapor deposition (CVD) and to the solvent based processes for SiC thin films deposition. The focus is put here on understanding the fundamental mechanisms and composition-structure functional relationships of the PS-
CVD prepared a-SiC films for electronic devices and various coating applications capable of sustaining harsh environment. The investigations in this thesis, firstly, focused on studying the stability of the PS-CVD a-SiC-metal interface as a function of targeted application of a prime. Secondly, the effect of thermal annealing on the mechanical (hardness, Young's modulus and density) and structural properties, as well as the surface morphology (roughness, dense or porous surface films) of the PS-CVD a-SiC thin films has been studied in detail. Thirdly, special focus is put on the induced modifications in the mechanical properties of nitrogenated a-SiC:H films (a-SiCN:H). A correlation between the mechanical properties and structural configurations of the a-SiCN:H films is established. Forth, a detailed analysis of the structural, bonding configuration and surface morphology of a-SiC with respect to nitrogen percentage introduced into the films was made. Fifth, the corrosion resistance of the prepared PS-CVD films was tested under selected harsh environmental conditions including, (i) very strong acidic environment and (ii) buffer saline solution for 300 days at a temperature of 75 °C.

PS-CVD, as any newly developed SiC deposition technique, is expected to face several challenges. This process, in particular is challenging since it is based on solid polymer sublimation without using any solvents or any toxic gas (silane) in the deposition of a-SiC:H thin films and many other potential derivatives. Such approach, to the best of our knowledge, is the first of its kind that makes the challenges even bigger (lack of prior art of such approach and the absence of clear characterization of the produced films). Even if the challenges might be bigger and the potential of success is lower, the potential competitive advantages expected to be achieved by the PS-CVD technique are the main
force behind pursuing this research. These advantages are also hard to achieve by other conventional CVD processes, as will be discussed in the details of this thesis.

The main focus of the work presented in this thesis is film characterizations rather than synthesis, since the details of the synthesis process are reported elsewhere.  

1.2. Overall Objectives

- The overall project objective is to contribute to the development of the PS-CVD technique as a safe substitute for all conventional SiC thin films deposition techniques. In other words, the work described in this thesis will assist in the development of methods to optimize efficient, practical and economically sensible SiC-based materials without the need of using any toxic gas or solvents.

- Achieve better understanding of the fundamental mechanisms and composition-structure functional relationships of the PS-CVD materials to enable further enhancements in the process as well as the produced thin films.

- Create and screen libraries of materials capable of meeting the industrial requirements for various harsh environment applications, where Si based electronic devices can not function (>300 °C ) and several thin film coatings fail to function adequately.

- Produce in-situ porous SiC based thin films without using any harsh chemicals (usually needed for chemical anodization to produce porous films) and consider applications where competitive advantages may be achieved.
1.3. Specific Aims and Objectives

- One of the main exploratory research objectives of the work described here focuses on studying the effectiveness of depositing a-SiC:H thin films on metallic electrodes in an attempt to use these electrodes as a back contact for future device applications without the need for using Si or SiC as substrate materials. Such approach is in contrast to most conventional SiC based electronic device fabrication, where Si and/or SiC wafers are used as an active part of the device of a prime.

- Evaluate the adhesion and interfacial interactions between PS-CVD thin films and various metallic substrates for coating applications, where the adhesion and bonding strength between the coating and the underlying metallic substrates are of major concerns.

- Study the stability of PS-CVD prepared a-SiC films as a candidate for high temperature applications by focusing on the effect of high temperature (800 °C, 2 hrs) thermal annealing on the interfacial interactions between PS-CVD prepared a-SiC and the various underlying metals. This aimed at identifying the most stable a-SiC-metal contact for the integration of a-SiC into various opto-electronic devices for high temperature device and coating applications.

- Characterize thermal annealing as a potential technique to control the mechanical properties of a-SiC films mainly hardness and Young's modulus, as an initial stage in establishing a clear correlation between the hardness, toughness and wear resistance intertwined relation for coating applications, especially in the drilling industry.
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- Design techniques to control the surface morphology of a-SiC films in the nanometer scale with the focus on controlling the surface roughness of the prepared films.
- Correlate a-SiC mechanical properties with Si–C bonding environment.
- Develop an in-situ technique, to produce porous thin films, with the ability to control the pores size and density of the prepared films for several states of the art applications as will be discussed in chapter 5 and in more details in chapter 7.
- Analyze the induced structural modifications and bonding configurations of the PS-CVD films due to annealing and nitrogen addition.
- Study the corrosion resistance of the PS-CVD prepared a-SiC films against strong acidic environments as a potential candidate for protective coating.
- Evaluate the potential of using PS-CVD prepared thin films for biomedical applications by performing fundamental testing of the corrosion resistance of PS-CVD a-SiC in buffer solution (30 μL phosphate buffered saline, pH 7.4).

1.4. Approach Followed

- Deposit a-SiC films on several metal-coated (Ti, Cr, Au, V, Pt, Ni, TiW, TiN, Pt-Rh, Ni-Cr, AuPd) and insulating (SiO₂ and Si₃N₄) substrates and expose these substrates to harsh annealing for 2 hrs at 800 °C.
- Carry out a series of measurements and characterizations to evaluate the a-SiC:H surface morphology and the possible impurities present in the a-SiC:H films, their level, as well as the origins of such impurities. Furthermore, special focus is put here on the structure of the a-SiC:H-metal interface.
- Prepare several a-SiC:H films on Si(100) substrates, then anneal these samples at different annealing temperatures ranging from 750 to 1200 °C. This is followed by performing nanoindentation measurements of the hardness and Young's modulus. Similarly, the effect of thermal annealing on the surface morphology, structural modifications, bonding configurations and density of the films are also performed.

- Identify the changes in Si–C bond density induced by thermal annealing and then establish a correlation between the hardness and Young's modulus of the a-SiC:H films from one side and the Si–C bond density from another side. Moreover, the established relation is then compared with similar relations established by other researchers for a-SiC films prepared by pulsed laser deposition (PLD) and PECVD techniques.\textsuperscript{3,11}

- Perform \textit{in-situ} nitrogenation of the a-SiC:H films (using different NH\textsubscript{3} flow rates) to produce a-SiCN:H followed by a series of characterizations to determine the impact of nitrogen addition on the electrical, mechanical and structural properties of the prepared films.

- Prepare several a-SiCN:H samples under various NH\textsubscript{3} flow ratios, to evaluate the use of NH\textsubscript{3} as a potential candidate for producing porous a-SiCN:H film, followed by the required characterization steps to evaluate the pores size and density.

- Prepare several a-SiC:H films and test the corrosion resistance of these films against acidic environment by immersing these films in strong acidic solution (1:1:1) by volume HF (50%), HNO\textsubscript{3} (70%), H\textsubscript{2}O\textsubscript{2} (32%) for 48 hour followed by several measurements to indicate any possible induced effects. (Si(100) substrates are used as a reference).
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- Immerse several a-SiC:H-coated Si(100) substrates (LPCVD prepared Si$_3$N$_4$ and SiO$_2$ films are included in the test as references) in buffer (30 μL phosphate buffered saline, pH 7.4) solution heated at 75 °C for 12 months period. Periodic testing of the corrosion resistance of these films is carried out for 12 months period at regular intervals.

- The surface morphology, cross sectional view and film thickness are measured using scanning electron microscopy (SEM). Atomic force microscopy (AFM) is used for more 2-D and 3-D mapping of the films. The impurity level is first measured using a capacitance-voltage (C-V) technique followed by measuring the composition of the films, as well as the interface structure using a combination of x-ray photoelectron spectroscopy (XPS) and elastic recoil detection (ERD). Nanoindentation measurements are performed to measure the mechanical properties (hardness and Young's modulus). Moreover, X-ray reflectivity (XRR) measurements are performed to measure the density of the films. In addition Fourier transform infrared (FTIR) spectroscopy is used to identify the structural properties of the films. Details of the different experimental procedures followed in the above techniques and a full analysis of the results are covered in the scope of the following chapters.

1.5. Accomplishments

- Work on the stability of a-SiC:H-metal contacts under harsh condition environments (temperature at 800 °C for 2 hours) clearly showed that it is feasible to achieve very stable interface (in terms of narrowness and abruptness) for electronic device
applications, between a-SiC:H films and the two metallic compounds TiN and Pt-Rh layers. Moreover, the a-SiC:H films deposited particularly in the case of TiN substrate are shown not only to contain the lowest oxygen content but also to exhibit the smoothest surface. (chapter 3)

- It is shown that for coating metallic substrates, where wider interface is required between a-SiC:H and the underlying metal (stronger adhesion), PS-CVD prepared a-SiC:H is an excellent candidate for coating a series of metals including Cr, Ti, V, and TiW. Also it is not surprising to find that these metallic substrates got oxidized before deposition of a-SiC:H films due to the high temperature of deposition. A reduction of deposition temperature may be needed to overcome such limitations and a better reactor sealing is still needed. (chapter 3)

- Identified the effects of short cycle thermal annealing on the structural properties of the a-SiC:H films. It is found 10 minutes thermal annealing under Ar flow at an annealing temperature (T_a) ranging from 750-1200 °C resulted in more ordered structured films. Moreover, a significant increase in the Si-C bond density accompanied by a significant decrease of the hydrogen content is clearly observed. (chapter 4)

- A direct relation between thermal annealing and film density is established. It is found that the a-SiC:H film density increased from 2.36 to 2.75 g/cm³ as a result of increasing T_a from 750 to 1200 °C. (chapter 4)

- Engineered an accurate control of the surface morphology of a-SiC:H. The studies have shown that the average root mean square roughness (R_{rms}) can be reduced from 20 nm to ~ 1 nm. (chapter 4)
Introduction

- It was found that both hardness and Young’s modulus increase from 15.5 to 17.6 GPa and from 155 to 178 GPa, respectively, as a result of increasing the annealing temperature (T_a) from 750 to 1200 °C. (chapter 4)

- We have established a constant-plus-linear relation between hardness and Young’s modulus with respect to Si–C bond density, which is found to be in good agreement with the same relation established by other researchers using pulsed laser deposition (PLD) and PE-CVD for depositing a-SiC films. This is a further indication that regardless of the SiC deposition process and/or film composition, the derived constant-plus-linear relation is a strong indication that the Si–C bond density is the major detrimental factor that control both hardness and Young’s modulus of SiC:H films. (chapter 4)

- We have demonstrated the effectiveness of using NH_3 as a nitrogen source to produce a-SiCN:H films based on the PS-CVD process. It is found that only a flow ratio of NH_3/Ar equal to 4x10^{-3} is needed to add 27 at.% nitrogen in the a-SiCN:H films. (chapter 5)

- Identified the nature of bonding configurations of the a-SiCN:H films by showing that the films consist of a complex bonding structure between Si–C–N and can not be considered as separate Si–C and Si–N bonds. (chapter 5)

- In addition to our effort of finding better performance SiC:H thin films by tuning the composition of the films, we have been developing a general method for the production of high surface area nanostructured films by utilizing in-situ nitrogenation of the films without the need for any further after-deposition electrochemical etching steps. Likewise, from the libraries of in-situ nitrogenation, whereby a new means of
Introduction

creating nano porous surfaces has been developed, the study shows that it is feasible
to achieve pore size in the range of 2-20 nm and pore density of 1-5%, without the
need to use electrochemical anodization techniques. (chapter 5 & 6)

• Demonstrated a clear approach of reducing both hardness and Young's modulus of the
formed films by the incorporation of nitrogen. The approach shows that where ever an
accurate control of hardness and Young’s modulus of the PS-CVD films for specific
applications is needed, the addition of nitrogen in the a-SiC:H films is an effective
approach. It is shown that that the hardness and Young’s modulus can be accurately
reduced from 16.6-13.4 and 158-136 GPA, respectively. (chapter 5)

• Confirmed again the validity of the constant-plus-linear relation between hardness and
Young’s modulus with respect to the decrease of Si–C bond density induced by the
increase of nitrogen atomic percentage. (chapter 5)

• Demonstrated a good agreement between the FTIR and XPS analyses of the bonding
configurations of the a-SiC:H and a-SiCN:H films. (chapter 6)

• Our work on testing the corrosion resistance of a-SiC:H in harsh acidic environment
showed that the prepared PS-CVD a-SiC:H films did not show any sign of corrosions,
pitting, peeling off or degradation after 48 hours immersion in (1:1:1) by volume HF
(50%), HNO₃ (70%), H₂O₂ (32%).

• Finally, work on testing the corrosion resistance of the a-SiC:H films in buffer (30 μL
phosphate buffered saline, pH 7.4) solution shows that the films are very stable after
360 days immersion in the buffer (30 μL phosphate buffered saline, pH 7.4) solution
heated at 75 °C. There is no degradation, pitting, etching or cracking observed.
1.6. Future Directions

- Continue and expand investigations of the characteristics of semiconductor materials following the proposed characterization map shown in Appendix A from which the fruit of this thesis is achieved.

- Continue to design and test additional a-SiC:H-metal junction systems for electronic and coating applications.

- Explore different routes of doping which include ion implantation, and in-situ doping using the conventional doping gases. More important, develop a safe substitute for the toxic gases used for doping purposes (i.e. B₂H₆, BCl₃) in conventional processes, by investigating different potential doping candidates. For instance, tris [dichloromethylsilyl]ethyl]borane has been used recently to achieve p-type doping of SiC. By doing so, it could be possible to produce semiconductor-quality SiC films without using any toxic gas, neither for film constituent nor for doping purposes.

- Evaluate the performance of TiN and Pt-Rh metallic thin films as potential candidates for Ohmic contacts for high temperature device applications. The essential characterization steps are included in Appendix C for reference purposes.

- Investigate library designs for Schottky contacts to both n-type and p-type a-SiC:H and a-SiCN:H for future electronic device applications.

- Design, fabricate and test the performance of an integrated test prototype device for high temperature applications based on the developed materials.

- Based on the initial results on the feasibility of controlling the hardness and Young's modulus of the a-SiC:H and a-SiCN:H films, conduct additional testing of the
toughness and wear resistance of these materials to complete screening evaluation of
the intertwined relation between hardness, fracture toughness and wear resistance
which are essential requirements for coating applications, especially tools coating.

- Coat tools such as drilling bits, cutting tools and perform the needed tests to evaluate
  the durability and performance of these tools and compare them to uncoated ones.
- Work with industrial partners to coat bigger parts such as car engine component. Such
  industry is getting more interested in SiC films for coating applications.

1.7. Summary and Layout of the Thesis

The background theory and the relevant literature survey are presented in chapter
two. The focus here is to bridge the prior art in the field with the subject of this thesis. An
extensive work on understanding the properties of the prepared films and the effects of
various experimental conditions on the quality of these films is performed. The details of
the experimental procedures, results and discussions are presented in chapters 3 to 7. In
particular, chapter 3 deals with the interfacial interactions between various metal-coated
substrates and the PS-CVD prepared a-SiC:H thin films. In chapters 4 and 5, the
mechanical properties (hardness and Young's modulus and density) as well as surface
morphology and structural properties of the PS-CVD prepared films are reported. More
specifically, chapter 4 contains several novel experimental results pertaining to the effect
of thermal annealing on hardness, Young's modulus, density and surface morphology of
a-SiC:H. In Chapter 5 the investigation is extended to cover the effect of introducing
nitrogen, as a constituent into the a-SiC:H films, on the hardness, Young's modulus,
surface morphology and the structural properties of the newly formed a-SiCN:H films. In
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Chapter 6, a detailed discussion on the FTIR and XPS comparative analysis of the structural and bonding configuration of a-SiCN:H film is presented. The findings presented in the thesis followed by chapter summaries and a discussion of future work are presented in Chapter 7. It is worth noting here that a comprehensive characterization map is designed and used as a guide through the work in this thesis (Appendix A). An example of a poster presentation presented at the International Conference on Silicon Carbide and Related Materials (ICSCRM) is presented in Appendix B. Mathematical derivations used in the subject of this thesis and/or needed for future characterizations of the electrical properties of the films especially for characterizing Schottky and Ohmic contacts, are included in Appendix C. The thesis ends with a bibliography of all used related literature.
CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

The objective of this chapter is to describe comprehensively the existent background on the synthesis and properties of amorphous silicon carbide thin films. The chapter provides the reader with a background of the techniques used for the growth of a-SiC:H films, challenges the a-SiC:H films facing including metal-SiC:H interface, Schottky, and Ohmic contacts. This chapter develops an introductory framework for understanding the mechanical and structural characteristics as well as the bonding configurations of the a-SiC:H film. It introduces the concepts of Polymer Source Chemical Vapor Deposition (PS-CVD) technique used to produce the films used in this thesis. The final topic in this chapter focuses on several potential applications of a-SiC:H thin films in various fields.

2.1. Introduction

Amorphous silicon carbide (a-SiC:H) thin films have attracted much attention because they are promising materials not only for making optoelectronics devices, but also many other applications as will be discussed throughout this chapter and subsequent chapters. The wide bandgap, high thermal conductivity, high breakdown electric field strength, high saturated drift velocity, high thermal stability and chemical inertness (due
to large Si–C bonding energies) of SiC:H all contribute to its unique and as yet untapped, potentials. Interest in SiC can be traced back to 1977 by Anderson, and Spear.\textsuperscript{14} Since then; there has been a growing technological interest in materials with these unique properties as evident by not only their increased numbers, but also the large variety of applications. Extensive work has been done on the deposition and characterisation of a-SiC as a potential candidate for many harsh environment applications, which is larger than the scope of this thesis to cover. Indeed, in this chapter, a brief description of a-SiC deposition techniques reported in literature based on the used precursors (gas, liquid and solid) is discussed. Several SiC characteristics and challenges are presented, which include: metal-SiC interface for active and passive applications, followed by a brief description of the mechanical properties (hardness and Young's modulus). Likewise, a description of a-SiC structural and bonding configurations, as well as various potential applications is covered in this chapter. More specific literature review is carried out and included in the fruit of this work that will be presented in the subsequent chapters.

2.2. Deposition Techniques

There are several deposition techniques known and available to those of skill in the art, for the preparation of thin films of amorphous silicon carbide. The choice of a particular deposition technique will be mandated by a number of factors including the need for a high deposition rate, the compatibility of the deposition process with other processing parameters, quality and reproducibility of the a-SiC films, homogeneity over a wide area, ease and cost of use, as well as detrimental side effects and limitations specific to each technique. A particular deposition process may be favored by a number of such
Background and literature review

considerations, but may also be otherwise unattractive since it may produce a semiconductor material having poor electronic properties. In addition, since the properties of a-SiC depends strongly on the microstructure, stoichiometry and the nature of the impurities present, it is inevitable that each deposition technique with its associated controlling parameters should yield films with different characteristics. The different deposition techniques presented in this chapter are divided into four categories based on the precursors used in each category; such distinction is only to achieve better understanding of different approaches and is not necessarily a comprehensive review of all available processes.

2.2.1 Gaseous-source Techniques

Among the deposition techniques; chemical vapor deposition (CVD) using separate precursors for Si and C have been widely used. The most commonly used gases are silane (SiH₄) and methane¹⁵ or propane.¹⁶,¹⁷,¹⁸,¹⁹,²⁰,²¹,²² Moreover, plasma enhanced chemical vapor deposition (PECVD), based on glow discharge decomposition of silane and methane has been investigated.²³,²⁴,²⁵,²⁶,²⁷ The fact that Si and C are supplied from two separate sources makes it easier to control the stoichiometry of the SiC films. On the other hand, all gas-based CVD techniques require the use of pyrophoric SiH₄ toxic gas as the source for Si. Such gas is not only undesirable for health issues, but also a highly corrosive gas which makes the cost of equipment maintenance relatively high.
2.2.2 Solvent-based source Techniques

Several attempts have been tested to deposit SiC films without using the pyrophoric SiH₄ toxic gas. Recently, studies of single-precursor CVD such as C₆₀₂₈ methylsilane,²⁹ hexamethyldisilane,³⁰ methyltrichlorosilane,³¹ dimethylisopropylsilane,³² diethylsilane,³³ silacyclobutane³⁴ and disilacyclobutane,³⁵ have been cited. Most liquid-based CVD processes are based on pyrolysis, which requires dissolving the polymer in a solvent, then depositing it on a surface (via spinning, dipping, or spraying) and then pyrolyzed.³⁶,³⁷ Indeed, most of the single precursors are either solvent dependent or produce toxic byproducts. The use of solvent to dissolve the single precursor and then to apply the thin film on a substrate has its own challenges that limit the use of such approach in any practical application. These limitations include the high density of texture defects, high density of pinholes due to the evaporation of solvents from the films, nonuniform deposition especially of thinner films, non conformable coatings, etc.

2.2.3 Solid Precursor Techniques (SiC Target Disk)

Recently several groups tried to use other approaches to prepare SiC films in order to overcome the limitations imposed by the gas-based and the liquid-based processes. Pulsed laser deposition (PLD)³ has been used to deposit a-SiC thin films. Moreover, sputtering³⁸,³⁹,⁴⁰ attracted some attention to deposit a-SiC, which involves knocking an atom or molecule out of a target material by accelerated ions from an excited plasma and condensing it on the substrate, either in its original or in a modified form. Both PLD and sputtering overcome several limitations of the gas and liquid-based processes, but new
challenges accompanied these approaches appeared as expected. To name a few, sputtering cause a high degree of damage to the surface of the prepared films. While PLD a-SiC films are hydrogen-free,\textsuperscript{3} a desirable requirement for coating applications, they have a significant drawback to any active device application due to the high dangling bonds (lack of hydrogen). The main role of hydrogen is the saturation of dangling bonds and the reduction in the number of defects, which relaxes the structure of the amorphous material.\textsuperscript{41} Moreover, both sputtering and PLD techniques are capable of coating planar surfaces and to the best of our knowledge, no conformable coating is reported using these techniques so far.

