Chemical Vapor Deposition and Characterization of Polysilanes Polymer Based Thin Films and Their Applications in Compound Semiconductors and Silicon Devices

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This thesis is dedicated to my sons Haron and Adam
and to the memory of my father
ABSTRACT

As the semiconductors industry is moving toward nanodevices, there is growing need to develop new materials and thin films deposition processes which could enable strict control of the atomic composition and structure of thin film materials in order to achieve precise control on their electrical and optical properties. The accurate control of thin film characteristics will become increasingly important as the miniaturization of semiconductor devices continue. There is no doubt that chemical synthesis of new materials and their self assembly will play a major role in the design and fabrication of next generation semiconductor devices.

The objective of this work is to investigate the chemical vapor deposition (CVD) process of thin film using a polymeric precursor as a source material. This process offers many advantages including low deposition cost, hazard free working environment, and most importantly the ability to customize the polymer source material through polymer synthesis and polymer functionalization. The combination between polymer synthesis and CVD process will enable the design of new generation of complex thin film materials with a wide range of improved chemical, mechanical, electrical and optical properties which cannot be easily achieved through conventional CVD processes based on gases and small molecule precursors.

In this thesis we mainly focused on polysilanes polymers and more specifically poly(dimethylsilanes). The interest in these polymers is motivated by their distinctive electronic and photonic properties which are attributed to the delocalization of the σ-electron along the Si-Si backbone chain. These characteristics make polysilane polymers very promising in a broad range of applications as a dielectric, a semiconductor and a conductor. The polymer-based CVD process could be eventually extended to other polymer source materials such as polygermanes, as well as and a variety of other inorganic and hybrid organic-inorganic polymers.

This work has demonstrated that a polysilane polymeric source can be used to deposit a wide range of thin film materials exhibiting similar properties with conventional ceramic materials such as silicon carbide (SiC), silicon oxynitride (SiON), silicon oxycarbide (SiOC)
silicon dioxide (SiO₂) and silicon nitride (Si₃N₄). The strict control of the deposition process allows precise control of the electrical, optical and chemical properties of polymer-based thin films within a broad range. This work has also demonstrated for the first time that poly(dimethylsilmaes) polymers deposited by CVD can be used to effectively passivate both silicon and gallium arsenide MOS devices. This finding makes polymer-based thin films obtained by CVD very promising for the development of high-κ dielectric materials for next generation high-mobility CMOS technology.

**Keywords:** Thin films, Polymers, Vapor Phase Deposition, CVD, Nanodielectrics, Organosilanes, Polysilanes, GaAs Passivation, MOSFET, Silicon Oxynitride, Integrated Waveguide, Silicon Carbide, Compound Semiconductors.
Au fur et à mesure que l'industrie des semi-conducteurs s'oriente vers les nanodispositifs, il y a un besoin croissant de développer de nouveaux matériaux et procédés de dépôt de couches minces qui pourraient permettre un contrôle strict de la composition et de la structure atomique des matériaux, ceci dans le but de réaliser un contrôle précis sur leurs propriétés électriques et optiques. Le contrôle précis des caractéristiques des couches minces deviendra de plus en plus important avec la miniaturisation des dispositifs semi-conducteurs. Il n'y a aucun doute que la synthèse chimique de nouveaux matériaux et leur auto-assemblage joueront un rôle très important dans la conception et la fabrication des dispositifs semi-conducteurs de la prochaine génération.

L'objectif de ce travail est d'étudier le procédé de dépôt en phase vapeur (CVD) des couches minces en utilisant un précurseur polymérique comme source. Ce procédé offre plusieurs avantages, notamment un coût de déposition relativement bas, un environnement de travail sans risque, et tout particulièrement la possibilité d'adapter le matériau de la source aux besoins à travers la synthèse et la fonctionnalisation des polymères. La combinaison entre la synthèse de polymère et le procédé de CVD permettra la conception d'une nouvelle génération de matériaux complexes avec un large éventail de propriétés chimiques, mécaniques, électriques et optiques améliorées qui ne peuvent pas être facilement obtenues par des procédés CVD conventionnels basés sur des gaz et des précurseurs moléculaires.