2.2.4 Solid Precursor Techniques (Powder Sublimation)

With increased development in electronic and coating technology, there is a need to develop a process that is capable of replacing the highly toxic silane based CVD processes and to eliminate the need of solvent in the a-SiC films synthesis. It is important to point out here that the work presented in this thesis is based on using a sublimation of powder that contains both Si and C. As a consequence, more focus is put in this section on the proposed technique to achieve basic understanding of SiC thin film synthesis. Scarlete et al.\textsuperscript{16} recently developed a process called Polymer-Source Chemical Vapor Deposition (PS-CVD) that is expected to overcome the limitations induced by the toxic silane gas and to eliminate the use of solvent in any stage of the a-SiC thin films deposition process. Furthermore, the proposed PS-CVD technique is reported to coat any substrate regardless of shape or orientation without causing any damage to the surface of the films as in the case of sputtering and PLD. In their PS-CVD technique,
[Polydimethylsilane (PDMS)] has been used as a single precursor for both Si and C. Figure 2-1 shows a schematic diagram of the PS-CVD system, which is based on converting PDMS, a solid polymer source, into gaseous precursors needed to produce a-SiC thin films. The PS-CVD system used in this study is a Lindbergh one-zone programmable furnace equipped with a Euorotherm PID temperature controller, with a maximum temperature of 1100 °C. The heating coils around the quartz tube supply the heat needed for the sublimation of the polymer source inside the tube as well as the energy needed to heat the substrate. The system is connected to an external source of carrier gas. The material to be deposited is inserted into the tube in a boat. The substrate is positioned near the polymer source closer to the gas exit. The deposition procedure is done by evacuating the chamber to a pressure lower than 0.1 Torr. Argon, being a noble gas which does not react with either the polymer source or the substrate, is then introduced into the chamber. The process of introducing Ar gas and then evacuating is done several times to reduce or eliminate the existence of O₂ gas in the tube. Once preconditioning is complete, the temperature is set to increase following specific ramp rate as needed. A carrier gas is introduced to the tube through bubblers. The work that has been done based on the reactor design presented in Figure 2-1 showed the feasibility of producing good quality SiC thin films from powder source. Even though, such process is in its early stages and tremendous work is still needed to make a clear assessment of such approach, the initial indications are very promising to believe that such approach could be a great alternative to several other processes discussed earlier. In addition to the obvious simplification of the experimental apparatus and the elimination of using the highly toxic
SiH₄ gas or solvents, the other principal advantages of using sublimation of a single powder precursor including deposition on any surface orientation, high deposition rate, cost effective, environmentally friendly process, cracks-free films and very low thermal budget due to the pre-exist bonding between Si and C in the starting precursors. These advantages, among others were the main motivations behind pursuing more detailed studies making the primary objective of this work is to assess the quality of PS-CVD a-SiC thin films, more specifically, to achieve greater understanding of the electrical, mechanical and structural properties of these films. With this goal in mind, the prior work focusing on the a-SiC films synthesis has been reported elsewhere.¹⁰

2.3. Silicon Carbide Characteristics and Challenges

The great potential of SiC as active thin films in electronic device and/or as passive layers for coating applications is challenged by several difficulties. To name just a few, we have selected (i) the control of metal-SiC contact properties (Schottky and


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Ohmic contacts for device applications; (ii) the ability to control the mechanical properties of these films (hardness and Young’s modulus) especially where the trade off between the hardness and toughness is needed; (iii) the ability to control the surface morphology (smooth, rough, porous), hydrophobicity and hydrophilicity; (iv) the control of structural properties and bonding configurations and (v) the corrosion resistance of these films in acidic, salt and Phosphate Buffer Saline (PBS) solutions are among other challenges. We will discuss some of these challenges in the following sections.

2.3.1 Metal-Silicon Carbide Contacts

The control of interface reactions between silicon carbide and metal is a significant issue and should be considered together with individual material properties for a successful design. The interdiffusion between metal and SiC can be considered advantageous in many coating applications. On the other hand, in SiC devices in general and more specifically for high temperature and power applications, the contact metallization of SiC degrades severely at high temperature because of factors such as the interdiffusion between layers and the compositional and microstructural changes at the metal/semiconductor interface. These mechanisms can be a device killer, which limits the temperature range at which a particular metallization can be used, especially for operation at elevated temperatures.

A. Active SiC-Metal Contacts (Schottky and Ohmic Contacts)

In any SiC device application, metal contacts (Schottky and Ohmic contacts) have to be provided to both sides of the device in order to connect the device to an external circuit. These contacts have to be as stable as possible, so that the current flow through a
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semiconductor device and, hence through the contacts, leads to the smallest contact resistance possible. The great potential of SiC as a semiconductor in electronic device applications is challenged by the difficulty of controlling metal-SiC contact properties. These properties of the metal-SiC interfaces include uniformity and thickness of the interfacial region and most importantly the stability of the interface especially at high temperatures (~ 600 °C) and the interfacial interdiffusion between the metal contacts and the SiC films.

A Schottky contact (rectifying contact) allows current to flow for only one sign (positive or negative) of voltage bias, thereby becoming a component of the active region of the device. Many authors have investigated Schottky diodes characteristics using I-V and C-V methods. Table 2.1 summarizes several studies on Schottky contacts: showing metals used, the achieved Schottky barrier heights and the characterization methods used for metal/3C-SiC. Schottky barrier height, \( \Phi_b \) which is an important factor used to determine the contact quality, is defined as the potential barrier to thermionic emission that naturally exists between an intimate metal and semiconductor contact at zero applied bias. Table 2.2 shows more specifically several metals used to form Schottky contacts with n-type 6H-SiC. Furthermore, Table 2.3 shows a list of metals used for forming Schottky contact with p-type 6H-SiC. It is worth to mention that very little focus was put in studying the stability of the metal-SiC contacts at high temperature for longer time. Platinum and copper layers are proven to function as good Schottky contacts at temperature up to 500 °C,\(^{33,44}\) and molybdenum-heterojunctions have shown Schottky behavior up to 900 °C.\(^{45}\)
Table 2.1: Schottky barrier heights of metal/3C-SiC systems

<table>
<thead>
<tr>
<th>Metal</th>
<th>Barrier height ($\Phi_b$) (eV)</th>
<th>Measurement methods</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>1.15 to 1.2</td>
<td>C-V</td>
<td>[46,47]</td>
</tr>
<tr>
<td>Pt</td>
<td>1.3-1.6</td>
<td>C-V</td>
<td>[48]</td>
</tr>
<tr>
<td>Au</td>
<td>1.0-1.6</td>
<td>C-V</td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>0.95</td>
<td>C-V</td>
<td>[49]</td>
</tr>
<tr>
<td>Pd</td>
<td>0.95 to 0.92</td>
<td>C-V, XPS</td>
<td>[50]</td>
</tr>
<tr>
<td>Au</td>
<td>0.78 to 0.87</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>0.69 to 0.73</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>0.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>0.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tb</td>
<td>0.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>0.16</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ohmic contacts play a vital role in controlling the performance of an electronic device. A satisfactory Ohmic contact should offer negligible contact resistance relative to the bulk or spreading resistance of the semiconductor. In addition, the voltage drop across the contact should be significantly small compared with the drop across the active region of the device. However, in practice when a metal film is deposited on a semiconductor, it is more likely to form a Schottky (rectifying) contact which impedes current flow across the metal–semiconductor interface. Either thermionic emission or tunneling is the dominant conduction mechanism in this case, depending upon the semiconductor doping level. According to Sze\textsuperscript{51} for semiconductors with low carrier concentrations ($<10^{18}$ cm$^{-3}$) conduction across the interface is normally dominated by thermionic emission. Therefore,
Table 2.2: Schottky barrier heights of metal/ n-type 6H-SiC

<table>
<thead>
<tr>
<th>Metal</th>
<th>Barrier height ($\Phi_B$) (eV)</th>
<th>Measurement methods</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>1.45</td>
<td>C-V</td>
<td>[52]</td>
</tr>
<tr>
<td>Ag</td>
<td>1.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>1.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>1.40</td>
<td>I-V, C-V</td>
<td>[53]</td>
</tr>
<tr>
<td>Al</td>
<td>1.7</td>
<td>C-V</td>
<td>[54]</td>
</tr>
<tr>
<td>Cr</td>
<td>0.82 to 0.85</td>
<td>I-V, C-V</td>
<td>[55]</td>
</tr>
<tr>
<td>Pd</td>
<td>1.11 to 1.27</td>
<td>I-V, C-V</td>
<td>[56]</td>
</tr>
<tr>
<td>Au</td>
<td>1.37 to 1.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>0.83 to 0.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.79 to 0.96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>0.26 to 0.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>0.27 to 0.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tb</td>
<td>1.04 to 2.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Er</td>
<td>1.04 to 2.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>0.79 to 0.97</td>
<td>I-V, C-V</td>
<td>[57,58]</td>
</tr>
<tr>
<td>Ti</td>
<td>0.73 to 0.75</td>
<td>C-V, XPS</td>
<td>[59]</td>
</tr>
<tr>
<td>Ni</td>
<td>1.24 to 1.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>0.82 to 1.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Er</td>
<td>1.40</td>
<td>XPS</td>
<td>[60]</td>
</tr>
<tr>
<td>Ti</td>
<td>0.79 to 0.88</td>
<td>I-V, C-V, XPS</td>
<td>[61]</td>
</tr>
<tr>
<td>Pt</td>
<td>1.06 to 1.33</td>
<td>I-V, C-V</td>
<td>[62]</td>
</tr>
<tr>
<td>Au</td>
<td>1.40</td>
<td>C-V</td>
<td>[63,64]</td>
</tr>
<tr>
<td>Mo</td>
<td>1.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>1.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>1.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td>0.57</td>
<td>XPS</td>
<td>[65]</td>
</tr>
</tbody>
</table>
Table 2.3: Schottky barrier heights of metal/ p-type 6H-SiC

<table>
<thead>
<tr>
<th>Metal</th>
<th>Barrier height ($\Phi_n$) (eV)</th>
<th>Measurement methods</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>1.07, 1.37</td>
<td>C-V</td>
<td>[66]</td>
</tr>
<tr>
<td>Ag</td>
<td>1.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>1.36, 1.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>1.73</td>
<td>I-C; C-V</td>
<td>[67]</td>
</tr>
<tr>
<td>Pd</td>
<td>1.61 to 1.63</td>
<td>XPS</td>
<td>[68]</td>
</tr>
<tr>
<td>Ni</td>
<td>1.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>1.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>1.72 to 1.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>2.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>2.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>2.47</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ohmic behavior can be achieved in low-doped semiconductors provided the barrier height for majority carriers is sufficiently low. As per the Schottky–Mott theory,$^{69}$ the metal which is likely to form an Ohmic contact to n-type semiconductor should have a work function equal to or less than the electron affinity of the semiconductor. However, the presence of interfacial states and the chemical reactivity between the metal and the semiconductor at a given temperature have significant influence in tuning the barrier height. Table 2.4 shows different metals reported to form good Ohmic contact with n- and p-type SiC, as well as the used annealing temperature and the achieved specific contact resistance (refer to Appendix. C for further details of the mathematical derivations of specific contact resistance). In addition to the metals described in Table 2.4, several other metallization schemes are described in the literature to serve as good
Table 2.4: Different metallization schemes used to form Ohmic contact on n- and p-type silicon carbide as well as the achieved specific contact resistance and the annealing temperature used.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Substrate</th>
<th>Annealing Temperature(°C)</th>
<th>Specific contact resistance ($\Omega$.cm$^2$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>n-type SiC</td>
<td>850</td>
<td>1.0x10$^{-7}$</td>
<td>[70]</td>
</tr>
<tr>
<td>Ti/Al</td>
<td>p-type SiC</td>
<td>850</td>
<td>1.0x10$^{-6}$</td>
<td></td>
</tr>
<tr>
<td>Ni/Al</td>
<td>p-type SiC</td>
<td>800</td>
<td>5.0x10$^{-3}$</td>
<td>[83]</td>
</tr>
<tr>
<td>Ni/Ti/Al</td>
<td>p-type SiC</td>
<td>800</td>
<td>6.6x10$^{-5}$</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>n-type 6H-SiC</td>
<td>950</td>
<td>3.9x10$^{-5}$</td>
<td>[71]</td>
</tr>
<tr>
<td>Ni/Al</td>
<td>p-type 4H-SiC</td>
<td>800</td>
<td>5.0x10$^{-3}$</td>
<td>[83]</td>
</tr>
<tr>
<td>Ni/Ti/Al</td>
<td>p-type 4H-SiC</td>
<td>800</td>
<td>6.6x10$^{-5}$</td>
<td></td>
</tr>
<tr>
<td>CoSi$_2$</td>
<td>n-type 6H-SiC</td>
<td>900</td>
<td>3.0x10$^{-5}$</td>
<td>[72]</td>
</tr>
<tr>
<td>Al/Ni/W</td>
<td>p-type SiC</td>
<td>900</td>
<td>1.0x10$^{-6}$</td>
<td>[73]</td>
</tr>
</tbody>
</table>

Ohmic contacts to n-type SiC. A single Ni layer or a Ni-based contact for Ohmic purposes has been used extensively due to the simple preparation method.\textsuperscript{24,75,76} TiN was proposed as Ohmic contact material for its stability and low resistivity at high temperature,\textsuperscript{18,77,78} Ni/3C.\textsuperscript{79} Tungsten disilicide and molybdenum disilicide contacts were prepared as well for Ohmic purposes.\textsuperscript{80} Different metallization schemes are used for p-type SiC where Al/Ti contacts are commonly used for Ohmic contacts.\textsuperscript{81,82,83,84}
B. Passive Silicon Carbide-Metal Contacts (Coating)

Indeed, while the interdiffusion between metal and SiC can be considered non desired in many a-SiC based devices intended for high temperature and high power applications, it is however advantageous in many applications such as joints between a-SiC and Ni-based super alloys\textsuperscript{85,86} and reinforcement in structural material.\textsuperscript{87} A fair number of studies have been reported on the interface reactions between SiC and metals, e.g. Ti,\textsuperscript{88} Cr,\textsuperscript{89} Ta,\textsuperscript{90} Mo,\textsuperscript{91} Ni-Cr alloy and TiAl.\textsuperscript{92} These reports have shown that the reaction products sequence and interface morphology in SiC/metal reactions are mainly dependent on the contact materials. It is possible that reactions in certain metal/SiC systems are limited by the dissociation of SiC because of the strength of the Si–C covalent bond. Evidence in support of this statement is provided by the initial formation of metal rich silicides, for example between SiC and Ni,\textsuperscript{93} Co\textsuperscript{94} and Pd,\textsuperscript{95} which in most cases was followed by the formation of less metal-rich silicides and ended by a periodic morphology composed of alternating carbon and silicide.\textsuperscript{95} Other metals such as Ti,\textsuperscript{51} Mo,\textsuperscript{96} Fe,\textsuperscript{97} Nb\textsuperscript{98} and W\textsuperscript{99} formed both carbides and silicides after annealing at temperatures between 570 and 1200 °C. The product phases in Ti/SiC were reported to be TiC and TiSi\textsubscript{n}.\textsuperscript{100,101}

2.3.2 Mechanical Properties of SiC

One of the major interests in amorphous silicon carbide films is that they combine not only unique electrical and optical properties, but also they exhibit excellent mechanical (hardness, Young's modulus, toughness) and morphological properties. In the following pages, we will discuss in more details hardness, Young's modulus and surface
morphology in order to achieve better correlation between what has been reported in the literature and what has been achieved in this work.

A. Hardness and Young’s Modulus

Hardness, fracture toughness and wear resistance are strongly inter-related properties. Higher hardness usually dictates higher wear resistance at the cost of fracture toughness. A trade-off must be made between wear resistance and toughness when selecting materials for specific applications. The challenges for researchers are not only to improve the hardness and Young’s modulus, but also to improve or to preserve the fracture toughness and the wear resistance. All these intertwined relationships between the microstructure, hardness, Young’s modulus, toughness and wear resistance present difficulties and also opportunities, for optimizing hardness, fracture toughness and wear resistance.

A summary of hardness and Young’s modulus of different states (amorphous, crystalline) of SiC films deposited using various techniques is shown in Table 2.5. Silicon and fused quartz were included in Table 2.5 for reference purposes. The high hardness (hardest material after diamond) and Young’s modulus of a-SiC, as shown in Table 2.5, makes it a suitable material for many mechanical applications. A further advantage of these materials, beside their excellent mechanical properties, is the ability to modify both the hardness and Young’s modulus by different methods. Among these methods is varying the a-SiC film composition which has been reported to be very effective in achieving good control of both hardness and Young’s modulus. Moreover, thermal annealing of the deposited films has been recently tested. The Young’s modulus of a given film is related to the microstructure and bonding configurations of the
### Table 2.5: A summary of mechanical properties: hardness and Young's modulus of SiC films deposited using various techniques

<table>
<thead>
<tr>
<th>Material</th>
<th>Hardness (GPa)</th>
<th>References</th>
<th>Young's modulus (GPa)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PECVD a-SiC</td>
<td>0.7-1.8</td>
<td>[27]</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>PECVD a-SiC</td>
<td>9</td>
<td>[104]</td>
<td>70.3</td>
<td>[104]</td>
</tr>
<tr>
<td>PECVD 3C-SiC</td>
<td>1-28</td>
<td>[105]</td>
<td>47-203</td>
<td>[82]</td>
</tr>
<tr>
<td>β-SiC</td>
<td>11-36</td>
<td>[106]</td>
<td>100-150</td>
<td>[107]</td>
</tr>
<tr>
<td>RF sputtering SiC</td>
<td>15-40</td>
<td>[108]</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>ECR-CVD a-SiC</td>
<td>---</td>
<td>---</td>
<td>400-600</td>
<td>[109,110]</td>
</tr>
<tr>
<td>LPCVD Poly-SiC</td>
<td>---</td>
<td>---</td>
<td>420-470</td>
<td>[111,112, 113]</td>
</tr>
<tr>
<td>Si</td>
<td>11.9</td>
<td>[114]</td>
<td>190</td>
<td>[3]</td>
</tr>
</tbody>
</table>

Film material and can be a helpful and an interesting macroscopic parameter when used to characterize the state of the material. Representing the main elastic properties of the material, Young's modulus of the film determines the mechanical behavior, especially the residual stress as well as the elastic energy induced by external loading. The later property is responsible for initiating cracks and micro-fractures. In the case of hard film
Background and literature review

materials, Young’s modulus correlates with hardness, which may be difficult to measure directly.

B. Porous Silicon Carbide

In order to produce porous SiC films to meet the specific requirements of the above applications, several techniques have been developed to achieve the needed porosity in the films. Among other techniques, anodization steps\textsuperscript{115,116} and chemical etching treatment\textsuperscript{117} has been used to get porous SiC samples. Recently, porous silicon carbide attracted great attentions in an emerging area of biotechnology, especially in the development of implantable sensors. These sensors measure molecules in the fluid that surrounds the cells comprising tissues and organs. The aim of developing such sensors is to detect diseases in their early stages. New materials are needed in order to create an interface between micro devices and living tissues. Nanoporous SiC is needed in biomedical field applications since it has many desirable properties and has proven biocompatibility, as evident by its successful use as a coating on vascular stents inserted into coronary arteries to maintain arterial patency.\textsuperscript{118} In addition, porous SiC could make an excellent medium for semi-permeable membranes for microdialysis.\textsuperscript{119} Moreover, porous SiC membranes would be robust, thus enabling long term continuous monitoring of tissues, for early disease detection and other biosensor applications. Furthermore, porous SiC is an attractive material for nanocatalysis in tissue engineering and formation and growth of bone.\textsuperscript{119,120} In addition to the biomedical applications of porous SiC, many other potential applications have been recently adapted: (i) porous SiC has been used as a substrate for GaN growth in an attempt to form high-density robust storage applications;\textsuperscript{121,122} (ii) in the fabrication of ammonia sensors;\textsuperscript{123} (iii) fuel cells\textsuperscript{120} (iv) high-
Background and literature review

temperature fuel; (v) visible luminescence at room temperature\textsuperscript{115,117} and (vi) humidity sensors for harsh environment applications.\textsuperscript{124,125} Of particular interest is the last application, since measurement of humidity is required in a wide range of applications, including meteorological service, food processing industry, air-conditioning, car exhaust and electronics processing to name but a few. It was established that for effective humidity sensing, the pore size distribution should include pore sizes in the range 2-10 nm for low relative humidity (RH) values and 20-100 nm for high RH values.\textsuperscript{126}

2.3.3 Structural Properties and Bonding Configurations

Among many advantages offered by the SiC- derived materials is the possibility to tailor their optical, electrical, and structural properties by controlling, in an appropriate way, its atomic composition. For example, the incorporation of hydrogen atoms into the film structure is known to saturate the dangling bond, thereby improving their optical\textsuperscript{127} and electronic properties.\textsuperscript{128} The introduction of fluorine atoms into the SiC matrix has been also reported to improve the thermal stability of the SiC films, resulting in both an optical band gap widening and a decrease in the electrical conductivity values.\textsuperscript{129,130} Incorporating nitrogen atoms in the SiC network has been shown to be effective in significantly increasing the optical band gap of SiC films.\textsuperscript{131} Moreover, Gomez \textit{et al.}\textsuperscript{132} proposed that a-SiCN based alloy should have properties between silicon nitride and carbon nitride. Indeed, optical investigation of the polycrystalline SiCN films indicated a direct band gap of about 3.8 eV and a strong optical emission around 2.8 eV.\textsuperscript{133,134} Thus, the ternary SiCN compound constitutes an excellent material, which exhibits not only a
wide band gap, but also good mechanical properties, excellent thermal stability and exceptional high-temperature creep resistance. In particular, it has been reported that SiCN films posses higher thermal stability in comparison with the binary Si-N or Si-C amorphous thin films.

2.4. Potential Applications of Silicon Carbide Films

Silicon carbide is becoming an integral part of modern electronic technology wherever there is a potential for improving optoelectronics devices or quantum efficiency of light emitting devices. However, with increased development in electronic and coating technology, there has come the need for a greater understanding of the electrical, mechanical and structural properties of a-SiC. Indeed, a-SiC films are extensively studied for many potential applications. The intention behind collecting many of these applications in one section is to achieve easier access to specific interest of a prime for the reader. With this goal in mind, it is expected that many of these application will be found in different sections in this thesis. These applications include optoelectronics devices, solar cell, photo transistors, light emitting diodes (LEDs), microelectronic devices, heterojunction bipolar transistor (HBT), image sensors, photoreceptors, high temperature sensors, photo modulator devices, near-visible color sensors, color sensors and flat-screen full color displays. Similarly, for its excellent mechanical properties, a-SiC has been used for high temperature, biocompatible implants and MEMS coatings, x-ray masks, dielectric copper diffusion barrier, sliding friction, wear resistance, protective coatings against corrosion of steel, protection of thermonuclear reactor walls SCALPEL mask membrane
and microelectronic dielectric layers. Recently, porous SiC has been used as a substrate for GaN growth in an attempt to form high-density robust storage applications.\textsuperscript{121,122} Among other applications of porous SiC, fabrication of ammonia sensors,\textsuperscript{123} humidity sensors for harsh environment applications\textsuperscript{124,125,126} and fuel cells.\textsuperscript{120} Furthermore, Sung \textit{et al.} developed tailored macroporous SiCN and SiC structures for high-temperature fuel reforming and intense visible luminescence.\textsuperscript{163} Also, recent application of porous SiC especially in an emerging area as biotechnology is arisen. Amorphous SiC has been successfully used as a coating on vascular stents,\textsuperscript{118} semi-permeable membranes for microdialysis,\textsuperscript{119} engineering the growth of new bone in tissue engineered bone grafts.\textsuperscript{120}

2.5. Highlights of the Chapter

The highlights of this chapter as follows:

- Various SiC thin films deposition techniques have been covered. These techniques are divided in this work, based on the precursors used: gaseous, liquid and solids.