Dans cette thèse nous nous sommes principalement concentrés sur des polymères de polysilanes et plus spécifiquement sur les poly(diméthylsilanes). L'intérêt porté à ces polymères est motivé par leurs propriétés électroniques et photoniques distinctives, qui sont attribuées à la délocalisation des électron-σ le long de la chaîne du polymère. Ces caractéristiques rendent les polymères de polysilanes très attrayants dans un grand nombre d'applications telles que les diélectriques, les semi-conducteurs et les conducteurs. Le procédé CVD à base de polymères peut être éventuellement étendu à d'autres matériaux polymériques tels que des poly-germanes, ainsi qu'à une vaste variété de polymères inorganiques et organique-inorganiques hybrides.
Ce travail a démontré que les polymères polysilanes peuvent être utilisés comme source pour déposer un large éventail de matériaux en couche mince présentant des propriétés semblables aux matériaux céramiques conventionnels tels que le carbure de silicium (SiC), l'oxynitrure de silicium (SiON), le dioxyde de silicium (SiO₂), l'oxycarbure de silicium (SiOC), et le nitrure de silicium (Si₃N₄). Le contrôle strict des paramètres de procédé de dépôt permet un contrôle précis des propriétés électriques, optiques et chimiques des couches minces dans un large intervalle. Ce travail a également démontré pour la première fois que les polymères de polysilanes déposés par CVD peuvent être utilisés pour passer efficacement des dispositifs MOS à base d'arséniure de gallium et de silicium. Ces résultats rendent les couches minces à base des polymères, obtenues par CVD, très prometteuses pour le développement de matériaux diélectriques hauts-κ pour la technologie CMOS à haute mobilité de la prochaine génération.

Mots-clés : Couches minces, Polymères, Dépôt en Phase Vapeur, CVD, Nanodiélectriques, Organosilanes, Polysilanes, GaAs Passivation, MOSFET, Oxynitrure de Silicium, Guide d'Ondes Intégrés, Carbure de Silicium, Semiconducteurs Composés
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<td>Atomic layer Deposition</td>
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<td>APPLD</td>
<td>Atmospheric Pressure Plasma Liquid Deposition</td>
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<td>ATM</td>
<td>Atomic Force Microscope</td>
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<td>CBE</td>
<td>Chemical Beam Epitaxy</td>
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<td>CMOS</td>
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CHAPTER 1

INTRODUCTION

1.1 Semiconductor technology status and trends

During the past few decades, the continuous increase in transistor density and performance guided by CMOS scaling process according to Moore's Law, has been a highly successful methodology in the rapid development of silicon technology. As the silicon industry is moving into the 22 nm node and beyond, significant technological challenges are imposed by silicon CMOS device scaling [1]. Two of the most important challenges are the continuous rising of power dissipation and the increasing variability in device characteristics. As the CMOS devices are approaching quantum-mechanical physics boundaries, it becomes evident that Moore's Law and CMOS scaling are coming to an end [2]. Industry directions for addressing these challenges are developing along two primary axes: extending silicon scaling through innovations in materials and device structure; and exploring post-silicon CMOS technology with new nanodevices based on distinctly different principles of physics, new materials, and new assembly processes.

1.1 Thin film materials technology

The large scale investment in the development of new thin film materials and new deposition processes has lead to explosion in scientific and technological breakthroughs in
microelectronics, optics and nanotechnology, over the past decade. The extension of synthesis flexibility has allowed the design and development of novel materials and precise control of their chemical composition and atomic nanostructure. As a result, a large number of new thin films material and deposition processes have been developed in recent years, which have enabled the fabrication of precisely controlled devices structure. Nowadays, there is now a much greater understanding of the link between film deposition parameters, film structure, and film properties. Such advances in the understanding of thin film preparation has been made possible by the development of broad range of deposition techniques such as molecular beam epitaxy (MBE) [3], atomic layer deposition (ALD) [4] and atmospheric pressure plasma liquid deposition (APPLD) [5], and also through advances in materials in-situ and ex-situ characterization tools such scanning tunneling microscope (STM) and atomic force microscope (ATM), to name only a few.