- Literature survey on various characterizations of a-SiC thin films has been carried out. More focus is put on the challenges that face SiC films to meet the industrial standards. For instance, the metal-SiC interface, Schottky contacts, and Ohmic have been covered for active applications of the SiC films. Moreover basic review of some passive challenges is also covered.

- Mechanical properties, mainly hardness and Young's modulus, are discussed in more details for their importance in many applications, especially where the SiC is used for details protective purpose.
• Other topics in this chapter are the methods used to produce porous SiC films and their potential use especially in biomedical applications.

• The structural properties and bonding configurations of a-SiC and some of its derivatives including a-SiCN have been discussed.

• The potential applications of SiC films in various applications have been included in the last section of this chapter to enable ease of access for those who are interested to explore the added value of such unique material.
CHAPTER 3

STABILITY OF METAL-SILICON CARBIDE INTERFACE AT HIGH TEMPERATURES

This chapter covers the interfacial interactions between PS-CVD a-SiC and metal-coated substrates. It describes the effect of high temperature thermal annealing on the stability of the metal-SiC interface, considers the evolution of the microstructural modifications in the films, discusses specific metallization used for contacts, evaluates the ramifications of the metal-SiC contact interactions, and discusses the principle of diffusions.

3.1. Introduction

The contact between the semiconductor films and a metal is a significant issue and should be considered together with individual materials properties in a successful design. In SiC devices for high temperature and high power applications, the contact metallization of SiC degrades severely at high temperature because of many factors such as the interdiffusion between layers, the compositional and microstructural changes at the metal-semiconductor interface. These reactions limit the temperature range at which a particular metallization can be used, especially for operation at elevated temperatures.
Stability of metal-SiC contact

The association of properties involving high hardness and thermal stability with low wear rates and friction coefficient is the main goal to achieve. Silicon carbide is a material that presents these features but has been quite unexplored, mainly due to its sometimes poor adhesion to metallic substrates. Amorphous silicon carbide (a-SiC) thin films continue to attract considerable attention because they are highly promising for a variety of applications spanning from passive coatings for very harsh environments to active optoelectronic devices. The wide range of applications of a-SiC is due to their unique combination of excellent properties, such as the wide bandgap,\(^1\) high breakdown electric field,\(^\text{164}\) unprecedented mechanical properties\(^3\) and chemical inertness (due to the covalent Si-C bonding energies). Indeed, a-SiC films have been extensively investigated for applications such as optoelectronics devices,\(^4\) solar cells,\(^5\) photo transistors,\(^6\) light emitting diodes,\(^7\) color sensors,\(^8\) photo modulator devices\(^2\) and flat-screen full color displays.\(^9\) In a large part of these applications, the a-SiC films have to be contacted with metal electrodes. As a consequence, the control of the quality of the a-SiC-metal interface is a crucial issue that should be addressed as a function of the targeted application. Indeed, while the interdiffusion between metal and SiC can be considered advantageous in some applications (for example, joint between a-SiC and Ni-based super alloys\(^\text{85,86}\)) it is however non desired in many a-SiC based devices intended for high temperature and high power applications. In fact, under high temperature conditions, the metallization contacts of a-SiC degrade severely because of many factors such as the interdiffusion between layers, compositional and structural changes, thermal and/or structural induced stress that can take place at the metal/semiconductor interface. Silver has been even reported to evaporate from the SiC surface at temperatures above 600 °C.\(^{165}\) A fair
number of studies have been reported on the interface reactions between SiC and metals (including Ti,\textsuperscript{88} Cr,\textsuperscript{89} Ta,\textsuperscript{90} Mo,\textsuperscript{91} Ni-Cr alloy or TiAl\textsuperscript{92}). These reports have shown that the reaction product sequence and the interface morphology in SiC/metal reactions are mainly dependent on the contact materials. For example, in the case of SiC and Ni,\textsuperscript{93} Co\textsuperscript{94} or Pd,\textsuperscript{95} the formation of less metal-rich silicides usually occurs and a periodic morphology composed of alternating carbon and silicide has been evidenced.\textsuperscript{95} Other metals such as Ti,\textsuperscript{61} Mo,\textsuperscript{96} Fe,\textsuperscript{97} Nb\textsuperscript{98} and W\textsuperscript{99} formed both carbides and silicides after annealing at temperatures between 570 and 1200 °C and the product phases in Ti/SiC were reported to be TiC,\textsuperscript{101} and TiSi\textsubscript{3},\textsuperscript{100} Thus, the reactions of a-SiC with many metals at a potential device operating temperatures of ~600 °C severely limit the use of a-SiC-based device. Therefore, it is important to develop contacts which are stable at high temperatures. Alternatively, one may consider the use of diffusion barriers to prevent the interdiffusion at the metal-SiC interface. In fact, different alloys including\textsuperscript{93} Al\textsubscript{2}O\textsubscript{3}, TiB\textsubscript{4}, VB\textsubscript{5}, and TaB\textsubscript{5} were tested as a diffusion barrier between Ti and SiC, but none of them was found to stop effectively the diffusion of Ti into the SiC layer at a temperature of 900 °C. Finally, it is to be emphasized that most of the work related to SiC/metal interface that has been covered in the literature is based on depositing metal films on SiC substrates, but very few started with the metal as a substrate.

The focus is put in this chapter on studying the interfacial interactions between a-SiC and various underlying metal coated substrates, with the aim to identify the most chemically stable metal electrodes for the integration of a-SiC into various opto-electronic devices.
3.2. Experimental

Amorphous SiC thin films were deposited from poly(dimethylsilane) (PDMS) using an in-house built reactor. Brief description of the reactor is given in chapter two. Further details on the reactor and deposition conditions were reported elsewhere.\textsuperscript{10} Prior to the deposition, the chamber was pumped to a background pressure of $2.5 \times 10^{-2}$ Torr. Ultra high purity (UHP) argon (99.999\%) gas was then introduced into the chamber. This process of pumping and reintroducing the UHP argon was repeated four times to ensure that no oxygen remained in the chamber. The substrates and the solid polymer source were introduced to the chamber from the opposite ends of the reactor through load lock systems. The deposition time was fixed at 15 min, at 800 °C and the samples were systematically left in the chamber for an incubation period of two hours at 800 °C before removing them from the furnace. This incubation time was chosen to investigate the stability of the interface between the metallized substrates and the PS-CVD deposited a-SiC films. The metallized substrates were prepared by depositing various metallic thin films on Si wafers. These metallic thin films include refractory metals (Cr, Ti and V), high oxidation resistant metals and alloys (Ni, Ni-Cr, Au and AuPd). Furthermore, two alloys (TiN and Pt-Rh) were also used as substrates for their known excellent oxidation resistance. In addition, Si substrates coated with 1μm-thick thermally grown SiO$_2$ and LPCVD Si$_3$N$_4$ were also used in this study. The thickness of all a-SiC films deposited on various substrates was 150 nm, except the case of TiN thin metallic films on which the a-SiC thin films were 200 nm as determined by cross sectional view of SEM. The impurity level in the a-SiC films was evaluated using capacitance-voltage technique (C-V). The C-
Stability of metal-SiC contact

V measurements are carried out using mercury probe technique. The DC bias voltage is varied from −10V to 10V. Increasing the voltage will result in an increase in the width of the depletion zone \( X_d \) which will alter the capacitance of C as given in the following equation

\[
X_d = A \frac{\varepsilon_s}{C} \tag{3-1}
\]

where \( X_d \) is the depth from the surface, \( C \) is the measured capacitance, \( A \) is the capacitor area and \( \varepsilon_s \) is the semiconductor permittivity. By measuring the capacitance, \( C \), of a semiconductor capacitor at applied bias, \( V_A \), the doping \( N_d(X_d) \) is obtained as a function of position, \( X \), by the following equations.\(^{166}\)

\[
N_d(X_d) = \frac{-C^3}{q \varepsilon_s \frac{dC}{dV}} \tag{3-2}
\]

where \( N_d \) is the doping (impurity) concentration and \( q \) is the electron.

A LEO 1530 field emission gun scanning electron microscope (SEM) was used to characterize the surface morphology and to obtain cross-sectional analysis. The XPS spectra were collected by using the ESCALAB 220i-XL spectrophotometer, equipped with an Al K\(_\alpha\) (1486.6 eV) monochromatic source. Before analysis, surface films were sputter-cleaned by an ion gun using ultra high purity Ar gas. Survey scans (0 to 900 eV) were recorded for each sample to obtain a qualitative elemental analysis. Elastic Recoil Detection (ERD) technique was used to further investigate the composition depth
profiles, especially for the light elements such as hydrogen. Finally, the surface microroughness of the a-SiC films was systematically characterized by means of atomic force microscopy (AFM).

3.3. Results and Discussions

The deposited a-SiC films were integrated into MIM (metal-insulator-metal) capacitor devices and their level of impurity determined from C-V characterizations. Figure 3-1 shows typical C-V curves obtained for two extreme cases corresponding to the highest and the lowest levels of impurities. Following these C-V characterizations, the a-SiC films deposited onto the various metallized substrates were divided into three sets based on their impurity level as well as their surface morphology. Table 3.1 depicts these sets with the corresponding surface morphologies and impurity levels. The initial C-V measurements of the deposited films showed at least a five orders of magnitude difference in the impurity level from $1 \times 10^{19}$ cm$^{-3}$ (set I) to $1.0 \times 10^{13}$ cm$^{-3}$ (set II & III). Figure 3-2 shows typical top-view micrographs of a-SiC films deposited on metallized substrates from two different sets namely on Cr (for sets I and III) and on Ni (for set II). These SEM images were taken as an example which represents well the entire elements in a given set. It is clearly seen that the surface morphology of a-SiC films is highly sensitive to the underlying metallized substrate changing from very rough surface due to the high density of micron-size features on the surface in the case of Ni (Fig. 3-2(a-b)) to a very smooth, in the case of Cr (Fig. 3-2(c-d)). It is worth mentioning that the low magnification SEM images were taken to achieve general view of the surface (Fig. 3-2a and Fig. 3-2c), while the high magnification ones (Fig. 3-2b and Fig. 3-2d) were included
Figure 3-1: Variation of high frequency capacitance with respect to bias voltage measured using mercury probe technique for a-SiC thin films deposited on (a) Cr-coated Si (set I), and (b) Pt-Rh-coated Si (from set III). The inset represents the carrier concentration with respect to depletion depth extracted from the corresponding C-V characteristic curves.
Table 3.1: Various thin films coated on Si used as substrates and the corresponding surface morphology and impurity levels in the deposited PS-CVD a-SiC on these substrates. Note: The word rough used in the table to describe surfaces having several micron features [Fig. 2(a-b)], while smooth refers to surface free from any textured defects [Fig. 2(c-d)]

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Surface morphology</th>
<th>Impurity level (cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set I</td>
<td>Cr, Ti, V,TiW, SiO₂, Si₃N₄</td>
<td>Smooth</td>
</tr>
<tr>
<td>Set II</td>
<td>Ni, Ni-Cr, Au, AuPd</td>
<td>Rough</td>
</tr>
<tr>
<td>Set III</td>
<td>TiN, Pt/Rh</td>
<td>Smooth</td>
</tr>
<tr>
<td>Reference</td>
<td>Si (100)</td>
<td>Smooth</td>
</tr>
</tbody>
</table>

to give better detailed views. The micron-size features shown in Fig. (a-b) are probably formed due to the diffusion of carbon from the SiC films to the surface, as will be discussed in more details later. Thus, based on the SEM results, the set II substrates (Ni, Ni-Cr, Au, AuPd) were excluded from any further analysis, since they lead to highly rough a-SiC surfaces limiting thereby their use as metal electrodes in any device applications.

XPS analysis has been performed on the a-SiC films deposited on substrates of both set I and set III, in an attempt to observe the changes in the elemental composition of the films that would explain such a large variation in the impurity level present in the films. Figure 3-3 shows the compositional depth profiles of the a-SiC deposited at 800 °C on different substrates and kept at an incubation temperature of 800 °C for a period of 2 hrs. One can see from these profiles that regardless of the nature of the underlying substrate, the carbon to silicon atomic ratio remains unchanged around a value of ~1.2.
Figure 3-2: Top-view SEM micrographs of PS-CVD a-SiC films deposited onto Ni (Set II, table 3.1) (a) low magnification and (b) high magnification and onto Cr (set I & III, table 3.1), (c) low magnification and (d) high magnification.

In contrast, the amount of incorporated oxygen in the films is seen to be somehow substrate dependent. Indeed, the oxygen content of the films deposited onto Cr is seen to be as high ~6 at.%, while it scarcely reaches ~1-2 at.% for those deposited either on silicon or on Pt-Rh (Set III). The relatively higher level of oxygen content in the a-SiC films deposited on Set-I substrates is thought to arise from their high chemical affinity for oxygen leading to their easy oxidization from the ambient prior to the a-SiC deposition. Thus, during the deposition process and more particularly during the incubation time, the
Figure 3-3: XPS depth profiling for PS-CVD a-SiC films deposited onto various substrates: (a) Si (100) shown here as a reference; (b) Cr-coated Si (from set I); and (c) Pt-Rh-coated Si (from set III)
oxygen diffuses from the metallic substrates into the deposited a-SiC films. In contrast, noble metal substrates (such as Pt, Ir, Os, Pd or Rh, which are well known for their outstanding chemical stability and oxidation resistance\textsuperscript{167,168}) are confirmed here to lead to a very low oxygen content in the a-SiC films.

To further refine the film composition analysis of the a-SiC films but more particularly to access the interfacial information, ERD analysis was used to determine the depth profiles of the various elements including hydrogen (not accessible by XPS). Figure 3-4 shows the obtained compositional profiles (from the film surface up to depth beyond the interface) of the a-SiC films deposited on various substrates, including silicon (for reference (Fig. 3-4a), Cr-coated Si (Fig. 3-4b), Pt-Rh-coated Si (Fig. 3-4c) and TiN/Cr-
Figure 3-4: ERD depth profile of a-SiC films deposited on (a) Si substrate (b) 200nm Cr/Si (c) 100nm Pt-Rh/Si and (d) 200nm TiN/200 nm Cr/ Si. Note that the interface is defined in this figure as the region at which the atomic concentration of both Si and C changed dramatically.
coated Si (Fig. 3-4d). Figure 3-4 clearly shows that not only the interface but also the a-
SiC film composition is clearly substrate dependent. Indeed, even if all a-SiC films are
found to be carbon-rich, their Si/C atomic ratio is found to increase from ~1.1 for Cr to
~1.5 for Pt-Rh while it is almost the same (~1.3) for TiN and silicon substrates.
Moreover, ERD not only confirms the higher oxygen content (~8 at.%) of the a-SiC films
deposited onto Cr-coated Si substrates, but also reveals a diffusion of Cr atoms into a-SiC films at the interface. This seems to lead particularly to the broadest interface among all the substrates investigated. The irregularity of Cr concentration across the interface and through the a-SiC films is poorly understood at this stage. Interestingly, the a-SiC films deposited onto Pt-Rh are found to present a very stable interface; their oxygen content (~1-2 at.%) is as low as that of those deposited onto TiN, but the interface between the Pt-Rh and the underlying silicon substrate showed a strong diffusion of Si from the silicon substrates into the Pt-Rh films which in turn alter the interface structure. It is found that TiN offers a sharp interface with a-SiC; a C/Si atomic ratio and an oxygen content that are the same as for the Si (100) reference substrate, and no metallic diffusion into the a-SiC is observed. Figure 3-5 shows the surface microroughness of the PS-CVD a-SiC films (200 nm-thick) deposited onto the two potential electrode candidates (namely TiN and Pt-Rh) was investigated by AFM, and compared to that of the films deposited onto the Si(100) reference substrates. The mean roughness (R_a) and root mean square (RMS) roughness values are 1.1 and 1.4 nm respectively, for films deposited on silicon substrates, 6.2 and 7.6 nm for films deposited on Pt-Rh, and 0.5 and 3.5 nm for films deposited on TiN/Cr stack. For both films deposited on Si and TiN, the films are very smooth compared to the films deposited on Pt-Rh. The roughness of the a-SiC films deposited on Pt-Rh could be possibly due to some initial roughness in the Pt-Rh films, which might need to be optimized prior to any a-SiC deposition. By adding this surface roughness criterion to those related to the interface quality (discussed above), TiN/Cr-coated Si definitely arises as the best metallic substrate for high temperature deposition (and/or harsh environment operation) of a-SiC films intended to opto-electronic device
Figure 3-5: Three-dimensional images of 10 μm scans for PS-CVD a-SiC films deposited on: (a) Si (100), (b) 200 nm TiN/200 nm Cr/Si and (c) 100 nm Pt-Rh. Note the different vertical scales on the AFM images.
applications. Finally, it is important to point out that in order to achieve better understanding of the stability of the a-SiC metal contact, a more systematic study on the effect of annealing time and different annealing temperature on the stability of the a-SiC-metal interface will be essential.

3.4. Highlights of the Chapter

The highlights of this chapter are as follows:

- Amorphous silicon carbide (a-SiC) thin films have been deposited onto a variety of substrates, including silicon, SiO₂, Si₃N₄, Cr, Ti and refractory metal-coated silicon, by means of Polymer-Source Chemical Vapor Deposition (PS-CVD), at a substrate temperature of 800 °C.

- The interface-interactions between various metallic substrates and PS-CVD-deposited a-SiC films have been investigated following their subjection to annealing temperature of 800 °C after a 2h incubation time.

- It is clearly shown that not only the film composition, but also the interface quality is highly sensitive to the nature of the underlying substrate. Three major metallic-substrate-sets (with comparable behavior within each set) have been identified: set I (Cr, Ti, V, TiW, SiO₂, Si₃N₄), set II (Ni, Ni-Cr, Au, AuPd) and set III (TiN, Pt/Rh).

- The interfacial behavior of each of these three sets can be summarized as follows: (i) the interface between set-I substrates and a-SiC is rather unstable due to metallic diffusion and oxidation; (ii) the set-II substrates are to be avoided because of their tendency to form silicides and to lead to very rough surfaces with micron-sized
protrusions [Fig.3-2(a-b)] and (iii) The set-III substrates offer the best interface quality (in terms of narrowness and abruptness) particularly in the case of TiN.

- The impurity levels of the a-SiC films were found to be clearly correlated with the nature of the underlying substrates. The Pt-Rh and TiN-coated Si substrates are shown to lead to the lowest impurity level (~1×10^{13} cm^{-2}) in the PS-CVD grown a-SiC films, while Cr and Ti-coated Si substrates induce much higher impurity concentrations. Such high impurity levels are shown to be a consequence of a strong metallic diffusion of the metallic species (Cr or Ti). In contrast, no diffusion was observed at the interface of a-SiC with either Pt-Rh or TiN.

- The a-SiC films deposited onto TiN substrate are shown to not only contain the lowest oxygen content, but also to exhibit the smoothest surface.

- Consequently, it can be concluded that for device applications, especially at high temperature where the stability of the interface between the metallic contact and the a-SiC is essential, TiN is found to be the most interesting metal electrode material which also acts as an efficient diffusion barrier.
CHAPTER 4

EFFECT OF THERMAL ANNEALING ON THE MECHANICAL AND
STRUCTURAL PROPERTIES OF AMORPHOUS SILICON CARBIDE

This chapter covers the effect of high temperature thermal treatment on the mechanical (hardness, Young’s modulus, density and surface morphology) and structural properties of the films and their relation to the treatment temperatures. The aim is to assess the PS-CVD prepared a-SiC films as a material for applications including electronic devices as well as metallurgical and protective coatings.

4.1. Introduction

Amorphous silicon carbide (a-SiC) thin films are widely employed in many applications due to their chemical stability, hardness and interesting optical and electronic properties. One of the major advantages offered by this kind of material is the possibility to tailor its properties by varying, in the appropriate way, the preparation conditions and/or the film composition. Amorphous SiC films are extensively studied for many potential applications such as optoelectronics devices, solar cell and visible light emitting diodes (LEDs). Consequently, for the excellent mechanical properties that a-SiC posses, which are just behind those of diamond, it has been also used for a variety of high
Mechanical and structural properties of amorphous silicon carbide

temperature and mechanically demanding applications, such as MEMS coatings,\textsuperscript{149} x-ray masks,\textsuperscript{110,153,162} dielectric copper diffusion barrier,\textsuperscript{104,155} sliding friction\textsuperscript{169} and wear resistance.\textsuperscript{170} It has been shown that both the hardness and Young's modulus of the a-SiC films can be increased by different approaches including the film composition control\textsuperscript{3} and post-thermal annealing.\textsuperscript{103} The mechanical properties of a-SiC films have been shown to scale up linearly with their Si–C bonding density.\textsuperscript{3,11} This fundamental correlation highlights the crucial role of the Si–C covalent bonds and the way they connect to each other on the mechanical properties of the a-SiC films. It is expected that thermal treatment of SiC films significantly improves the thermal conductivity, creep resistance and strength retention of these films with minimal degradation in their ultimate tensile strength. Moreover, thermal treatment is expected to reduce defects and improve the mechanical and structural properties of SiC films.

The aim of the present work is to report on the effect of thermal annealing (750-1200 °C) on the microstructural and mechanical (hardness, Young's modulus) of a-SiC films deposited by means of a newly developed polymer-source chemical vapor deposition (PS-CVD) process. Our results confirm that the annealing induced enhancement of the mechanical properties of the a-SiC films correlates well with the measured film densification.

4.2. Experimental

The a-SiC films were grown using an in-house built PS-CVD system that was previously described.\textsuperscript{10} Poly(dimethylsilane) (PDMS) is used as a single polymeric source
Mechanical and structural properties of amorphous silicon carbide

for both Si and C. Argon is used as a carrier gas. Unless otherwise specified, all films were grown on Si (100) substrates for a deposition time of 15 minutes. The as-deposited films were subsequently subjected to post-deposition annealing treatments at $T_a$ ranging from 850 to 1200 °C for 10 min. in a 3"-diam. quartz tube furnace under ultra high purity (UHP) Ar flow. The IR absorption experiments were carried out using a Fourier transform infrared (FTIR) spectrometer (Matterson Instruments 6020 Galaxy series). The spectra were performed over the 400-4000 cm$^{-1}$ spectral range at a resolution of 4 cm$^{-1}$. X-ray photoelectron spectroscopy (XPS) was used to acquire structural spectra using the ESCALAP 220I-XL spectrophotometer, equipped with an Al K$_\alpha$ ($h\nu=\text{1486.6 eV}$) as excitation energy. Before analysis, surface films were sputter-cleaned by an ion gun using UHP Ar gas. High-resolution scans (0 to 900 eV) were recorded for each sample to obtain a qualitative elemental analysis. Detailed scans over narrow energy ranges were recorded around each peak of interest: Si$_{2p}$ (98.0-103.0 eV) and C$_{1s}$ (280.0-288.0 eV) core levels were measured. A spectral decomposition process was used to extract the overlapped components of the FTIR and XPS experimental spectra of PS-CVD a-SiC films for the as-deposited and annealed samples. To characterize the density changes associated with the annealing process, we performed x-ray reflectometry (XRR) measurements on the a-SiC layers annealed at different temperatures. The surface topography of a-SiC grown films was investigated by tapping mode AFM. The AFM images were obtained under ambient laboratory conditions and the scans were 20 μm in size.

The mechanical properties (hardness ($H$) and Young's modulus ($E$)) of the a-SiC films were determined by using the nanoindentation method. The nanoindentation tests
were carried out by using a commercially available ultra low load indentation system, the Nano-Indenter II, at Nano Instruments, Inc. Each indent gives hardness and Young's modulus as a continuous function of the indenter's displacement into the sample. Ten indentations were performed on each sample. Loading was controlled such that the loading rate divided by the load was held constant at 0.05/sec. Experiments were terminated at a depth of approximately 270 nm. A sample of fused silica was used as a reference for the mechanical testing. A diamond indenter was used with a load of up to 19 mN. The load and displacement were recorded continuously throughout the loading/unloading sequence to produce load-displacement curves. The results for $H$ and $E$ versus penetration depth for the ten indentation experiments on a particular sample were averaged together using discrete displacement windows of approximately 5 nm. The bond density of Si–C (N_{Si-C}) and Si–H (N_{Si-H}) were extracted from FTIR spectra and the relations between the bond density and both $H$ and $E$ were established.

4.3. Results and Discussions

4.3.1 IR Absorption Analysis

The films deposited at 750 °C and then annealed at various annealing temperatures were investigated by IR absorption spectroscopy. Special attention is given to the evolution of Si–C and Si–H absorption bands as a function of annealing temperature. Figure 4-1(a) shows the FTIR spectra of the PS-CVD a-SiC films, deposited on Si (100) substrates, as a function of $T_a$. The FTIR spectra [Fig. 4-1(a)] of the as-deposited films is seen to consist mainly of one prominent band centered around 778 cm$^{-1}$ which is the
Figure 4-1: FTIR spectra of PS-CVD α-SiC films deposited at 750 °C and annealed for 10 min at different annealing temperatures ranging from 850 to 1200 °C. (a) Full range scanned spectra from 400-4000 cm⁻¹ (For the sake of clarity, the spectra are vertically shifted, and the part of the spectra 1900-2300 cm⁻¹, magnified by a factor of 10 in the absorption coefficient) (b) Si-C band position and bond density [extracted from Fig. 4-1(a)] as a function of annealing temperature.

characteristic of the stretching vibrations of Si–C bonds.⁹⁵,¹⁷¹ The FTIR spectra of the as-deposited films shown in Fig. 4-1(a) is best fitted by a Gaussian band which, gradually narrows and becomes more intense as Tₐ is increased from 850 to 1200 °C. Obviously, the absorption peak centred around 2100 cm⁻¹, which is due to the stretching vibration of the Si-H bands,¹⁷¹ gradually disappears as Tₐ is increased from 850 to 1200 °C. The Si-C
absorption bands were quantitatively analyzed and both the Si-C absorption band position (\(v_o\)) and the absorption coefficient \(\alpha(v_o)\) were deduced as a function of \(T_s\). In addition, the Si–C bond density \(N_{Si-C}\) of the PS-CVD a-SiC films as well as the Si–H bond density \(N_{Si-H}\) were determined using the inverse cross section and the integrated absorbance of the Si-C stretching absorption band.\(^{172}\) A deconvolution of the Si-C band, for as-deposited and selected films annealed at 1200 °C, is carried out to further analyze the structural changes induced by \(T_s\). Figure 4-1(b) shows quantitatively that, as \(T_s\) is increased from 850 to 1200 °C, the peak position \((v_o)\) and the bond density of a-SiC dominant spectra follow the same trend. The \((v_o)\) is linearly increased from 776 (for as-deposited films) to 795 cm\(^{-1}\) (for films annealed at 1200 °C). Similarly, the bond density continuously increases \([(11-13)\times10^{22} \text{ bond cm}^{-3}]\) when \(T_s\) increased from 850 to 1050 °C and then abruptly increases to much higher value \(~23\times10^{22} \text{ bond cm}^{-3}\) as a result of increasing the \(T_s\) from 1050 to 1200 °C. From the integrated absorbance of the Si-C and Si-H bands, we estimated the Si–C and Si–H bond densities (according to the procedure previously described in Ref. [173]) of the films and plotted it as a function of \(T_s\). Figure 4-2 confirms that the Si–C bond density of the a-SiC films significantly increases with \(T_s\).

This result shows that thermal annealing at increasing \(T_s\) leads to a more dense and possibly more ordered microstructure of the a-SiC films. It is worth noting that after annealing at 1200 °C, the Si–C bond density is seen to increase in a more abrupt way and the band has become narrower. Prado et al. reported similar results, where it was shown
that the heat-treated SiC phase is more similar to the crystalline SiC. In contrast, the Si–H bond density varies in a different way: as the films are annealed at 850 °C, the Si–H bond density ($N_{\text{Si-H}}$) decreases about 16% from its original value before annealing (2.5 x10$^3$ bond-cm$^{-3}$ for as-deposited samples). The $N_{\text{Si-H}}$ decreases much steeper (~70% of the original ($N_{\text{Si-H}}$) as $T_a$ increases from 850 to 1050 °C. A less pronounced decrease of $N_{\text{Si-H}}$ can be seen for $T_a$ above 1050 °C. Similar results are found for a-SiC films deposited by PECVD in others work. The observed gradual decrease of $N_{\text{Si-H}}$, suggests that the increase of $T_a$ induces Si–H bonds breaking, which is expected to lead to more hydrogen release and subsequent Si–C bond formation in the film.

More precise information on the evolution of the film structure was obtained from
the deconvolution of the IR absorption envelopes (ranging from 400 to 1200 cm\(^{-1}\)) into the component absorption bands. This is illustrated in Fig. 4-3, which shows decomposition of the FTIR absorption band of the as-deposited [Fig. 4-3(a)] and annealed at 1200 °C [Fig. 4-3(b)] films. The relative integrated intensities of the component bands are determined as their integrated areas. In Fig. 4-3(a), three Gaussian peaks were needed to achieve good fit of the integrated absorption spectrum of as deposited films. The main peak centered around 778 cm\(^{-1}\) (denoted by ‘G1’) is attributed to SiC lattice mode\(^{172}\) and represents about 75% of the total peak area. Moreover, the shoulder located at around 940 cm\(^{-1}\), (denoted by ‘G2’) represents about 23% and can be attributed to a combination of Si-CH\(_n\) wagging vibration and the (SiH\(_x\))\(_n\) bending modes located at around 915 cm\(^{-1}\) position,\(^{173}\) and a-SiC:H wagging mode\(^{175,176}\) centered at 990 cm\(^{-1}\), but in some cases assigned to non-hydrogen Si-O stretching vibration\(^{171}\) or CH\(_n\) wagging and/or rocking mode.\(^{177}\)

Finally, the shoulder located around 625 cm\(^{-1}\), (denoted by ‘G3’) represents about 2% of the total area and could be assigned to Si-H\(_n\) wagging mode.\(^{129}\) Likewise, Figure 4-3 (b) shows a deconvolution of the FTIR absorption band of the a-SiC sample annealed at 1200 °C. In this case, a forth band (Lorentzian band denoted by ‘L1’) peaked at 799 cm\(^{-1}\) is needed to fit the Si-C band [(Fig. 4-3(b)]. The two dominant Si-C bands in Fig. 4-3(b) are a Gaussian band centered at 783 cm\(^{-1}\) (denoted by ‘G1’) and a Lorentzian band centered at 799 cm\(^{-1}\) (denoted by ‘L1’) represent about 92% of the total area under the band. Furthermore, the band centered at 940 cm\(^{-1}\) before annealing (‘G2’), is not only shifted to a lower wave number but the relative area percentage of this peak is drastically
Figure 4-3: Typical deconvolution of the dominant Si-C band for (a) as-prepared a-SiC film [three contribution peaks: (G1) Si-C stretching vibration, (G2) Si-CH₃ wagging vibration and (G3) Si-H₃ wagging vibration] (b) films annealed at 1200 °C [Four contributions: (G1) Si-C stretching vibration, (L1) Si-C Lorentzian stretching vibration band, (G2) Si-CH₃ wagging vibration and (G3) Si-H₃ wagging vibration]
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decreased from about 25% before annealing to \(-4\%\) after annealing. Hence, the decrease of the relative area percentage of the peak centered at 940 cm\(^{-1}\) and the increase of the area percentage of the SiC dominant peaks centered at (783 and 799 cm\(^{-1}\)) further confirm hydrogen related bonds breaking and evolution of hydrogen, which in turn lead to more Si–C bond formation.\(^{172}\) In a similar manner, the third band centered at 625 cm\(^{-1}\) before annealing (denoted by ‘G3’) is shifted to a higher wave number (634 cm\(^{-1}\)) and its relative area slightly increased (from 2.5 to 4\% of the total area).

4.3.2 XPS Analysis

The increase of Si–C bond formation observed in the analysis of FTIR in the previous section is further confirmed in much the same way by XPS spectra for the selected Si\(_{2p}\) and C\(_{1s}\) core levels for as-deposited films compared to annealed ones at 1200 \(^\circ\)C as illustrated in Fig. 4-4. The spectrum of the Si\(_{2p}\) core level shown in Fig. 4-4(a) (before annealing) was decomposed into two Gaussian peaks: the first component (dotted line) with a low-energy (100.15 eV) represents about 71\% of the total Si\(_{2p}\) line area with FWHM of about 1.49 eV and is attributed to the Si\(_{2p}\) peak in \(\beta\)-SiC.\(^{178}\) The second component (dashed line) which has a higher-energy of (101.2 eV) and a FWHM of 1.61 eV, can be assigned to the Si\(_{2p}\) in SiC\(^{131,179}\) or an overlap of three components: Si-C, SiOC and SiO\(_2\) bands.\(^{180,181}\) As a result of annealing [Fig. 4-4(b)], several points can be pointed out; (i) the total area under the as observed Si\(_{2p}\) component (solid lines) increased by about 12\%; (ii) the area under the low-energy Si\(_{2p}\) component (dotted line) increased by about 17\% accompanied by a decrease of the area under the higher-energy Si\(_{2p}\) component.
Figure 4-4: XPS spectra acquired from the PS-CVD a-SiC for (a) Si_2p core levels for as-deposited films (b) Si_2p core levels for annealed films at 1200 °C (c) C_1s core levels for as-deposited films and (d) C_1s core levels for annealed films at 1200 °C. (The solid lines represent as observed spectra, while the dotted and dashed lines (Si_2p spectra) represent low energy Si-C and higher energy SiC components, respectively. The dotted, dashed and dotted-dashed lines (C_1s spectra) represent the carbide components (in the Gaussian approximation) given by a C-Si, C-C and C-O, respectively)

(dashed line) of about 17%; (iii) the FWHM of the lower energy component decreased by about 0.15 eV from 1.49 to 1.34 eV. In the same manner, the FWHM of the Si_2p higher-component decreased by at least 0.55 eV. Such transformation from the higher energy component of Si_2p (101.2 eV assigned to a-SiC by Santoni et al.\textsuperscript{179} and Trusso et al.\textsuperscript{131}) to the lower energy component (100.15 eV assigned to β-SiC by Tabata et al.\textsuperscript{179}) is a further indication of microstructural change and more ordered Si–C bonds.\textsuperscript{181}
Preliminary fit results of the C_1s [Fig. 4-4(c-d)] have shown that a satisfactory fit of the C_1s core levels of the as-deposited and annealed films requires three components: (i) the first component (dotted line), whose peak energy is slightly decreased from 283.5 to 283.4 eV and its relative area decreased from 91 to about 84% as the samples annealed at T_a of 1200 °C, is assigned to C–Si bonds in the SiC films;^{182} (ii) the second component centered at 284.6 eV (dashed line) is attributed to C–C bonds in the SiC films.\(^{183}\) This component represents about 6% of the total C_1s line (as-deposited) and increased to more than 14% after annealing; (iii) the third component peaked at 286 eV (dotted-dashed line) and represents about 2.3% of the total C_1s line before annealing (assigned to C-O).\(^{183}\) The peak position of this component shifted slightly from 286 to 286.2 eV and its area increased from 2.3% to ~3.0% after annealing. This is probably due to additional oxygen contamination.\(^{184}\) The presence of one component at higher binding energy at about 284.3 eV could indicate the presence of sp\(^2\) carbon species or graphite\(^{172}\) in the a-SiC films,\(^{185}\) where the coexistence of graphitic environments and sp\(^3\)-carbon environments has been suggested on the basis of data obtained by infrared spectroscopy and XPS.\(^{186}\) The observed component centered at 284.6 eV (represent about ~ 6% of the total C_1s before annealing) is probably due to excess carbon in the films (Si:C as 1:1.3) as confirmed by XPS and ERD analysis (not shown). The increase of the area under the C-C peak from about 6 to 14% was attributed to carbon contamination originating from the residual gas contamination. Such increase of the area under the component centered at 284.6 as a result of annealing is in agreement with a previous work on the effect of rapid thermal annealing on the stress and bonding states of a-SiC:H films prepared by PECVD.\(^{172}\)
4.3.3 Film Density

The observed effect of $T_a$ on the Si–C bond density shown in the FTIR and XPS spectral analysis is also confirmed by measuring the film density. Figure 4-5 represents can be noticed that there is a linear correlation between the film density and $T_a$. For

![Graph showing density of SiC films vs. annealing temperature](image)

**Figure 4-5:** Density of PS-CVD a-SiC films deposited at 750 °C and annealed for 10 min as a function of annealing temperature. The inset in Fig. 4-5 represents AFM image of films annealed at 1200 °C.

Instance, the density of the a-SiC films increased from 2.36 to $\sim$ 2.75 g/cm³ as a result of increasing $T_a$ from 750 °C to 1200 °C. In fact, the density of 2.75 g/cm³ (films annealed at 1200 °C) is about 16% less than that of the value of 3.2 g/cm³ given in the literature for crystalline SiC.$^{187}$ The inset of Fig. 4-5 shows AFM image of a-SiC films after annealing
at 1200 °C. It is noteworthy that the surface morphology of the films annealed at 1200 °C stayed smooth and the root-mean-square ($R_{\text{rms}}$) of about ~1 nm stayed constant.

4.3.4 Hardness and Elastic Modulus

Figure 4-7 shows a typical load–displacement curve generated during loading and unloading of a diamond indenter used to determine $H$ and $E$ of the as-deposited and annealed a-SiC films at 1200 °C with penetration depth of 277 nm. It is noted that the load needed to achieve the same penetration depth is higher for the annealed films (16.4 mN), compared to as-deposited films (15.9 mN). At the outset of the indentation, the loading path usually exhibits non-linear behavior caused by the loose structure. Generally, the elastic modulus is calculated from the unloading curve and the penetration depth is used to acquire the hardness value.

In view of the effect of thermal annealing on both $H$ and $E$, the depth dependence of $H$ and $E$ for the as-deposited and annealed a-SiC films is presented in Fig. 4-7(a) and Fig. 4-7(b). It can be noted that there is a clear increase of both $H$ and $E$, particularly when $T_a$ is increased to 950 °C and above. The initial variations of $H$ and $E$ values over the first 30 nm are most probably due to the surface roughness and/or contamination. For higher penetration depths, the values of both $H$ and $E$ are constant through the a-SiC films over the 30-150 nm indentation depth range. Indeed, it also can be noted that as the indenter penetration increases beyond 150 nm, the measurements are increasingly affected by the underlying substrate. This is evident by comparing the a-SiC indentation curves with bulk silica reference sample, which shows constant values of both $H$ and $E$ over the entire indentation depth. In this perspective and for more reliable determination
Figure 4-6: Typical force versus displacement curves used to measure hardness and Young’s modulus of PS-CVD a-SiC. Note that as-deposited and annealed at 1200 °C a-SiC films are included for comparison.

of the \( H \) and \( E \), only the data covers a penetration depth of 30-150 nm is considered in all cases to avoid any effect of surface contamination and/or substrate effects. The correlation between the average \( H \) and \( E \) with respect to \( T_a \) is presented in Fig. 4-8. It can be observed that the average of the \( H \) and \( E \) increases from 15.5 to 17.6 and from 155 to 178 GPa, respectively, with increasing \( T_a \) from 750 to 950 °C. However, for \( T_a \geq 950 \) °C, the increase of both \( H \) and \( E \) is less marked and almost reaches a plateau.

By comparing the effect of increasing \( T_a \) from 750-950 °C on \( H \) and \( E \) (Fig. 4-8) from one side and \( N_{Si-C} \) and \( N_{Si-H} \) (presented in Fig. 4-4) from another side, a reasonable hypothesis is that increasing the annealing temperature, while it promotes Si–C bond
Figure 4-7: Nanoindentation measurements (a) hardness (b) Young's modulus as a function of indentation depth of PS-CVD a-SiC deposited on Si (100) at 750 °C and then annealed for 10 min. at different annealing temperatures. As a control, a sample of fused silica (amorphous SiO₂) was tested and included with this set of samples.
formation, also decreases the hydrogen content in the films. It is well established in the literature that the hardness of amorphous SiC reaches a maximum for hydrogen-free films.\textsuperscript{188} Further support to such hypothesis is the increase of film density observed as a result of annealing temperature (Fig.4-5) and the increase of area under the Si-C observed bands (Fig.4-2). A possible explanation for the less marked effect of annealing on both $H$ and $E$, especially at $T_a > 950 \, ^\circ C$ is the increase of the formation of graphitic bonding (Fig. 4-4) as a result of annealing which might reduce the $H$ and $E$ at elevated $T_a$. The increase of C–C bonds in SiC is well known to reduce both $H$ and $E$.\textsuperscript{189} As a consequence, a compensation between the increase of the Si–C and C–C bond densities may takes place.
which in turn limit the increase of both $H$ and $E$ at $T_s > 950 \, ^\circ\text{C}$.

### 4.3.5 Dependence of both Hardness and Young’s Modulus upon the Si–C Bond Density

In order to further understand the dependence of both $H$ and $E$ on Si–C bond density, the average values of $H$ and $E$ are plotted against $N_{\text{Si-C}}$ as illustrated in Fig. 4-9. For that matter, our previously established constant-plus-linear dependence of both $H$ and $E$ upon the $N_{\text{Si-C}}$, over the $[(4-24)\times10^{22} \, \text{cm}^{-3}]$ range$^{3,11}$ for both PECVD a-SiC:H and hydrogen-free LAD a-SiC, are added to the figure. It can be noted in much the same way that the established constant-plus-linear relation fits with PS-CVD a-SiC films the same way with both PECVD and LAD a-SiC films. It is expected that the established constant-plus-linear relation between both $H$ and $E$ with the Si–C bond density will fit with any SiC thin films regardless of the preparation method or film structure. By comparing Figs. 4-2, 4-5 and 4-8, it is not surprisingly apparent that annealing induced similar effect on the variations of bond density (Fig. 4-2), film mass density (Fig. 4-5) and both hardness and Young’s modulus (Fig. 4-8).

### 4.4. Highlights of the Chapter

The highlights of this chapter are as follows:

- Synthesis of amorphous SiC films was performed by PS-CVD under Ar gas ambient.
- The effect of annealing temperature, $T_s$ over the 850-1200 °C range on the structural and mechanical (hardness and Young’s modulus) properties of the PS-CVD a-SiC films has been investigated. The increase of $T_s$ (from 850-1200 °C) resulted in a shift of a-SiC integrated absorption FTIR bands from 778 up to 799 cm$^{-1}$. Moreover the
Figure 4-9: Constant-plus-linear dependence of both (a) the hardness and (b) the elastic modulus of a-SiC films upon their Si–C bond density. Data from Ref. 3 (closed circle) and Ref. 11 (open circle) were added to the data of the present work (filled square). The dashed lines represent visual fitting curves.
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increase in $T_a$ favors the formation of Si–C bonds, leading thereby to a significant increase in the Si–C bond density from 101.6 to $224.5 \times 10^{21}$ bond·cm$^{-3}$. Moreover, a reduction of Si–H bond density from 2.58 to $0.46 \times 10^{21}$ bond·cm$^{-3}$ is also observed, which is probably due to the release of hydrogen from the a-SiC:H.

- The XPS results also confirm the increase in Si–C related bonds observed from FTIR analysis. At the same time, an increase in carbon concentration in the form of C–C bonds was also observed, especially at $T_a > 950 \, ^\circ$C.

- Annealing-induced film densification is confirmed by the XRR measurements, as the a-SiC film density is found to increase from 2.36 to $\sim 2.75$ g/cm$^3$ when $T_a$ is raised from 750 to 1200 °C. In particular, in the high temperature regime, the density of PS-CVD a-SiC is about 16% less than that reported for c-SiC.

- The measurements of both $H$ and $E$ over an indentation depth of 277 nm and the calculated average $H$ and $E$ over the indentation depth of 30-150 nm clearly show that both $H$ and $E$ increase from 15.5 to 17.6 GPa and from 155 to 178 GPa, respectively as a result of increasing $T_a$ from 750 to 1200 °C.