1.2 The nanotechnology era

As we enter the nanotechnology era it is becoming clear that the precise control of the atomic structure of thin film materials will become increasingly important to further the miniaturization of semiconductor devices [6]. The ability to understand and control the structure of materials at the atomic level will be essential if the semiconductor industry is to continue on its historical growth. Today, all the tools required to manipulate and observe the matter at the atomic level are available, and the ability to manipulate atoms at the atomic scale has been recently demonstrated [7]. While constructing a nanostructured block one atom at a time appears to be very attractive process for building nanodevices, it is unlikely that this process will be practical for large scale industrial fabrication of nanodevices, at least
in the near future. In contrast, nano-structured, self-assembled polymer materials, obtained through chemical synthesis, are expected to play a major role in shaping the future of semiconductor devices and nanotechnology [6, 8].

1.2 Polymer-based thin film materials

1.2.1 Brief introduction to polymers

Polymers have traditionally been used in electrical applications as the insulating materials that surround metal wires in order to prevent short-circuit between conductors, primarily because most polymers are electrically insulating. However, Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa (Chemistry Nobel prize laureates in 2000) changed this point of view nearly three decades ago when they observed a tremendous conductivity increase, by a factor of more than one billion, upon chemical oxidation of a polymer known as polyacetylene [9]. The relatively high conductivity observed in this polymer was later attributed to \( \pi \)-conjugated double bonds [10]. Since then, polymer-based electronic material and devices have quickly evolved into a well-established research and industrial field [11].

Today, there is a huge number of polymer materials available in the market, obtained either through chemical synthesizes or from natural processes [12]. Despite a broad spectrum of chemical structures and material properties possessed by various polymers, they are all built up from nanostructured units which are self-assembled to each other to form a long macromolecular chain upon polymerization. The result is usually an amorphous material that often can be processed from solution into very thin and flexible films by using a wide range of coating and deposition processes. The ability to process the polymers from solutions is a
key factor in manufacturing flexible polymer electronic devices at very low cost [13]. The other most important feature of polymers is the predictable variation of their optical and electronic properties with the molecular mass and chemical structure, which, in conjunction with the progress of the chemical synthesis procedures, have allowed the preparation of novel polymeric materials, with precise properties and functionalities, tailored for a wide range of applications [14].

1.2.2 Organic polymer thin films

Currently, polymer materials have found use in the electronics industry in both manufacturing processes used to generate today’s integrated circuits and as component in the device structure [15, 16]. The electronic properties of polymer-based thin films have been the subject of intense research because of the potential application of these materials as alternatives to conventional semiconductors for building low-cost, large area, flexible electronic devices [17].

Today a wide range of semiconductors, dielectrics and conductors based on polymer materials are available, and they have been successfully used to fabricate a growing number of semiconductor devices such as organic thin film transistor (OTFT) [18], organic solar cell [19], organic light emitting diode (OLED) [20], organic nonvolatile memory [21], organic waveguide [22], etc. The majority of these devices are prepared at relatively low temperature and in many cases at room temperature. As a consequence of the bonding structure of active organic materials, the semiconductor devices based on organic polymers have very low performance and are temperature and radiation sensitive, which make them relatively unstable and susceptible to degradation over somewhat short period of time [23].
1.2.3 Inorganic polymer thin film

In spite of the growing importance of organic polymers, attention is being focused increasingly on polymers that contain inorganic elements as well as organic components [24]. The main reason for the interest in this class of hybrid polymers is that inorganic polymers combine the advantages of inorganic materials and at the same time minimize some of the disadvantages of organic polymers [25]. The organic materials are usually easy to fabricate and process, but they become relatively unstable when exposed to high temperature, strongly oxidizing agents, high energy radiation and high intensity of light [26]. In inorganic polymers, combinations of properties can be achieved and tuned by combining the properties of inorganic backbone and the organic substituent [27]. While the backbone of inorganic polymer provides highly stable polymer structure with superior, mechanical, thermal, chemical and electrical properties, the organic constituents enable the reactive functionalities of the polymer.

Presently, inorganic polymers find application in nearly every industry and in a growing number of commercial products commonly used today. The majority of these applications consist of protective coating and materials reinforcement [28]. In semiconductor industry these polymers are mainly used in devices packaging and as a low-\(k\) interlayer dielectric materials in integrated circuits. However, in recent years, several emerging applications are being investigated such as nanolithography, integrated planar waveguide, high-\(\kappa\) dielectric for embedded capacitors, etc [29, 30].