- It is also confirmed that the constant-plus-linear-relation derived in our previous work applies for PS-CVD a-SiC films, which is a further indication that regardless of the SiC deposition process and/or film composition, the derived plus-linear relation is a strong indication that the Si–C bond density is the major detrimental factor that control both hardness and Young’s modulus of SiC films.
CHAPTER 5

CORRELATION BETWEEN STRUCTURAL AND MECHANICAL PROPERTIES OF HYDROGENATED AMORPHOUS SILICON CARBONITRIDE FILMS

This chapter correlates between the structural and mechanical properties of the a-SiCN:H films, and correlated these properties with the nitrogen concentration induced into the films. Main focus is put on the hardness, Young's modulus, and surface morphology of these films. More detailed study on the structural properties and bonding configurations is discussed in chapter six.

5.1. Introduction

Amorphous silicon carbide (a-SiC) thin films are widely employed in many applications due to their chemical stability, hardness and interesting optical and electronic properties. One of the major advantages offered by this material is the possibility to tailor its optical, electrical and structural properties by controlling, in an appropriate way, its atomic composition. For example, the incorporation of hydrogen atoms into the films is known to saturate the dangling bond, thereby improving their optical and electronic
Structural and mechanical properties of silicon carbonitride

properties. The hydrogen content also has a dominant effect on the film density, its refractive index, and on photoluminescence efficiency. The introduction of fluorine atoms has been also reported to improve the thermal stability of the a-SiC films, resulting in both an optical band gap widening and a decrease in the electrical conductivity values. Incorporating N atoms in the SiC network has been shown to be effective in significantly increasing the optical band gap of SiC films. Gomez et al. proposed that a-SiCN based alloy should have properties between silicon nitride and carbon nitride. Indeed, optical investigation of the polycrystalline SiCN films indicated a direct band gap of about 3.8 eV and a strong optical emission around 2.8 eV. Thus, the ternary SiCN compound constitutes an excellent material which exhibit not only a wide band gap, but also good mechanical properties, excellent thermal stability and exceptional high-temperature creep resistance. In particular, it has been reported that SiCN films posses higher thermal stability in comparison with the binary Si-N or Si-C amorphous thin films. Composite materials containing silicon, carbon and nitrogen demonstrate high-performance mechanical and chemical properties including hardness, fracture toughness and corrosion resistance. This combination of mechanical, chemical and to some extent electrical properties makes these composites useful in applications where high-performance materials are needed due to exposure to extreme conditions such as high temperatures, mechanical stresses and corrosive environments such as heat engines, cutting tools, wear and friction surfaces and space vehicles. In recent years, the use of ceramics has extended into the fields of microtechnology and nanotechnology. The need for these qualities extends to medicine as well, since a variety of medical devices, such as
implants, prostheses and surgical devices, would benefit from a combination of high strength and chemical inertness (as previously discussed in Chapter 2).

Silicon carbonitride (SiCN) films have been prepared by using either physical or chemical-based vapor deposition techniques. As an illustration, amorphous and hydrogenated SiCN films were grown by ion-plasma sputtering of a-SiC target.\textsuperscript{193} Plasma-assisted chemical vapor deposition (PA-CVD) was also used to grow a-SiCN:H films from SiH\textsubscript{4}-NH\textsubscript{3}-C\textsubscript{2}H\textsubscript{4} or (CH\textsubscript{4}-H\textsubscript{2}) precursor gases.\textsuperscript{194,195}

In the following sections, the focus is put on the effect of the increasing N incorporation in the a-SiCN:H films on their structural and mechanical (hardness, Young's modulus, and surface morphology) properties. A correlation between the structural and mechanical properties of the prepared a-SiCN:H films is presented.

5.2. Experimental

The deposition of a-SiCN:H films onto silicon (100) substrates has been carried out using a PS-CVD system.\textsuperscript{10} This reactor uses poly(dimethylsilane) as a single precursor for both Si and C, NH\textsubscript{3} as nitrogen source and argon as a carrier gas. The level of nitrogen in the films was controlled by adjusting the NH\textsubscript{3}/Ar ratio in the PS-CVD reactor. Thus, the N content of the a-SiCN:H films can be controlled. All films were grown on Si(100) substrates for a growth time of 15 min. Mass flow controllers were used to control the NH\textsubscript{3}/Ar flow ratio. The IR absorption spectra were recorded at room temperature in the 400-4000 cm\textsuperscript{-1} range, at a resolution of 4 cm\textsuperscript{-1}, with a bare silicon wafer used as a reference. The XPS spectra were acquired with VG ESCALAB MKII system equipped
with an Al Kα (1486.6 eV) monochromatic radiation source to measure the atomic percentage of the film composition. A spectral decomposition process was used to extract the FTIR and XPS components in order to achieve better understanding of the microstructural modifications induced in the a-SiCN:H films as a result of increasing the N at.% in the films. Subsequently, atomic force microscope (AFM) is used to obtain 2-D and 3-D images of the prepared films and to calculate the average root mean square roughness (Rrms) with respect to N at.%. The mechanical properties [hardness (H) and Young’s modulus (E)] of the PS-CVD a-SiCN:H films were characterized by using a commercially available ultra low load nanoindentation system (the Nano-Indenter II, at Nano Instruments, Inc). With this technique, each indent gives hardness and Young’s modulus as a continuous function of the indenter’s displacement into the samples. Ten indentations were performed on each sample. Loading was controlled such that the loading rate divided by the load was held constant at 0.05/sec. Experiments were terminated at a depth of approximately 270 nm. The average H and E were calculated at a depth of 30-150 nm in the films. At the same time, the Si–C bond density is calculated from the FTIR extracted components and a correlation between the average H and E with respect to Si–C bond density was established. It is worth mentioning here that Fused silica was used as a reference for the mechanical testing.

5.3. Results and Discussions

The nitrogen content in the a-SiCN:H films was measured with respect to the NH₃/Ar ratio in the flow using XPS. The average concentrations of the nitrogen [N] were
then calculated from the values measured in the bulk of the films and a relation between the [N] and NH$_3$/Ar flow ratio is established as presented in Fig. 5-1. It can be observed that N content in the a-SiCN:H films steadily increased from 0 to 27 at.% as a result of increasing the NH$_3$/Ar flow ratio from 0 to 4×10$^{-3}$. Obviously, the high atomic percentage

![Graph showing nitrogen atomic percentage as a function of NH$_3$/Ar flow ratio](image)

**Figure 5-1:** Nitrogen atomic percentage in the a-SiCN:H films as a function of NH$_3$/Ar flow ratio. The [N] values are measured by XPS.

of nitrogen incorporated into the a-SiCN:H films as a result of introducing a very small NH$_3$/Ar flow ratio is an indication of the effectiveness of NH$_3$ as source for nitrogen.
5.3.1 FTIR Spectroscopy Measurements

Figure 5-2 shows the FTIR spectra of the a-SiCN:H films as a function of their [N]. When [N] = 0 at.%, the films are then characterized by the presence of two main bands: (i) the absorption band centered around 779 cm\(^{-1}\), which is due to the stretching vibrations of Si-C bonds\(^{109,172,173}\) and (ii) the absorption band covering the region from 2000 - 2200 cm\(^{-1}\), which is due to Si-H stretching vibrations.\(^{169}\) On the contrary, no bands of C-H (around 2900 cm\(^{-1}\))\(^{130}\) or N-H (around 3400 cm\(^{-1}\))\(^{196}\) were detected in the spectra for samples without nitrogen content. Consequently, as the [N] is increased from 0 to 27 at.%; three main changes are observed in the FTIR spectra: (i) the maximum of the main SiC stretching vibrations band shifts to higher wave numbers as [N] is increased; (ii) an increase of Si–H (~2100 cm\(^{-1}\)) band and a shift of the maximum of this band to a higher wave number is also observed as a result of increasing N concentration in the a-SiCN:H films and (iii) the formation of a new band centered around 3400 cm\(^{-1}\), which is assigned to N–H stretching vibration.\(^{196}\) Although the relative intensity of this band is smaller than Si–H for all values of [N], the N–H is evident in the spectra of a-SiCN:H at all values of [N]. The shift of the main dominant absorption bands (779–850 cm\(^{-1}\)) together with their intensity decrease are evidenced in Fig. 5-2(a) and more quantitatively in Fig. 5-2(b). The shift of the band maximum from 779 cm\(^{-1}\) (for [N] = 0 at.%) to 850 cm\(^{-1}\) (for [N] = 27 at.%) strongly suggests that N atoms are substituting C atoms in the Si-C local environments, since the Si-N stretching vibration in a-SiN films are known to occur in the range of 840-910 cm\(^{-1}\).\(^{197}\) Furthermore, the band intensity decreased by ~50% as a result of increasing the N content in the films from 0 to 27 at.%. The inset of Fig. 5-2(b) shows
Figure 5-2: (a) Infrared spectra of the PS-CVD a-SiCN:H series of samples as a function of [N]. The atomic percentages of nitrogen shown in the figure (0-27 at.%) are measured by XPS with respect to NH₃/Ar flow ratio as detailed in Fig. 5-1. For the sake of clarity, the 3200-3400 cm⁻¹ region is amplified by a factor of 5, and the spectra are vertically shifted. (b) Si-C absorption bands position and intensity as a function of N at.%. [The data is extracted from the FTIR spectra of Fig. 5-2(a)]. The inset of Fig. 5-2(b) is a deconvoluted spectrum of a-SiCN:H at [N] = 20 at.%. 
the deconvolution of a selected band in FTIR spectrum of the a-SiCN:H films ([N] = 20 at.%). In fact, the deconvoluted spectrum has five major components: (i) a weak component at 630 cm⁻¹ is attributed to SiH₆ wagging mode,;¹²⁹ (ii) the absorption band centered around 786 cm⁻¹, is due to the stretching vibrations of Si–C bonds,;¹⁰⁹,¹⁷² (iii) the component around 878 cm⁻¹ is assigned to Si-N (850-910 cm⁻¹ is assigned for Si-N, Ref. 183); (iv) the component at ~ 972 cm⁻¹ is attributed to the wagging vibration of C–H₆ bonds in Si–CH₆ groups.¹⁷⁶,¹⁹⁸ It could be also assigned to the (SiH₂)ₙ bending modes located at around 915 cm⁻¹ position¹⁰⁹ and a-SiC:H wagging mode¹⁷⁶ centered at 990 cm⁻¹. In some cases, this band is also assigned to non-hydrogen Si–O stretching vibration.¹⁷¹ (v) a very weak band centered at 1140 cm⁻¹ is believed to be due to N–N bond.¹⁹⁹ The rare occurrence of the N–N bonds in the material can be assumed to be the result of a solid matrix resulting from a process driven by thermodynamic control, due to the fact that the N–N binding energy is the weakest in the system: \( E(\text{N–N}) = 1.65 \text{ eV} \), with respect to other bonds actually present in the films: \( E(\text{Si–N}) = 3.45 \text{ eV} \), \( E(\text{N–H}) = 4.05 \text{ eV} \), \( E(\text{Si–H}) = 3.34 \text{ eV} \) and \( E(\text{Si–Si}) = 2.3 \text{ eV} \).²⁰⁰ As a matter of fact, Fig. 5-3 shows a quantitative representation of the Si-H [Fig. 5-3(a)] and N-H [Fig. 5-3(b)] absorption bands position and intensity extracted from Fig. 5-2. The shift of Si–H absorption to a higher wavenumber is in agreement with the increased force constant due to the formation of H–Si–N groups, while the increase of IR-intensity can be attributed to increased N and H incorporation (from NH₃) that leads to the Si–H bonds formation.¹⁷¹ In much the same manner, the increase of N–H bond density could also be due to the increase of H percentage which lead to more N–H formation. The fluctuation of the N–H band position is poorly understood and further investigation is needed.
Figure 5-3: Position and intensity of the Si-H and N-H absorption bands as a function of N content. [The data extracted from the spectra presented in Fig. 5-2(a)]. As indicated by the arrows, closed circles are used for the position of band maximum, while open circles are used for the band intensity.
In sum, the FTIR results clearly show that as [N] increased in the a-SiCN:H films from 0 to 27 at.%, N and H incorporation (from NH$_3$) occur through the formation of Si–N, Si–H and N–H bonds, at the detriment of the Si–C bonds. This would explain the global lowering of the intensity of the Si–C stretching absorption band and the shift of the main absorption band to higher wavenumber. Moreover, the bonding configuration between the three major constituents: Si, C and N do not form separate phases (Si–C and Si–N for example), but rather a complex structure in the inter-bonded Si–C–N.

5.3.2 XPS Analysis

In order to determine the state of chemical bonding and the compositional changes of the films, XPS analyses of the prepared films are performed. Figure 5-4 illustrates selected XPS spectra of a-SiCN:H films and the major deconvoluted components of the Si$_{2p}$, C$_{1s}$ and N$_{1s}$ peaks for samples with [N]= 0 at.% [Fig. 5-4(a)-5-4(c)] and with [N] = 27 at.% [Fig. 5-4(d)-5-4(f)]. The Si$_{2p}$ peaks presented in Fig. 5-4(a) show that two major components are needed to fit the as observed Si$_{2p}$ peak of the a-SiC:H films obtained under inert atmosphere (without NH$_3$): one is a low-energy peaked at 100.1 eV and it is the dominant peak of the total Si$_{2p}$ line attributed to Si–C.$^{20}$ Another minor peak, which has a higher-energy (101.2 eV), can be assigned a higher binding energy Si–C bond. This component is poorly understood and further work is needed to explain such peak. Furthermore, Fig. 5-4(b) illustrates the as observed C$_{1s}$ spectrum (centered at 283.4 eV) which is fitted by two components: The first peak (centered at ~ 283.3 eV) is assigned to C–Si bonds in the SiC films.$^{180}$ The relative intensity of this component represents ~78%
Figure 5-4: As observed (solid lines) XPS spectra and the deconvoluted components of Si$_{2p}$, C$_{1s}$, N$_{1s}$ of a-SiCN:H films deposited using [N] = 0 at.% [Fig. 5-4(a)-Fig. 5-4(c)] and [N] = 27 at.% [Fig. 5-4(d)-Fig. 5-4(f)].
of the total area under C$_{1s}$ spectra. The second component (centered at 284.9 eV) is attributed to C–C bonds in the SiC films$^{202}$ and represents ~22% of the total area. As expected, no N$_{1s}$ peak is observed for sample with [N] = 0 [Fig. 5-4(c)]. The deconvolution of the XPS spectra for films containing nitrogen [N= 27 at.% is presented in Fig. 5-4(d)- 5-4(f)]. It is worth mentioning that the Si$_{2p}$ deconvoluted spectrum consist of three components [Fig. 5-4(d)]; (i) the first component, centered at 100.5 eV and its relative area ~44%, is assigned to Si–C$^{201}$ (ii) the second component, centered at 101.5 eV with relative area ~ 48%, could be assigned to Si–N$^{131,183}$ and (iii) a third minor component centered at ~102.5 eV and its relative area represents ~7.8%). This component may be due to silicon present in the form of Si–O or Si–N.$^{131}$ Fig. 5-4(e) shows the effect of N addition on the C$_{1s}$ deconvoluted spectra, which has three components: (i) the first component centered at 283.3 eV and its relative area ~68% assigned to C–Si$^{180}$ (ii) a second component centered at 285 eV and its relative area ~15% which could be assigned to C–C$^{202}$ and (iii) a third component centered at 286.1 eV and its relative area is ~16.8% eV, which could be attributed to C–N.$^{203,204,205}$ For accurate fit of the corresponding N$_{1s}$ core level spectrum, two states are also needed as represented in Fig. 5-4(f). The first component centered at 398.1eV is assigned to N–Si.$^{202}$ The area under this peak represents about 88% of the total area. The second component is centered at 399.2 eV and its relative area ~11.6%, is normally assigned to N–C bond in a- SiCN:H films.$^{206,207,208,244}$ Table 5.1 summarize the XPS deconvolution of the Si$_{2p}$, C$_{1s}$ and N$_{1s}$ components and their relative areas. The significant decrease of Si–C relative area (97 to 44.2% of the Si$_{2p}$) accompanied by a much higher increase of Si–N (48% of the Si$_{2p}$) and
### Table 5.1: The results of deconvolution and relative concentration of Si$_{2p}$, C$_{1s}$ and N$_{1s}$ binding states of the XPS spectra of a-SiCN:H films grown with [N] = 0 and 27 at.\%.

<table>
<thead>
<tr>
<th>Element line</th>
<th>Bonding type</th>
<th>$E_b$ (eV)</th>
<th>Relative area (%)</th>
<th>$E_b$ (eV)</th>
<th>Relative area (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si$_{2p}$</td>
<td>Si-C</td>
<td>100.1</td>
<td>97</td>
<td>100.5</td>
<td>44.2</td>
<td>[201]</td>
</tr>
<tr>
<td></td>
<td>Si-N</td>
<td>101.2</td>
<td>3</td>
<td>101.5</td>
<td>48</td>
<td>[131, 183]</td>
</tr>
<tr>
<td></td>
<td>Si-O</td>
<td>--</td>
<td>0</td>
<td>102.5</td>
<td>7.8</td>
<td>[131]</td>
</tr>
<tr>
<td>C$_{1s}$</td>
<td>C-Si</td>
<td>283.3</td>
<td>78.0</td>
<td>283.3</td>
<td>68.0</td>
<td>[180]</td>
</tr>
<tr>
<td></td>
<td>C-C</td>
<td>284.2</td>
<td>22</td>
<td>285.5</td>
<td>15.2</td>
<td>[244]</td>
</tr>
<tr>
<td></td>
<td>C-N</td>
<td>--</td>
<td>0</td>
<td>286.0</td>
<td>16.8</td>
<td>[244, 207]</td>
</tr>
<tr>
<td>N$_{1s}$</td>
<td>N-Si</td>
<td>--</td>
<td>0</td>
<td>398</td>
<td>88.4</td>
<td>[203, 208, 209]</td>
</tr>
<tr>
<td></td>
<td>N-C</td>
<td>--</td>
<td>0</td>
<td>399.2</td>
<td>11.6</td>
<td>[204, 205]</td>
</tr>
</tbody>
</table>

N–Si (88.4% of the N$_{1s}$) compared to lower increase of C–N (16.8% of the C$_{1s}$) and N–C (11.6% of the N$_{1s}$) is a clear indication that N preferential bonding is to Si rather than C. Figure 5-5 illustrates clearly a shift of the binding energy of Si$_{2p}$, C$_{1s}$ and N$_{1s}$ peaks to a higher binding energy as the N content in the films increases from 0 to 27 at.%. Xiao et al.\(^{196}\) attributed such shift to the difference in the electronegativity of elements which plays a crucial role in the chemical shift of corresponding bonding state in XPS spectrum. The chemical shift of Si–C in Si$_{2p}$ to higher position is a result of partial replacement of C in Si–C bonding by N whose electronegativity is much higher than that of C. He et al. further attributed such shift to the presence of N and C complexes that are somewhat
Figure 5-5: Si$_{2p}$, C$_{1s}$ and N$_{1s}$ binding energy variations with respect to [N] contents in the PS-CVD a-SiCN:H. The lines are guides for the eye.
5.3.3 Surface Morphology.

Figure 5-6 shows quantitatively the surface roughness measured by AFM, as root mean square ($R_{\text{rms}}$), as a function of nitrogen [N] in the films. The $R_{\text{rms}}$ increases from 4 to 12 nm as a result of increasing [N] from 0 to 27 at.%. The increase of the films roughness as a result of increasing [N] is probably due to formation of spongy films as can be seen in the inset of Fig. 5-6. It can be also noted from the inset of Fig. 5-6 that, not only the
surface roughness increases, but also the surface becomes porous and more nano-scaled, well-shaped and defined features appeared. Such porous textured films, with a porous network could be advantageous in many potential applications. For example, Sung et al. developed tailored macroporous SiCN and SiC structures for high-temperature fuel reforming. It also has been reported in many photoluminescence studies, that porous SiC generally exhibits much more intense visible luminescence than non porous films at room temperature. Further anodization steps\textsuperscript{115,116} and chemical etching treatment\textsuperscript{117} has been used to get porous SiC samples to improve the intensity of SiC emission.

5.3.4 Hardness and Young’s Modulus

Figure 5-7 shows a typical load-displacement curve generated during loading and unloading of a diamond indenter used to determine the hardness ($H$) and Young’s modulus ($E$) of the films having $[N] = 0$ and 20 at.%. It can be noted that the load needed to achieve the same penetration depth (270 nm) is lower for nitrogen-containing films (15.1 mN) compared to nitrogen-free films (15.9 mN). At the outset of the indentation, the loading path usually exhibits non-linear behaviour caused by the loose structure. Generally, the elastic modulus is calculated from the unloading curve and the penetration depth is used to acquire the hardness value.

The remarkable change of mechanical properties due to different film composition is best illustrated in Fig. 5-8 in which the depth-dependence of both the hardness [Fig. 5-8(a)] and the Young’s modulus [Fig. 5-8(b)] of a-SiCN:H prepared under various [N] concentrations is presented. It can be noted that there is a clear decrease of both hardness
Figure 5-7: Typical force versus displacement curves used to measure hardness and Young's modulus of PS-CVD a-SiCN:H for films having [N] = 0 at. % (solid line) and [N] = 20 at. % (dashed line).

and Young's modulus as a result of increasing [N] in the films. The initial variations in \( H \) and \( E \) values over the first 25 nm are due to the surface roughness and/or contaminations.

For higher penetration depths, the values of both hardness and modulus are constant through the a-SiCN:H films over the 25-175 nm indentation depth range. It can also be noted that as the indenter penetration increases beyond 175 nm, the measurements are increasingly affected by the underlying substrate. This is evident by comparing the a-SiCN:H indentation curves with the bulk silica reference sample, which shows constant values of both hardness and Young's modulus over the entire indentation depth. For a reliable determination of the average of both \( H \) and \( E \), only the data covering a depth from
Figure 5-8: Variation of the (a) hardness, (b) Young's modulus as a function of the indentation depth for a-SiCN:H films having [N] ranging from 0 to 27 at.%. As a control, a sample of fused silica was tested and included with this set of samples.
25-175 nm was considered in all cases to avoid any effect of surface contamination and/or substrate effects. The correlation between the average $H$ and $E$ with respect to [N] are presented in Fig. 5-9. Hence, it can be noted from the extracted data presented in Fig. 5-9 that increasing the [N] from 0 to 27 at.% results in a decrease of the hardness from 17 to 13 GPa and the Young’s modulus from 160 to 136 GPa. There are several reasonable hypotheses behind the decrease of both $H$ and $E$ with increasing [N] in the films. As previously discussed in the FTIR and XPS sections, Si–N, Si–H and N–H bonds are incorporated at the expense of Si–C bonds. Therefore, the decrease in Si–C bonds is believed to be the major factor behind the decrease in both hardness and Young’s modulus knowing that Si–C bonds is the stiffest one, the formation of Si–N, Si–H and N–H bonds at the detriment of Si–C would definitely lead to lowering the mechanical properties of a-SiCN:H in comparison with a-SiC. In addition, the incorporation of hydrogen (from NH$_3$) in the films, represented in Si–H, N–H bonds, further decrease both $H$ and $E$ as reported by Kulikovsky et al.$^{188}$ Furthermore, the decrease of both $H$ and $E$ could be also related to the difference in microstructure (fully dense or porous films) as discussed previously in the surface morphology section, since textured films with a porous network possess limited mechanical properties, due to a moderate coordination number.$^{210}$ As previously discussed, the decrease in Si–C bond density is the major detrimental factor in reducing both hardness and Young’s modulus of PS-CVD a-SiCN:H film. The relation between the average hardness and Young’s modulus with respect to Si–C bond density is best illustrated in Fig. 5-10. It is worth mentioning here that the $N_{Si-C}$ is calculated from the extracted FTIR components in the range 779-786 cm$^{-1}$ (an example of the extracted components is shown in the inset of [Fig. 5-2(b)]). It can be noticed that
Figure 5-9: Variation of the average hardness and Young's modulus of PS-CVD a-SiCN:H films having [N] ranging from 0 to 27 at.%. The closed circles represent the average hardness, while the open circles represent the average Young's modulus. Regression lines represent the best fit for the data.

decreasing the Si-C bond density [(12-0.3)×10^{22} bond·cm^{-3}] resulted in the decrease of both $H$ and $E$ from 17 to 13 and from 160 to 136 GPa, respectively. This is in agreement with the same constant-plus-linear relation established in our previous work,$^{3172}$ in which hardness as well as Young's modulus were found to increase linearly from (10-50 GPa) and from (100-380 GPa) respectively, by increasing the Si-C bond density [(10-50)×10^{22} bond·cm^{-3}) in PECVD and PLD a-SiC. The inset of Fig. 5-10 shows the effect of reducing the Si-C bond density with increasing [N] content on the plasticity index ($H/E$) of the PS-CVD a-SiCN:H films. The $H/E$ ratio linearly decreased from 0.114 to 0.105 as a result of decreasing the Si-C bond density from (12-0.3)×10^{22} bond·cm^{-3} (increasing the [N] from 0 to 27 at.%). This shows in particular that the increase of nitrogen at. % in the
Figure 5-10: Average hardness and Young's as a function of Si–C bond density, \( N_{\text{Si-C}} \). The \( N_{\text{Si-C}} \) is calculated from the extracted FTIR components peaked at (779-786) cm\(^{-1}\). The inset of Fig. 5-10 shows the plasticity index \((H/E)\) as a function of \( N_{\text{Si-C}} \).

PS-CVD derived a-SiCN:H films induces a larger decrease in the hardness relative to Young's modulus.

5.4. Highlights of the Chapter

The highlights of this chapter are as follows:

- Amorphous silicon carbonitride thin films with nitrogen content up to 27 at.% have been deposited by polymeric-source chemical vapor deposition technique using NH\(_3\) as nitrogen source.
Structural and mechanical properties of silicon carbonitride

- FTIR measurements indicated not only a shift in the main SiC absorption band toward SiCN ones, but also the intensity of these peaks decreased by increasing the percentage of [N] in the films from 0 up to 27 at.%. On the microstructural level, the increasing incorporation of N in the a-SiCN:H films is found not only to lead to C atoms substitution by N atoms in the local Si–C–N environment, but also to an enhanced incorporation of hydrogen bonded to both Si and N.

- XPS studies confirmed the substitution of C atoms by N atoms. Furthermore, the addition of nitrogen resulted in the formation of Si–N, Si–H and N–H bonds at the detriment of the stiffer Si–C bonds, which can be considered the main detrimental factor behind the observed lowering of the mechanical properties of the a-SiCN:H films as their N content increased.

- Both $H$ and $E$ of the a-SiCN:H films were found to be sensitive to their N content, as they decrease from $-17$ GPa and $160$ GPa to $-13$ GPa and $136$ GPa, respectively when the N content is increased from 0 to 27 at.%. 

- Increasing incorporation of N in the a-SiCN:H films resulted in an increase of the average $R_{\text{ms}}$ surface roughness from 4 to 12 nm and the films became porous with pore size and density increase as a result of increasing N at.% as determined by AFM measurements.

- It is also confirmed that the constant-plus-linear-relation derived in our previous work applies for PS-CVD a-SiCN:H films, which shows that regardless of the SiC deposition process and/or film composition, the derived constant-plus-linear relation is a strong indication that the Si–C bond density is the major detrimental factor that
controls both hardness and Young's modulus of a-SiCN:H films.
CHAPTER 6

IR AND XPS COMPARATIVE STUDY OF SILICON CARBONITRIDE FILMS

The work presented in this chapter is a continuation of chapter five. Indeed the focus is placed here on the induced modifications in the structural and bonding configurations of the PS-CVD derived a-SiCN:H films as a result of introducing NH₃ in the deposition reactor as a source of nitrogen. This chapter forms a basis for assessing the use of NH₃ as a nitrogen source in producing a-SiCN:H films.

6.1. Introduction

The synthesis of ternary Si–C–N materials has been attracting growing interest due to their excellent properties, such as high hardness, high temperatures and corrosive environments resistance. In addition to mechanical properties, crystalline SiCₓNᵧ films exhibit a wide band gap of 3.8 eV, which is suitable for optoelectronics applications in the blue-UV range. It is well known that SiC and Si₃N₄ compounds are electronic materials with excellent performance. As a wide band gap semiconductor, SiC is widely used in extreme conditions such as high temperature and high power devices, as well as solar cell and many other optoelectronics applications. On the other hand, Si₃N₄ is a main component in electrical insulators and diffusion barriers. The band gap of SiC
located at 2.86–3.2 eV and that of Si$_3$N$_4$ is near 5.0 eV indicating that the ternary compound SiCN could be an example for photoelectron material with an adjustable band gap between 2.86 and 5.0 eV.\textsuperscript{132} Therefore, SiCN materials have potential applications in microelectronics and coating technologies. The properties of SiCN material could be an interesting combination of silicon carbide, a semiconductor, and silicon nitride, a dielectric. In this respect, it might be a hard material with a wide band gap having interesting optical and electronic properties.\textsuperscript{218}

The aim of this study is to report on the FTIR and XPS structural and bonding configurations analysis of a-SiCN:H films synthesized by polymer-source chemical vapor deposition (PS-CVD).

6.2. Experimental Method

The PS-CVD system was employed to grow the a-SiCN:H films on Si(100) substrates. Details of the PS-CVD system have been described elsewhere.\textsuperscript{10} In brief, poly (dimethylsilane) (PDMS) has been used as a single source for Si and C, and NH$_3$ added as the N source. An in-house designed 3"-diam. quartz tube reactor heated by heating coils was employed to convert the PDMS into a gaseous precursor. High purity NH$_3$ gas diluted by electronic grade Ar was used to control the nitrogen content of the a-SiCN:H films. The N at.% was controlled by varying the NH$_3$/Ar ratio in the range of 0 to 4×10\textsuperscript{3}. The substrate temperature was set at 750 °C and the chamber pressure was kept at about 2.5 × 10\textsuperscript{2} Torr during deposition. The deposition conditions are optimized to achieve a deposition rate of 50 nm/min. The thickness of the films ranges from 200-250 nm as
determined by cross section measurements of the samples using SEM. The IR absorption measurements were carried out at room temperature in the 400 to 4000 cm\(^{-1}\) range, at a resolution of 4 cm\(^{-1}\), using a Matteson Instruments 6020 Galaxy series spectrometer. Moreover, the IR spectra were recorded using uncoated silicon wafer as a reference. The XPS spectra were collected by using the ESCALAB 220I-XL spectrophotometer, equipped with an Al K\(_\alpha\) (1486.6 eV) radiation source to measure the atomic percentage of the chemical composition and bonding states of the a-SiCN:H films. Before analysis, surface films were sputter-cleaned by an ion gun using ultra high purity Ar gas. Survey scans (0 to 900 eV) were recorded for each sample to obtain a qualitative elemental analysis. A spectral deconvolution fitting process was used to extract the components of the FTIR and XPS spectral bands of the PS-CVD prepared a-SiCN:H films.

6.3. Results and Discussions

For the sake of clarity, this section has been divided into two subsections. The first subsection deals with the analysis of the FTIR measurements to verify the effect of increasing the NH\(_3\)/Ar ratio on the bonding configuration of the a-SiCN:H films. The second subsection discusses the results obtained from high resolution XPS measurements and the analysis performed to verify the FTIR observations. A correlation between the FTIR and XPS analysis is presented.

6.3.1 FTIR Spectroscopy Measurements

The IR spectroscopy measurements were performed in order to investigate the
effect of introducing NH$_3$ in the gas stream, on the microstructural changes of the prepared films. The absorption spectrum of a-SiCN:H films prepared without introducing NH$_3$ during the films growth [(Fig. 6-1) consists of three bands: the most dominant band centered at 778 cm$^{-1}$ assigned to Si–C vibration mode.$^{172}$ The second band which centered at 1500 cm$^{-1}$ could be assigned to C=C$^{219}$ and the third band centered at 2050 cm$^{-1}$ assigned to Si-H.$^{220}$ As shown in Fig. 6-1, changes in the NH$_3$/Ar ratio [(0.5 to 4)$\times$10$^{-3}$], result in striking changes in the absorption spectra. In particular, the first band (which centered at 778 cm$^{-1}$ before adding NH$_3$ in the gas stream) is shifted continuously to a higher wave number and reaches ~855 cm$^{-1}$ for the samples prepared using NH$_3$/Ar ratio of 4 $\times$10$^{-3}$. The second remarkable feature of the IR spectra is the clear separation of the bands, especially those in the high wave number domain between 1500 and 3400 cm$^{-1}$: (i) a clear shoulder at ~1200 cm$^{-1}$ which is assigned to C-N$^{221,222,223}$ is evident in all spectra; (ii) several sub peaks cover the band between 1500 and 1850 cm$^{-1}$ are associated with carbon-carbon and carbon-nitrogen bonds in different environments including C=N$^{224,225}$ and C=C$^{226,227,228}$ (iii) a third band centered at 2200 cm$^{-1}$ associated with C=N$^{219,229}$ (iv) a forth band centered at 3340 cm$^{-1}$ which could be assigned to N-H.$^{196}$ It is worth mentioning that all observed bands in the range of 1500-3400 cm$^{-1}$ retain almost their position regardless of the NH$_3$/Ar ratio used. Furthermore, an evident increase of the intensity of these bands with respect to the NH$_3$/Ar ratio used can be observed.

More precise information on the evolution of the film structure was obtained by the deconvolution of the IR absorption envelopes (ranging from 400 to 1300 cm$^{-1}$) into the component absorption bands. This is exemplified in Fig. 6-2, which shows an
Figure 6-1: Infrared spectra of PS-CVD a-SiCN:H series of samples from 400-4000 cm\(^{-1}\). The films have been prepared under NH\(_3\)/Ar ratio of (a) 0; (b) 0.5\(\times\)10\(^{-3}\); (c) 1\(\times\)10\(^{-3}\); (d) 2\(\times\)10\(^{-3}\); (e) 3\(\times\)10\(^{-3}\) and (f) 4\(\times\)10\(^{-3}\). Note that all the deconvoluted peaks are shown as dashed and dotted lines, while the as observed FTIR bands are shown as solid lines.

Example of deconvoluted FTIR spectra of the films grown without using NH\(_3\) in the gas stream and under NH\(_3\)/Ar ratio of 4\(\times\)10\(^{-3}\). The absorption band without introducing NH\(_3\) in the films [(Fig. 6-2(a))] consists of three bands: the most dominant band is centered at 778 cm\(^{-1}\) which is assigned to Si–C vibration mode.\(^{11}\) The second band centered at 580 cm\(^{-1}\), is assigned to Si–H\(_a\) wagging mode.\(^{230}\) The third peak centered at 956 cm\(^{-1}\) could be an overlap of many components including (SiH\(_3\))\(_2\) bending modes at 915 cm\(^{-1}\),\(^{173}\) Si–CH\(_a\) wagging vibration at 940 cm\(^{-1}\),\(^{132}\) Si–H stretching mode at 978 cm\(^{-1}\),\(^{196,231}\) a-SiC–H wagging mode\(^{232}\) centered at 990 cm\(^{-1}\) and C–H\(_a\) wagging and/or rocking mode centered at 990 cm\(^{-1}\).\(^{233}\) The last minor peak centered at 1140 cm\(^{-1}\) could be attributed to Si–O.\(^{234,235}\)
Figure 6-2: An example of IR deconvoluted spectra of a-SiCN:H films prepared (a) without NH₃ in the gas stream; (b) with NH₃/Ar ratio of 4×10⁻³.
As a result of introducing NH$_3$/Ar ratio of 4$\times$10$^{-3}$ [Fig. 6-2(b)], several points could be pointed out (i) the intensity of the first peak centered at 778 cm$^{-1}$ (assigned to Si–C) decreases continuously and reaches a value of about 67% of its original value as a result of increasing the NH$_3$/Ar ratio from 0 to 4$\times$10$^{-3}$; (ii) the band centered at 956 cm$^{-1}$ before NH$_3$ addition (assigned to several components as discussed earlier) broadened, and the relative area under this peak increases from 19% (at NH$_3$/Ar ratio =0) to 55%; (iii) a newly developed dominant band centered around 836 cm$^{-1}$ is essentially needed to better fit the FTIR spectra for all films prepared under NH$_3$/Ar ratio >0. In addition, since N is the only element added to the a-SiC films, it is reasonable to assume that the newly developed band at 836 cm$^{-1}$ and the increase of the relative area under the band centered at 956 cm$^{-1}$ is a signature of Si–N bonds (centered at 875, 234 at 910, 173 and at 980$^{236}$ cm$^{-1}$).
formation among other possible bonds including (SiH₂)₉ bending mode centered at 915 cm⁻¹, SiCH₃ wagging vibration centered at 940 cm⁻¹ and Si-H centered at 978 cm⁻¹. Hence, it is fair to assume that the prepared films cannot be considered two separate phases of Si–C and Si–N, but rather a complex structure of several components. In order to confirm such assumption, a correlation between the FTIR dominant band and the nitrogen atomic percentage incorporated in the films is drawn. From Fig. 6-3, it can be observed that there is a good agreement between the shift of the FTIR spectra to a higher wave number and the N at.% incorporated in the prepared a-SiCN:H films with respect to NH₃/Ar ratio used. Thus, it is fair to assume that the dominant component formed is the bonding between silicon and nitrogen.

6.3.2 X-Ray Photoelectron Spectroscopy Results

In order to determine the state of chemical bonding and the compositional changes of the films, XPS analysis of the prepared a-SiCN:H films are performed. The average concentration of each element was calculated from the values measured in the bulk of the films. Table 6.1 shows the elemental composition of a-SiCN:H films prepared using NH₃/Ar ratio from 0-4×10⁻³. This is rather a good agreement between NH₃/Ar ratio and the N at.% in the films. This indicates that, in the present case, the use of NH₃ is a very effective in the nitrogenation of a-SiC films. In fact, the [N] content in the a-SiCN:H films steadily increased from 0 to 27 at.% as a result of increasing the NH₃/Ar ratio from 0 to 4×10⁻³. Nevertheless, the carbon content decreases gradually from ~52 to 29 at.%, while the silicon content remains at a constant value of (43. ± 1.0 at.%). The increase of
Table 6.1: XPS elemental composition profile of the prepared a-SiCN:H films using different NH$_3$/Ar gas ratio

<table>
<thead>
<tr>
<th>(NH$_3$/Ar) $\times 10^3$</th>
<th>Elemental composition (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.5</td>
<td>11.7</td>
</tr>
<tr>
<td>1</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>24</td>
</tr>
<tr>
<td>4</td>
<td>27</td>
</tr>
</tbody>
</table>

N content accompanied by a decrease in carbon content and unchanged Si content is a clear indication that N substitutes C rather than Si. Such findings contradict Machorro et al. who observed that the concentration of both Si and C continuously decreased by increasing N percentage using Pulsed laser deposition (PLD). Figure 6-4 shows the depth profile of the elemental composition of a-SiCN:H films prepared under a ratio of NH$_3$/Ar equal to 2.0$\times 10^3$. For instance, atomic percentage of the tested a-SiCN:H films reveals uniform distribution of silicon, carbon, and nitrogen through the bulk of the films with a small amount of oxygen at the surface which decreases rapidly to low levels in the bulk (~1.5%). It is worth noting that the first few nanometers from the surface contain relatively high atomic percentage of oxygen (<5 at.%). The high oxygen content, which is limited to the surface, is presumably due to ambient air contamination that occurs during sample handling after deposition. Figure 6-5 shows the XPS spectral bands of Si$_{2p}$, C$_{1s}$, N$_{1s}$, and O$_{1s}$ levels as a function of NH$_3$/Ar ratio. Before introducing NH$_3$ in the gas stream, the Si$_{2p}$ spectra show a symmetric line shape centered at 100.1 eV, corresponding
Figure 6-4: Film chemical composition as measured by XPS in the depth-profiling mode. The film deposited in a system with \((NH_3/Ar) = 2.0 \times 10^3\)

to Si-C, while the \(C_{1s}\) spectrum is centered at 283.3 eV, corresponding to C-Si,\(^{208}\) while \(N_{1s}\) spectrum is centered at 397.3 eV. Successive increase of \(NH_3/Ar\) ratio from 0 to \(4 \times 10^3\) reveals a definite trend. Careful examination of the binding energy of \(Si_{2p}, C_{1s}\) and \(N_{1s}\) shows several points: (i) a recognizable shift to a higher binding energy for all \(Si_{2p}, C_{1s}, N_{1s}\) and \(O_{1s}\) (ii) the peak intensity of these spectra is highly dependent on the \(NH_3/Ar\) ratio used. For instance, the intensity of the \(Si_{2p}\) peak decreased by \(\sim 33\%\) from its original value compared to \(\sim 70\%\) decrease in the \(C_{1s}\) intensity. On the other hand, the intensity of \(N_{1s}\) spectra increased significantly and (iii) high energy tails in the \(C_{1s}\) spectra (\(>285\) eV as well as \(N_{1s}\) spectra (\(>398.0\) eV) are observed in all \(NH_3/Ar\) ratio used. Figure 6-6 shows
Figure 6-5: The recorded high resolution of Si2p, C1s, N1s, and O1s core levels in XPS spectra of PSCVD a-SiC:N:H films prepared with NH3/Ar ratio: (a) 0; (b) 0.5x10⁻³; (c) 1x10⁻³; (d) 2x10⁻³; (e) 3x10⁻³ and (f) 4x10⁻³.
the variation of the binding energy as a function of NH$_3$/Ar ratio. For instance, the binding energy of Si$_{2p}$ (Fig.6-6a) exhibit a clear shift from \(-100.1\) to 101.3 eV. Fig.6-6(b) shows the evolution of the C$_{1s}$ binding energy as a function of NH$_3$/Ar ratio. The binding energy of C$_{1s}$ is about 283.3 at NH$_3$/Ar ratio of 0 and increases as the NH$_3$/Ar ratio increases, reaching 283.7 eV for a-SiCN:H films prepared under NH$_3$/Ar ratio of $4 \times 10^{-3}$. In addition, the binding energy of N$_{1s}$ spectra shift from 387.3 to 397.8 eV, while the binding energy of O$_{1s}$ spectra shift from 531.7 to 532.6 eV. One can note that the shift to a higher binding energy in the Si$_{2p}$ (1.3 eV) spectra is much higher than that in the C$_{1s}$ (0.4 eV) and N$_{1s}$ (0.5 eV) spectra. This suggests that the tendency of silicon-nitrogen bond formation is much higher than the nitrogen-carbon ones. Xiao et al. attributed the shift to higher binding energy in the XPS spectra as a result of increasing N is due to the difference in the electronegativity of elements.$^{106}$ For example, the chemical shift of Si$_{2p}$ band as assigned to Si-C to higher position is due to the partial replacement of C in Si–C bonding by N whose electronegativity is much higher than that of C (C: $\chi_p = 2.55$, N: $\chi_p = 3.04$). He et al. further attributed such shift to the presence of N and C complexes that are somewhat peripheral to the Si bonding site in a-SiCN.$^{238}$ The same rule also applies to the case of C$_{1s}$ and N$_{1s}$ bands as shown in Fig. 6-5. It can be also observed that the line shapes of the Si$_{2p}$, C$_{1s}$ and N$_{1s}$ spectra shows overall widths exceeding 2.5 eV which indicates the presence of several contributions.

More qualitative trends were investigated by carrying out a deconvolution of the Si$_{2p}$, C$_{1s}$ and N$_{1s}$ spectral bands (Fig. 6-7) using Gaussian curve fits. The ratio of peak area reflects the relative fraction of bonding types contributing to the XPS spectra of Si$_{2p}$, C$_{1s}$,
Figure 6-6: Variation of the (a) Si$_{2p}$, (b) C$_{1s}$, (c) N$_{1s}$, and (d) O$_{1s}$ binding energies of the a-SiCN:H films as a function of NH$_3$/Ar ratio used during deposition.
and N\textsubscript{1s}. For films prepared without introducing NH\textsubscript{3} in the gas stream (Fig. 6-7a-c), two major and one minor components are needed to fit the as observed Si\textsubscript{2p} spectrum: one is a low-energy peaked at 99.9 eV, which is assigned to Si–Si component\textsuperscript{239} A second component peaked at 100.3 eV which could be attributed to Si–C\textsuperscript{240} A minor component at a binding energy of 102.3-102.5 eV with a small amount of silicon present in the form of Si–O presents\textsuperscript{241} The C\textsubscript{1s} XPS band was fitted by two components: (i) the first peak at 283.3 eV, corresponding to C–Si bonds in the SiC films\textsuperscript{242} The relative intensity of this component represents ~ 78% of the total area; (ii) the second component centered at 284.3 eV was attributed to C–C bonds in the SiC films\textsuperscript{183} and could also be attributed to C=C bonds\textsuperscript{243} As expected, for samples prepared without introducing NH\textsubscript{3} in the gas stream; no N\textsubscript{1s} peak can be detected in the XPS spectra. The deconvolution of O\textsubscript{1s} spectra (not shown) shows a dominant component peaked at 531.5 eV, corresponding to SiC:O or Si-O-C (oxygen in silicon oxycarbide)\textsuperscript{244} a minor component peaked at 532.5 eV, corresponding to O-Si (oxygen in silicon oxide)\textsuperscript{245} A minor shoulder at 533.8 eV corresponds to O-C\textsuperscript{244} Fig. 6-7(d-f) shows an example of Si\textsubscript{2p}, C\textsubscript{1s} and N\textsubscript{1s} XPS spectra for films prepared under NH\textsubscript{3}/Ar ratio of 4×10\textsuperscript{3}. For instance, Fig. 6-7d shows the Si\textsubscript{2p} band which deconvoluted intro three components: the first peaked at 100.3 eV, corresponding to Si-C bonds, the second is an intermediate component peaked at (100.5-101.5) eV depending on the neighboring C/N ratio, corresponding to SiCN (i.e. silicon bonded to both carbon and nitrogen), the third peaked at 101.8 eV was assigned to Si–N\textsuperscript{183} The shift of Si\textsubscript{2p} to high binding energy with the successive increase of NH\textsubscript{3}/Ar ratio, corresponding to elimination of Si-Si, decrease of Si-C and an increase of Si-N components. For all
Figure 6-7: Deconvolution of Si\textsubscript{2p}, C\textsubscript{1s}, N\textsubscript{1s} XPS spectra of a-SiCN:H films prepared at NH\textsubscript{3}/Ar ratio of 4×10\textsuperscript{3}.

NH\textsubscript{3}/Ar ratio, the Si\textsubscript{2p} binding energy is between SiC (100.3 eV) and Si\textsubscript{3}N\textsubscript{4} (101.8), but cannot be deconvoluted into two discrete Si–C and Si–N components. Hence, the films could be considered a mixture of Si–C, C–Si–N and Si–N. Meanwhile, the C\textsubscript{1s} spectrum (Fig.6-7e) exhibits a dominant component with binding energy at 283.3 eV. Nevertheless, the need for a second component peaked at 284.2 eV, even after increasing the NH\textsubscript{3}/Ar ratio to 4×10\textsuperscript{3} indicating the existence of pure carbon in the film. Moreover, a high energy tail above 285 eV is evident in the line shape of all C\textsubscript{1s} spectra (Fig. 6-6 and Fig
6-7e). The high-energy tails indicate carbon to nitrogen bonds formation with different possible configuration as discussed previously. For instance, the high energy tail in the C₁s spectra suggests the coexistence of graphitic environment (mainly C=C\(^{172}\)) and carbon bonded t nitrogen environment C(sp\(^3\))-N, and/or C(sp\(^3\))-N. \(^{246}\) The N₁s spectra (Fig. 6-7f) can be deconvoluted into a main sub peak at 397.3 eV, corresponding to Si-N bonds\(^{247}\) and a minor peak representing the high energy tail (>398 eV), which is an indication of nitrogen bonded to carbon. (The nitrogen to carbon bond under the high energy tail could take several minor peaks including: (398.2-399.1) eV normally assigned to N–C bond in the a-SiCN films,\(^{248,249}\) 398.8 eV assigned to N-C (sp\(^3\)),\(^{249}\) and/or 400.3 eV assigned to N-C (sp\(^2\)).\(^{249}\) The formation of nitrogen carbon bonds in the high energy tail of the N₁s spectra (>398 eV) is in agreement with the binding energy and line shape of the C₁s spectra (Fig. 6-6 and Fig. 6-7e) since the C₁s binding energy has a high energy tail (>285 eV) which would yield a carbon to nitrogen bond formation. The intensity of the O₁s spectra decreased significantly after introducing NH\(_3\) in the gas stream. It is worth mentioning that introducing NH\(_3\) in the gas stream significantly lowered the O in the SiC:O and O-Si bonds. The O bonded to C (at 533.8 eV) remains insignificant before and after introducing NH\(_3\) in the gas stream. Figure 6-8 represents a further analysis of the XPS spectra which shows the effect of increasing NH\(_3\)/Ar ratio from 0 to 4×10\(^3\), on the full-width-at-half-maximum (FWHM) of Si₂p, C₁s and N₁s spectra. In particular, the Si₂p peak increased from 1.42 eV for a-SiC (NH\(_3\)/Ar =0) to 1.86 eV for the a-SiCN:H films (NH\(_3\)/Ar = 4×10\(^3\)). Similarly, the FWHM of C₁s peaks increased from 1.56 eV to 1.89 eV. Furthermore, the FWHM of N₁s followed the same trend and increased from 1.16 eV
to 1.35 eV. The increase in the FWHM (Fig. 6-8) accompanied with the shift to higher binding energy (Fig. 6-6) are attributed to the inter-bonded Si–C–N covalent structure that broadens the Si$_{2p}$, C$_{1s}$ and N$_{1s}$ peaks in the a-SiCN:H film.$^{250,251}$

In sum, all Si$_{2p}$, C$_{1s}$ and N$_{1s}$ spectral bands of the prepared a-SiCN:H suggests that nitrogen preferential bonding is to silicon rather than to carbon. XPS analysis clearly shows that the two dominant bonds are Si–C and Si–N, at the same time, many less dominant peaks (C=C, C=N, C≡N, Si-O, SiC-O) are presented. In the same manner, FTIR analysis (Fig. 6-1) showed a broad peak shifted from 787 to 856 cm$^{-1}$. This suggests that the prepared a-SiCN:H films lies between the vibration modes of Si–C (787 cm$^{-1}$)$^{172}$ and Si–N (900-980 cm$^{-1}$)$^{252,253}$ phases, respectively. The clear presence of several components
in the FTIR analysis (Si–N, C–N, C≡N, C≡N and N–H) confirms the same finding in the XPS analysis.

6.4. Highlights of the Chapter

The highlights of this chapter are as follows:

- The a-SiCN:H films are prepared using polymer-source chemical vapor deposition. The PS-CVD a-SiCN:H films with up to 27 at.% N have been prepared.

- Compositional and bonding structure properties of the films have been investigated as a function of their nitrogen contents by FTIR and XPS techniques. According to FTIR analysis of the prepared films, nitrogen atoms displace carbon atoms.

- The FTIR spectra show a remarkable drop in the intensity of Si–C vibration accompanied by the formation of further bonds including Si–N, C–N, C≡N, C≡N and N–H with increasing NH₃/Ar ratio.

- Furthermore, the formation of Si–N, C–N, C≡N, C≡N and N–H bonding network take place in detriment of Si–C bonds. The results of XPS analysis revealed the formation of complex networks among the three elements Si, C and N and the existence of different chemical bonds (Si–C, N–Si–C, Si–N, N–C, N≡C, C≡C, N≡C) in the a-SiCN:H films.

- Based on the XPS and with reference to the FTIR data consideration, it could be assumed that the synthesized a-SiCN:H films are not only mixture of SiC and Si₃N₄ but also some intermediate compounds in the inter-bonded Si–C–N covalent structure.
CHAPTER 7

CONCLUSIONS AND FUTURE WORK

This thesis ranges across a series of characterization studies of SiC based films produced by the newly developed technique (polymer-source chemical vapor deposition). The unique aspect of this thesis lies in the fact that it evaluates the PS-CVD a-SiC:H and other SiC based thin films (a-SiCN:H) towards applications in new industries by a new approach of depositing such films without the need of using either toxic silane gas or solvents in any step of preparing these films. The technical work presented in this thesis is expected to demonstrate an understanding of several properties of PS-CVD films and the commercial advantages which can emerge from the development of such simple deposition process. The first part of this discussed is the stability of PS-CVD a-SiC-metal contacts under high temperature annealing for prolonged time. Followed by studying the effect of thermal annealing on the mechanical and structural properties of the prepared a-SiC:H films. In addition, the induced changes in the mechanical properties (hardness, Young’s modulus and surface morphology) and a correlation of these properties with the structural properties, as well as bonding configurations as a result of nitrogen addition into the a-SiC:H films to produce a-SiCN:H have been discussed. Moreover, a detailed FTIR and XPS structural studies of the a-SiCN:H films were carried out. Similarly, the stability of the a-SiC in strong
Conclusions and Future works

acidic solutions as well as the phosphate buffer saline solutions was briefly discussed.

7.1. Key Findings

The research presented in this thesis has examined several key areas of inquiry including:

1. This work has shown that TiN and Pt-Rh thin films are the most stable metallic contact (in terms of narrowness and abruptness) for a-SiC high temperature device applications without interdiffusion between layers and with oxygen level < 1 at.%. Moreover, the a-SiC films deposited particularly in the case of TiN substrate are shown to not only contain the lowest oxygen content, but also exhibit the smoothest surface.

2. Ultimately, it is shown here that it is possible to utilize amorphous silicon carbide thin films pertaining excellent adhesion and very smooth surface (R_m of 1 nm) on several metals including Ti, TiW, Cr and V. This proves that the PS-CVD a-SiC is an excellent candidate for many potential applications ranging from protective coatings against corrosion of steel to microelectronic devices, where the interface between the SiC films and the metallic substrates is a matter of a concern.

3. It was found that 10 minutes of thermal annealing under Ar flow at annealing temperature (T_a) ranging from 750-1200 °C resulted in more ordered structured films. Moreover, a significant increase in the Si–C bond density accompanied by a significant decrease of hydrogen content is clearly observed.

4. A direct relation between thermal annealing and a-SiC film density was established. It was found that the a-SiC film density increased from 2.36 to 2.75 g/cm³ as a result of
Conclusions and Future works

increasing $T_s$ from 750 to 1200 °C.

5. Eventually, the surface morphology of the a-SiC films can be smoothed to average root mean square ($R_{rms}$) of 1 nm by annealing and roughened to ($R_{rms}$) of 50 nm by nitrogen addition. The addition of nitrogen to the films not only roughened the surface, but also increased its pore-density by 1-5%.

6. Likewise, it is found that both hardness and Young's modulus increase from 15.5 to 17.6 GPa and from 155 to 178 GPa respectively, as a result of increasing $T_s$ from 750 to 1200 °C. The ability to control the mechanical properties mainly hardness and Young's modulus adds further values to the PS-CVD prepared a-SiC films and many other derivatives. For example, these films can be applied as coating to protect tool materials against severe mechanical degradation resulting of high temperature (above 500 °C) oxidation. Before full assessment of the protection properties of the a-SiC films, further tests of toughness and wear resistance, and a clear correlation between these major requirements are still needed.

7. Our work on establishing a correlation between the Si–C bond density and the mechanical properties of the PS-CVD films showed a constant-plus-linear relation, which indicates that Si–C bond density can be considered the major detrimental factor that controls both hardness and Young's modulus of SiC films regardless of the SiC deposition process and/or film composition. Such relation is in good agreement with the same relation established by other researchers for PE-CVD and PLD a-SiC films.3,11

8. We have demonstrated the effectiveness of using NH$_3$ as a nitrogen source to produce a-SiCN:H films based on PS-CVD process. It is found that only a flow ratio of NH$_3$/Ar
equal to $4 \times 10^{-3}$ is needed to increase \([N]\) in the a-SiCN:H films up to 27 at.\%.

9. We have identified the nature of bonding configurations of the a-SiCN:H films by showing that the films consist of a complex bond structure between Si–C–N and can not be considered a mixture of separated SiC and Si$_3$N$_4$ phases.

10. The work presented here proved the usefulness of a simple approach for the production of high surface area nanostructured films by utilizing \textit{in-situ} nitrogenation of the films without the need for any further after-deposition electrochemical etching steps. The surfaces show pores density of 1-5\%. The ability of producing porous SiC films by \textit{in-situ} nitrogenation of the films eliminates one major processing step (anodization) in the fabrication of several devices, which require porous films such as humidity sensors that could withstand very harsh chemical environments.\textsuperscript{117} It could be very advantageous to explore such approach in more details, in order to be able to answer specific industrial requirements. It is important to mention in this regard that porous SiC films are recently introduced in the market. For instance, MIRATECH Corporation\textsuperscript{254} has introduced two porous silicon carbide element soot trap product lines for diesel engines. Both new MIRATECH soot trap products feature wall-flow porous silicon carbide filters, which provide superior thermal durability. Both product groups incorporate design from Swiss based HUG Engineering, a world leading manufacturer of emission solutions for power plants, diesel-powered generation sets, ships and locomotives.

11. Our work has also demonstrated a reliable approach to reduce both hardness and Young’s modulus of the deposited films through the incorporation of nitrogen. This approach shows that if an accurate control of hardness and Young’s modulus of the PS-CVD films is needed for specific applications, the addition of nitrogen in the a-SiC films is an
Conclusions and Future works

effective approach. It was shown that the hardness and Young's modulus can be accurately reduced from 16.6-13.4 and 158-136 GPA, respectively.

12. This studies presented in this thesis confirmed the validity of the constant-plus-linear relation between hardness and Young's modulus with respect to the decrease of Si–C bond density induced by the increase of nitrogen atomic percentage.

13. Our work has demonstrated a good agreement between the FTIR and XPS analysis of the bonding configurations of the a-SiC:H and a-SiCN:H films. Both FTIR and XPS results show that annealing of the a-SiC resulted in a more ordered structure.

14. Our work on testing the corrosion resistance of a-SiC in harsh acidic environment showed that the prepared PS-CVD a-SiC did not exhibit any deterioration in (1:1:1) by volume HF (50%), HNO₃ (70%), H₂O₂ (32%). Thickness measurements and SEM measurements did not show any corrosion or etching of the protective a-SiC coated films even after 48 hours immersion in the solution, compared to few minutes of complete etching of Si counterpart.

15. Finally, our work on testing the corrosion resistance of the a-SiC films in buffer solution (30 µL phosphate buffered saline, pH 7.4) shows that the films are very stable after 360 days immersion in the buffer solution heated at 75 °C. No degradation, etching or cracking is observed. This confirms that the PS-CVD a-SiC is not only a potential candidate for harsh environment coating and microelectronics devices, but also a great candidate for medical implants especially in severe heart problems. heart problems. For instances, BIOTRONIK Inc. Germany based company lunched the first a-SiC coated STENT technology.²³⁵
7.2. Chapters Summary

This section is a review of the chapters summarizing the key parts of the work: Chapter one set out the context of the work and framed the way in which the work was undertaken. It also provided a brief description of the research problem investigated. In addition, the Chapter identified the overall objectives and focused more on the specific aims and scope of this thesis. Also, a concise description of the approach was summarized and the achieved results were given. Finally, the Chapter covered future directions and ended by a summary and layout of the thesis. Meanwhile, Chapter two contained a comprehensive literature review search across seven key themes: (i) silicon carbide deposition techniques based on the precursors (gas, liquid, and solid); (ii) more specifically, general description of the PS-CVD process used to prepare the films used in this work; (iii) various SiC characterization analysis and challenges that SiC technology still facing. In particular, the prior literature related to metal semiconductor contacts where more attention was put on Ohmic and Schottky contacts as essential requirements in any device fabrications; (iv) mechanical properties of the a-SiC:H and a-SiCN:H films especially hardness and Young's modulus; (v) different processes used to produce porous silicon carbide and some details of chosen applications of such porous structures; (vi) general discussion of the structural properties and bonding configuration of a-SiC film as well as a-SiCN films; (vii) a collection of most applications discussed throughout this thesis. Subsequently, Chapter three discussed the effect of thermal annealing on the interfacial interaction between PS-CVD prepared a-SiC with metallic substrates. Ultimately, understanding the effect of thermal annealing on the mechanical properties (hardness, Young’s modulus, density and surface morphology) of PS-
Conclusions and Future works

CVD a-SiC films is covered in Chapter four. At the same time, Chapter five discussed the induced changes in the mechanical properties and surface morphology as a result of adding nitrogen in the a-SiC films. Chapter six provided detailed FTIR and XPS comparative studies of the structural and bonding modifications of the a-SiC films as a result of introducing nitrogen as a major constituent in the films. To sum up, chapter seven concluded the work and proposed future outlook mainly in the device fabrication and coating field applications as the two major potentials for PS-CVD thin films. While Appendix A shows a proposed characterization chart to achieve full evaluation of the new PS-CVD a-SiC films followed during the work in this thesis, Appendix B contains an example of a poster presented in the International Conference on Silicon Carbide and Related Materials (ICSCRM). Lastly, basic mathematical derivations are included in Appendix C for future Schottky and Ohmic contacts characterizations. Finally, the bibliography of cited literature studies.

7.3. Future Work

The key findings of the work have led to the following ideas for future research.

7.3.1 Films Compositions

A very good understanding of the structural properties and bonding configurations has been achieved in this study, though a very specific issue needs to be addressed in the future to extend the understanding of the characteristics of the a-SiC:H with respect to its hydrogen contents. The early stage measurements of PS-CVD a-SiC hydrogen content shows that the hydrogen content in the a-SiC can range from 3-20 at.% (i.e. Fig. 3-4), which covers the
optimum reported values (8-12 at.%) for electronic devices.\textsuperscript{256,257} The hydrogen content of hydrogenated semiconductor alloy materials is an important factor, which controls their electronic and optical properties. It is speculated that hydrogen plays a role in passivating defective bonding states and relieving stress in the matrix of the semiconductor materials, thereby improving their electronic properties. Presence of less hydrogen attributes to low interface trap density, smooth interface and a reduction in the number of trapping sites in the films.\textsuperscript{258} The hydrogen concentration in the HDPCVD silane-based SiC is measured\textsuperscript{27,155} to be in the range of 12-20% which is lower than in the results of same references (25-30\% for PECVD 3MS-based SiC) and Racine et al. work\textsuperscript{259} (30-40\% for PECVD silane based SiC). Less hydrogen content means low interface trap density,\textsuperscript{260} smoother interface and fewer carrier-trapping sites.\textsuperscript{261} Less hydrogen reduces the defect sites in the film, increasing its resistance to copper penetration.\textsuperscript{262} Further studies on optimizing hydrogen contents in the PS-CVD films with respect to specific applications is highly recommended and more work on studying whether the hydrogen is bonded or free is essential.

7.3.2 Further Characterization Studies

The extension of the comprehensive characterization studies on the properties of the deposited films is needed especially films characterizations with respect to the process variables. A proposed characterization chart is included in Appendix B.

7.3.3 Device Fabrications

As a result of this research, one of the main concerns in device fabrication, the reactivity and diffusivity between deposited silicon carbide films and metallization, is being
Conclusions and Future works

discussed and an optimum solution is found. Such understanding should be used as a foundation for further improvements in the material itself, as well as interface with other metals if full potential of SiC devices is to be realized. The ability to create Ohmic contacts with low contact resistivities (≤ 10^4 Ω.cm²) and Schottky contacts with the optimum Schottky barrier height will be one of the major challenges in the foreseeable future. The following work is recommended as a follow-up to this study in order to fabricate and test the performance of the PS-CVD in device applications:

- Identify and characterize possible doping routes to produce semiconductor materials; the simplest approach is to use ion implantation and the ultimate goal is to develop in situ doping process of the prepared films. Such doping could be done using the conventional gases such as B_2H_6, PH_3.

- Use non toxic gases for doping, which is a big challenge that needs to be addressed in order to achieve safety processes for producing high quality semiconductor thin films based on PS-CVD technique.

- Deposit TiN contacts on a-SiC films to optimize the performance of Ohmic contacts.

- Similarly, it would be very desirable to optimize Schottky contacts by testing the performance of several metallic contacts. The metallic contacts could be chosen from Table 2.1 to 2.3, but the focus should be on those metals that were proven to be stable Schottky contacts at high temperature as detailed in Chapter 2.

- After performing the above three steps, the fabrication of small geometry metal/Schottky diodes should be possible.

- Testing the performance of the fabricated Schottky diode.
7.3.4 Coating Applications

There are still important questions left unanswered regarding SiC deposition and characteristics for potential coating applications. However, important strides have been achieved, which have provided opportunities for further research.
Characterization chart to assess the newly developed polymer source chemical vapor deposition (PS-CVD) technique.
APPENDIX. B

POSTER PRESENTATION


U.S.A

Physical and Optical Properties of In-situ Nitrogenated SiC Films Prepared by Polymer Source CVD Technique

Yousef Awad, My Ali El Khakani, Nathalie Camiré, Maxime Lessard, Gecin Aktik and Mihai Scarlete

Novel process of producing SiC thin films without toxic gases or solvents

<table>
<thead>
<tr>
<th>Process Features and Benefits</th>
<th>SIC accomplished derivatives</th>
<th>Potential Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>✔ Single source for Si &amp; C (PDMS)</td>
<td>✔ a-SiC film</td>
<td>✔ White LED</td>
</tr>
<tr>
<td>✔ High deposition rate (&gt;70nm/min)</td>
<td>✔ β-SiC (crystalline fraction 0-70%)</td>
<td>✔ UV LED</td>
</tr>
<tr>
<td>✔ Scaleable and adaptable process</td>
<td>✔ SiCN (at. % of Nitrogen up to 27%)</td>
<td>✔ Nanocomposite coating</td>
</tr>
<tr>
<td>✔ Cost effective</td>
<td>✔ SiOC (at. % of Oxygen up to 30%)</td>
<td>✔ Hydrophobic/hydrophilic coating</td>
</tr>
</tbody>
</table>

Characterizations

<table>
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<tr>
<th>Mechanical</th>
<th>Photoluminescence</th>
<th>Strategy</th>
</tr>
</thead>
<tbody>
<tr>
<td>✔ Hardness 15-20 GPa</td>
<td>✔ Color Flexibility including many &quot;Whites&quot;</td>
<td>Includes partnering with (fill-in-blank) manufacturers and/or suppliers to develop application-specific thin films or components/devices with significant cost/performance ratios</td>
</tr>
<tr>
<td>✔ Elastic modulus (160-200)</td>
<td>✔ Color Tuneability Possible</td>
<td></td>
</tr>
<tr>
<td>✔ Surface roughness (1-50 nm)</td>
<td>✔ Luminescent Intensity Control Possible</td>
<td></td>
</tr>
</tbody>
</table>

Contact

SIXtron Advanced Materials
2100, King St. West Suite 20
Sherbrooke, Quebec
Canada J1J 2E8
Phone: (613) 620-2105
Fax: (613) 620-3230
E-mail: info@sixtron.com
Web: www.sixtron.com

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APPENDIX. C

MEASUREMENTS TECHNIQUES

There are several experimental techniques available for measuring the electrical properties of a-SiC films, among these methods, the following four methods are either used in this study or will be needed for further future characterizations.

- TLM method\textsuperscript{263}
- Current voltage method \textsuperscript{264}
- Resistivity and hall measurements (Van der Pauw technique)\textsuperscript{265, 266, 267}

C.1: Transmission Line Model-TLM

Transmission Line Model (TLM) theory proposed by Reeves and Harrison\textsuperscript{263} was used for assessing the quality of Ohmic contacts as well as electrical properties of a-SiC films used in this study. Fig. C. 1 shows a schematic diagram of a semiconductor material with Ohmic contact pads prepared for TLM analysis. In this study, the TLM pattern consists of a rectangular contact pads and the pad spacing were 0.05 mm, 0.1 mm, ... 0.25 mm and 0.3 mm (corresponding to d_1, 2d_1, ... 5d_1 and 6d_1 respectively). The contact surface area is 1.0×10^4 cm^2 (0.2 cm×0.05 cm). Once the sample to be tested was fully prepared,
Appendix C

Fig. C. 1: A schematic diagram of a-SiC with Ohmic contact pads prepared as well as the respective resistance circuit for TLM measurements.

two probes were connected to two adjacent pads and a known voltage was applied. The respective current is then measured. The total resistance is then calculated by dividing the applied voltage by the resulted current. The process is repeated and the total resistance is plotted on a linear graph as a function of pad spacing. It can be seen from Fig. C. 1 that the total resistance, \( R_T \), between two adjacent pads, is given by:

\[
R_T = \frac{\Delta V}{\Delta I} = 2R_m + 2R_c + R_{sh} \tag{C-1}
\]

where \( R_m \) is the resistance of the metal pad, \( R_c \) is the contact resistance between the metallic pads and the semiconductor, \( R_{sh} \) is the semiconductor sheet resistance. TLM relies on resistance measurements between a series of pads with varying spacing.

Assuming the resistance of the metal pad to be essentially zero, this assumption is
valid since a very accurate measurement of the resistance is not critical. This reduces equation (C-1) to

\[ R_T = \left( \frac{\Delta V}{\Delta I} \right) = 2R_c + R_{sh} \]  \hspace{1cm} (C-2)

Now, if we assume that the contribution from \( R_s \) is linearly dependent on the distance between two pads, which is only a fair assumption in this case since the pads were not placed upon a mesa and the charge is not restricted to flow in straight lines between pads, then at a pad spacing of zero, \( R_{sh} = 0 \). This assumption is valid since a very accurate measure of contact resistance is not necessary for the purposes of this study. By separating the two contributions of the contact and sheet resistance, the contact resistance \( R_c \) can be calculated. The \( y \)-intercept of a plot of \( R_T \) vs. pad separation (see Fig. C. 2) is then approximately equal to \( 2R_c \), according to (Eq. C-2). Thus,

\[ R_c = \frac{y_0}{2} \]  \hspace{1cm} (C-3)

\( R_c \) describes the contact resistance.

The contact resistance extracted from I-V measurements is then multiplied by the contact surface area (A) which in turn gives the specific contact resistance \( \rho_c \), as given in the following equation
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![Graph showing total resistance as a function of TLM pad spacing](image)

**Fig.C. 2:** An example of a plot of total resistance as a function of TLM pad spacing

\[ \rho_c = R_c \times A \]  \hspace{1cm} (C-4)

From a purely experimental point of view, one has to be very careful about deformation to metal pad shape especially after anneal treatments. Deformed pads alter many of the vital dimensions, which are pre-set in the analysis. Hence, in such cases, inspection under the microscope is required to obtain more realistic values for these dimensions. The TLM method has various advantages: (i) sample shapes and sizes are always identical as they are produced using the same TLM mask set. Hence no correction factors have to be taken into account; (ii) many accurate measurements can be made from...
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a relatively small sample area (1 cm² sample contains 20 TLM mesas allowing as many independent measurements); (iii) repeatable results were obtained with acceptable standard deviation (below ±5%) for samples from the same deposition run.

C.2: Current-Voltage Measurements (I-V)

Current-voltage (I-V) measurements refer to d.c. characterizations of devices for the purposes of performance analysis and parameter extraction. All the measurements are done at room temperature. The I-V measurements are performed with the Precision Semiconductor Parameter Analyzer (HP-4156). The upper electrode is biased from -5 to +5 V in steps of 0.2V and the lower electrode is connected to the ground. In this section, various Schottky diode parameters are briefly discussed.

C.2.1. Schottky Diode Parameters Extraction

A number of good publications are available in the literature, which deal with various general[258,269] and specific extraction techniques where diodes suffer from high series resistance.[270] In practice, most of the diode parameters are extracted by first plotting its I-V characteristics on a log₁₀(I) vs. V graph as shown in Fig_C. 3.

The semi-logarithmic I-V plot in Fig_C. 3 which is a typical Schottky or a p-n junction plot, can be divided into three distinct regions: region (1) is the non-linear region due to non-exponential behavior of diodes at low voltages (leakage currents amongst other factors); region (2) is the linear region and region (3) where the current is limited by
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Fig. C. 3: Semi-logarithmic I-V plot for a typical Schottky or a p-n junction diode

the series resistance ($r_s$). The saturation current ($I_s$) can be estimated from the extrapolation of the exponentially increasing region of the I–V plot onto the y-axis.

The general diode equation is given by

$$I = I_0 \left[ \exp \left( \frac{qV}{nK_BT} \right) - 1 \right]$$  \hspace{1cm} (C-5)

with

$$I_0 = AA' T^2 \exp \left( -q \frac{\Phi_{bs}}{K_BT} \right)$$  \hspace{1cm} (C-6)

and
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\[ A^* = \left( \frac{4 \pi q m^* K_B 2}{h^3} \right) \]  

(C-7)

where \( I_0 \): the saturate reverse current; \( q \): the electron charge; \( V \): the voltage; \( n \): the ideality factor; \( K_B \): the Boltzmann constant \(1.374 \times 10^{-23} \text{ J/K}\); \( A^* \): the effective Richardson constant \(\text{120 A/cm}^2 \cdot \text{K}^2\); \( T \): the effective absolute temperature \(\text{(Kelvin)}\); \( \phi_0 \): the barrier height; \( q \): electron charge; \( m^* \): effective electron mass and \( h \): plank constant.

• Ideality factor, \( n \)

The ideality factor, \( n \), in the general diode equation \((C-5)\) gives a measure of the quality of the junction which is highly process dependent. For an ideal Schottky junction, \( n = 1 \). The diode equation is then become,

\[ I = I_0 \exp\left( \frac{qV}{K_B T} \right) - 1 \]  

(C-8)

In practice, however, larger values are obtained due to the presence of non-ideal effects or components to the current through the junction. Such non ideal effects may come from the interface states\(^{273}\) residual defects\(^{274}\) and surface roughening\(^{275,276}\) of the Schottky barrier diode, or components to the current through the junction. This mode of current transport is commonly referred to as the "thermionic emission" current.\(^{166}\) Again, using the linear fit to region 2 of Fig. C. 3 and the general diode equation, a clear expression

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for the ideality factor can be derived as follows:

Take the natural logarithm of both sides of the diode equation (C-8),

\[
\ln(I) = \ln(I_0) + \frac{qV}{nK_BT} \quad (C-9)
\]

derive both sides with respect to V,

\[
d\ln(I) = \frac{q}{nK_BT} dV \quad (C-10)
\]

divide both sides by dV

\[
\frac{d\ln(I)}{dV} = \text{slope} = S = \frac{q}{nK_BT} \quad (C-11)
\]

By simple rearrangements n becomes;

\[
n = \frac{q}{SK_BT} \quad (C-12)
\]

if the slope S is derived from log(I) base 10 instead of ln(I) based e versus V graph then a conversion factor from ln(I) to Log(I) is needed as shown in the following equation,

\[
n = \frac{q}{2.3SK_BT} \quad (C-13)
\]
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- **Series Resistance, \( r_s \)**

The series resistance is determined from region 3 of Fig. C. 3 where at high current, the plot becomes flat and is assumed to be dominated entirely by the \( r_s \). A plot of \( V/I \) can be made and \( r_s \) is extracted from the point where this curve saturates to a steady minimum value as illustrated in Fig. C. 3. Beside the experimental method of determining the series resistance, it can be also calculated mathematically: The diode voltage (V) in the diode equation (C-5) does not include any resistance effects. If both \( I_0 \) and \( (n) \) are constant over some current range, then a plot of \( \log(I) \) versus \( V \) yields a straight line. When series resistance contributes to device behavior the diode equation (C-5) can be modified as

\[
I = I_0 \exp \left( q \frac{V - I r_s}{n K_b T} \right) - 1
\]  
\[
(C-14)
\]

After taking the natural logarithm of both sides of equation (C-14), it becomes

\[
\ln(I) = \ln(I_0) + \frac{q(V - I r_s)}{n K_b T}
\]  
\[
(C-15)
\]

since \( I_0 \) is constant; \( \ln I_0 = 0 \)
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\[ \ln(I) = \left( \frac{q(V - Ir_s)}{nK_BT} \right) \]  \hspace{1cm} (C-16)

derive Equation (C-16)

\[ \frac{dI}{I} = \left( \frac{q}{nK_BT} \right) (dV - r_s dl) \]  \hspace{1cm} (C-17)

then simple re-arrangement of Equation (C-17)

\[ \left( \frac{1}{I} + \left( \frac{q}{nK_BT} \right) r_s \right) dl = \frac{q}{nK_BT} dV \]  \hspace{1cm} (C-18)

The final equation then,

\[ \frac{dV}{dl} = \frac{nK_BT}{q} \left( \frac{1}{I} + r_s \right) \]  \hspace{1cm} (C-19)

Equation (C-19) can be expressed as a plot of \( dV/dl \) versus \( 1/I \) which gives \( nk_BT/q \) as the slope and \( r_s \) as the intercept as shown in Fig. C. 4.
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![Graph showing the relationship between voltage and current with a slope equal to \( nK_B T/q \).]

Fig. C. 4: An illustration of the series resistance measurements based on equation C-19 where the variation of the voltage \( V \) with respect to the measured current \( I \) is plotted against the inverse of the measured current. The intercept of the curve with the y-axis gives the series resistance.

C.3: Resistivity and Hall Measurements (Van der Pauw Technique)

This section is intended to describe the Hall measurement technique for determining the carrier density and mobility in semiconductor materials. For those who are interested to read the original published work done by Van der Pauw, the original paper can be found on the web, or in the original journal for those who can access such journal.

In order to determine both the mobility \( (\mu) \) and the sheet density \( (n_s) \) a combination of resistivity measurements to determine the sheet resistance \( (R_s) \) and Hall measurements to determine \( n_s \) are needed. As originally devised by van der Pauw, one uses an arbitrarily shaped (but simply connected, i.e., no holes or nonconducting islands or inclusions), thin-plate sample containing four very small Ohmic contacts placed on the periphery (preferably in the corners) of the plate.
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The Hall mobility is given by

\[ \mu = \frac{|V_H|}{R_s I B} = \frac{1}{q n_s R_s} \quad (C-20) \]

where \( \mu \) is the mobility, \( V_H \) : Hall voltage, \( R_s \) : sheet resistance, \( I \) : the measured current, \( B \) : the applied magnetic field, \( q \) : electron charge and \( n_s \) : sheet density.

A schematic of a rectangular van der Pauw configuration is shown in Fig. C. 5

![Schematic diagram of a rectangular van der Pauw configuration](image)

**Fig. C. 5:** A schematic diagram of a rectangular van der Pauw configuration

C.3.1. Resistivity Measurements

The objective of the resistivity measurements is to determine the sheet resistance \( R_s \). Van der Pauw demonstrated that there are actually two characteristic resistances \( R_s \) and \( R_b \) associated with the corresponding terminals shown in Fig. C. 5. \( R_s \) and \( R_b \) (called the characteristic resistance, more details will follow) are related to the sheet resistance \( R_s \).
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through the van der Pauw equation

\[ \exp\left(\frac{-\pi R_A}{R_c}\right) + \exp\left(\frac{-\pi R_B}{R_c}\right) = 1 \]  \hspace{1cm} (C-21)

which can be solved numerically for \( R_c \). The bulk electrical resistivity \( \rho \) can be calculated using

\[ \rho = R_c d \]  \hspace{1cm} (C-22)

where \( d \) is conducting later thickness (in cm).

The following details will lead to calculate the two characteristic resistances \((R_A \text{ and } R_B)\) needed in Equation C-21.

- Definitions for Resistivity Measurements

Four leads are connected to the four Ohmic contacts on the sample. These are labeled 1, 2, 3 and 4 counterclockwise as shown in Fig. C. 5. It is important to use the same batch of wire for all four leads in order to minimize thermoelectric effects. Similarly, all four Ohmic contacts should consist of the same material. We define the following parameters (see Fig. C. 5):

\[ \rho = \text{sample resistivity (in } \Omega \cdot \text{cm)} \]

\[ d = \text{conducting layer thickness (in cm)} \]

\[ I_{12} = \text{positive dc current injected into contact 1 and taken out of contact 2.} \]
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Likewise for $I_{23}, I_{34}, I_{41}, I_{12}, I_{14}, I_{43}, I_{32}$ (in amperes, A)

$$V_{12} = \text{dc voltage measured between contacts 1 and 2 (} V_1 - V_2 \text{) without applied magnetic field (} B = 0 \text{). Likewise for } V_{23}, V_{34}, V_{41}, V_{21}, V_{14}, V_{43}, V_{32} \text{ (in volts, V).}$$

- Resistivity Measurements

The data must be checked for internal consistency, for Ohmic contact quality and for sample uniformity.

- Set up a dc current $I$ such that when applied to the sample the power dissipation does not exceed 5 mW (preferably 1 mW). This limit can be specified before the automatic measurement sequence is started by measuring the resistance $R$ between any two opposing leads (1 to 3 or 2 to 4) and setting

$$I < (200R)^{-0.5} \quad \text{(C-23)}$$

Apply the current $I_{21}$ and measure voltage $V_{34}$

- Reverse the polarity of the current ($I_{12}$) and measure $V_{43}$

- Repeat for the remaining six values ($V_{41}, V_{14}, V_{12}, V_{21}, V_{23}, V_{32}$)

- Eight measurements of voltage yield the following eight values of resistance, all of which must be positive:
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\[ R_{21,34} = \frac{V_{34}}{I_{21}}, \quad R_{12,43} = \frac{V_{43}}{I_{12}} \]
\[ R_{32,41} = \frac{V_{41}}{I_{32}}, \quad R_{23,14} = \frac{V_{14}}{I_{23}} \]
\[ R_{43,12} = \frac{V_{12}}{I_{43}}, \quad R_{34,21} = \frac{V_{21}}{I_{34}} \]
\[ R_{14,23} = \frac{V_{23}}{I_{14}}, \quad R_{41,32} = \frac{V_{32}}{I_{41}} \]

Note that with this switching arrangement the voltmeter is reading only positive voltages, so the meter must be carefully zeroed. Because the second half of this sequence of measurements is redundant, it permits important consistency checks on measurement repeatability, Ohmic contact quality and sample uniformity.

- Measurement consistency following current reversal requires that:

\[ R_{21,34} = R_{12,43} \]
\[ R_{32,41} = R_{23,14} \]
\[ R_{43,12} = R_{34,21} \]
\[ R_{14,23} = R_{41,32} \]

The reciprocity theorem requires that:

\[ R_{21,34} + R_{12,43} = R_{43,12} + R_{34,21} \]
\[ R_{32,41} + R_{23,14} = R_{14,23} + R_{41,32} \]
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• Resistivity Measurements

The sheet resistance $R_s$ can be determined from the two characteristic resistances and via the van der Pauw equation [Eq. (C-21)]. One can calculate $R_s$. If the conducting

\[
R_a = \frac{R_{21,34} + R_{12,43} + R_{34,12} + R_{34,21}}{4}
\]

\[
R_b = \frac{R_{32,41} + R_{23,14} + R_{14,23} + R_{41,32}}{4}
\]

(C-27)

layer thickness $d$ is known, the bulk resistivity $\rho = R_s d$ can be calculated from $R_s$.

C.3.2. Hall Measurements

The objective of the Hall measurements in the van der Pauw technique is to determine the sheet carrier density $n_s$ by measuring the Hall voltage $V_h$ as shown in the following equation

\[
n_s = \frac{IB}{q|V_h|}
\]

(C-28)

The Hall voltage measurement consists of a series of voltage measurements with a constant current $I$ and a constant magnetic field $B$ applied perpendicular to the plane of the sample. Thus, by measuring the Hall voltage $V_h$ and from the known values of $I$, $B$ and $q$, one can determine the sheet density $n_s$ of charge carriers in semiconductors. The Hall voltage is negative for $n$-type and positive for $p$-type semiconductors.
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• Definitions for Hall Measurements

The Hall measurement, carried out in the presence of a magnetic field, yields the sheet carrier density \( n \), and the bulk carrier density \( n \) or \( p \) (for \( n \)-type or \( p \)-type material) if the conducting layer thickness of the sample is known. The Hall voltage for thick, heavily doped samples can be quite small (of the order of microvolts). The most common way to control this problem is to acquire two sets of Hall measurements, one for positive and one for negative magnetic field direction. The relevant definitions are as follows (Fig. C. 5):

\[
I_{13} = \text{dc current injected into lead 1 and taken out of lead 3. Likewise for } I_{31}, I_{42}, I_{24}.
\]

\[
B = \text{constant and uniform magnetic field intensity (to within 3\% applied parallel to the } z\text{-axis}. B \text{ is positive when pointing in the positive } z \text{ direction and negative when pointing in the negative } z \text{ direction.}
\]

\[
V_{24p} = \text{Hall voltage measured between leads 2 and 4 with magnetic field positive for } I_{13}. \text{ Likewise for } V_{42p}, V_{13p} \text{ and } V_{31p}.
\]

Similar definitions for \( V_{24n}, V_{42n}, V_{13n} \) and \( V_{31n} \) apply when the magnetic field \( B \) is reversed.

• Hall Measurements

The procedure for the Hall measurement is:

- Apply a positive magnetic field \( B \)

- Apply a current \( I_{13} \) to leads 1 and 3 and measure \( V_{24p} \)

- Apply a current \( I_{31} \) to leads 3 and 1 and measure \( V_{42p} \)

- Likewise, measure \( V_{13p} \) and \( V_{31p} \) with \( I_{42} \) and \( I_{24} \), respectively
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- Reverse the magnetic field (negative $B$)

- Likewise, measure $V_{24N}$, $V_{42N}$, $V_{13N}$ and $V_{31N}$ with $I_{13}$, $I_{31}$, $I_{42}$ and $I_{24}$, respectively

  This sequence of measurements is redundant in that for a uniform sample the average Hall voltage from each of the two diagonal sets of contacts should be the same.

- Hall Calculations

Steps for the calculation of carrier density and Hall mobility are:

- Calculate the following (be careful to maintain the signs of measured voltages to correct for the offset voltage):

  $$
  V_C = V_{24P} - V_{24N},
  V_D = V_{42P} - V_{42N},
  V_E = V_{13P} - V_{13N},
  V_F = V_{31P} - V_{31N}.
  \tag{C-29}
  $$

- The sample type is determined from the polarity of the voltage sum $V_C + V_D + V_E + V_F$.

  If this sum is positive (negative), the sample is $p$-type ($n$-type).

- The sheet carrier density (in units of $\text{cm}^{-2}$) is calculated from

  $$
  p_s = 8 \times 10^{-8} \frac{IB}{q(V_C + V_D + V_E + V_F)} \tag{C-30a}
  $$

  if the voltage sum is positive, or

  $$
  n_s = 8 \times 10^{-8} \frac{IB}{q(V_C + V_D + V_E + V_F)} \tag{C-30b}
  $$

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where $B$ is the magnetic field in gauss (G) and $I$ is the d.c current in amperes (A).

- The bulk carrier density (in units of cm$^{-3}$) can be determined as follows if the conducting layer thickness $d$ of the sample is known:

$$n = \frac{n_s}{d}$$

$$p = \frac{p_s}{d}$$

(C-31)

- The Hall mobility $\mu = 1/(qn_s R_s)$ (in units of cm$^2$V$^{-1}$s$^{-1}$) is calculated from the sheet carrier density $n_s$ (or $p_s$) and the sheet resistance $R_s$.

There are practical aspects which must be considered when carrying out Hall and resistivity measurements. Primary concerns are (1) Ohmic contact quality and size; (2) sample uniformity and accurate thickness determination; (3) thermomagnetic effects due to nonuniform temperature; (4) photoconductive and photovoltaic effects which can be minimized by measuring in a dark environment; (5) the sample lateral dimensions must be large compared to the size of the contacts and the sample thickness and (6) finally, one must accurately measure sample temperature, magnetic field intensity, electrical current and voltage$^{280}$.

The next worksheet simplifies step by step the needed measurements to achieve reliable results.
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Van der Pauw Hall Measurement Worksheet

Sample Identification

Thickness if known (cm) Dimensions

Contact Metal Contact Process

Comments

Resistivity Measurement

Temperature (°C)

\[
\begin{align*}
I_{21} & \quad V_{34} & R_{21,34} \\
I_{32} & \quad V_{41} & R_{32,41} \\
I_{23} & \quad V_{14} & R_{23,14} \\
I_{43} & \quad V_{12} & R_{43,12} \\
I_{34} & \quad V_{21} & R_{34,21} \\
I_{41} & \quad V_{23} & R_{41,23} \\
I_{41} & \quad V_{32} & R_{41,32}
\end{align*}
\]

\[ R_A = \quad \text{(Eq. C-27)} \]

\[ R_B = \quad \text{(Eq. C-27)} \]

\[
\exp(-\pi R_A/R_g) + \exp(-\pi R_B/R_g) = 1
\]

\[ (\text{Eq. C-21}) \]

\[ R_s = \quad \text{(Ω/square)} \]

For known thickness \( \rho = R_s \cdot d \) (Ω.cm)

\[ \mu = 1/(q \rho R_s) = \quad \text{(cm}^2\text{V}^{-1}\text{s}^{-1}) \]

\[ (\text{Eq. C-20}) \]

Hall voltage measurements

Temperature (°C)

\[ +B \text{ Field (G)} \]

\[
\begin{align*}
I_{13} & \quad V_{24P} \\
I_{31} & \quad V_{42P} \\
I_{42} & \quad V_{13P} \\
I_{34} & \quad V_{31P}
\end{align*}
\]

\[ \Sigma V_i \]

\[ (\text{Eq. C-29}) \]

\[ n_s = \quad 8 \times 10^8 \text{l.B/q/} \Sigma V_i \]

\[ (\text{Eq. C-30b}) \]

\[ n_s = \quad \text{cm}^2 \]

For known thickness \( n = n_s / d \)

Prepared by
Yourself
Auch
Feb. 2005

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[254] www.miratechcorp.com