A large number of inorganic polymers with a variety of chemical composition and structural configuration are available today. Organosilicon polymers (also known as
organosilane) in particular, are by far the most extensively studied inorganic polymers, due to their unique properties, which cannot be easily matched by other organic polymers [31]. Because of the importance of organosilicon polymers to the work presented in this thesis, further attention will be given to this class of polymers in the following sections.

1.3 Deposition of Polymer-based thin films

A large number of deposition processes have been developed for coating polymer thin film on a variety of substrates. The choice of the most advantageous deposition process for a particular polymer depend greatly on the polymer chemical and physical properties, the deposition temperature and the type of substrates to be coated, in addition to film quality such as uniformity, planarity, and defects concentration. The deposition processes of polymer thin films are broadly classified into two general categories: liquid phase deposition processes and vapor phase deposition processes.

1.3.1 Liquid phase deposition processes

The liquid phase deposition process is a relatively simple and mature process traditionally used for coating decorative materials on a variety of objects. The deposition process is achieved by dipping the object to be coated into a liquid solution of the coating material and then dried naturally or in a furnace to enhance the mechanical strength of the coating material. Today this process has greatly evolved and became a driving technology in polymer industry. A large number of liquid phase deposition techniques of thin films are available today including spin-coating, dip-coating, spray-coating, roll-coating, screen-printing, inkjet-printing, etc [32, 33].
In recent years sol-gel process, which combines liquid phase deposition techniques and polymer materials synthesis, has emerged as a very promising process for the deposition of ceramic thin film materials [34]. The sol-gel process offer many advantages, including low processing temperature, low deposition cost, large area coating, and very low equipments investment, in addition to the availability of unlimited number of pure and stable organic and inorganic materials, which can be easily obtained via chemical synthesis. Currently, the sol-gel process is widely used to prepare polymer-based ceramic thin films materials. The process has also demonstrated its potential towards commercial manufacturing in various fields of applications such as low-κ interlayer dielectrics and planar waveguides [35], and it is very promising technology for printed microelectronic devices and for block copolymers self-assembly in future nanoelectronic devices [36].

1.3.2 Vapor phase deposition processes

Vapor phase deposition processes have been widely used in semiconductor industry for several decades as the preferred method for coating the majority of inorganic materials commonly used in the fabrication of integrated circuits. The high quality of the thin films obtained through thermal evaporation in vacuum, and the ability to control precisely the thickness and the roughness of thin films are some of the many advantages offered by vapor phase deposition processes. Today, there are a large number of vapor phase deposition processes, which are widely used semiconductor industry; such as plasma enhanced chemical vapor deposition (PECVD) [37, 38], low pressure chemical vapor deposition (LPCVD) [38], metal organic chemical vapor deposition (MOCVD) [39], molecular beam epitaxy (MBE) [3.
Chemical Beam epitaxy (CBE) [39], atomic layer deposition (ALD) [4], and many others.

The majority of polymers thin films can be deposited by liquid phase deposition processes. However, these processes present several problems such as non-uniform film thickness, pinholes, non-conformality of the polymeric film to the substrate, as well as the residual solvent in the films [40]. In addition there are many attractive organic and inorganic polymers which cannot be easily dissolved to form a solution. In order to solve these problems and meet the demand for high performance organic polymer devices, several vapor phase deposition processes, adapted for coating polymer thin films materials, have been developed in recent years [41]. These processes have enabled better control of thickness, composition, structure, purity and morphology of polymer thin films. Some of the chemical vapor deposition processes include low pressure organic vapor phase deposition (OVPD) [42], and atmospheric pressure plasma liquid deposition (APPLD) [5]. Polymer thin films have also been obtained by physical vapor deposition of monomers using electron beam evaporation (EBE), sputtering, and pulsed laser deposition (PLD), in the presence of an activating source such as a hot filament or quartz lamps which act as initiators for polymerization [43]. While these depositions methods are widely investigated for the growth of organic polymer, our research have been focused on the development of chemical vapor deposition (CVD) process of inorganic polymer materials, such as polysilanes. Figure 1.1 shows the CVD system setup used in our laboratory for the deposition of polymer-based thin films.
Figure 1.1: Typical setup of the chemical vapour deposition (CVD) system used for the deposition of polymer-based thin films. The top image shows the three-zone furnace with a horizontal quartz tube, and the polymer powder dispensing system. The bottom image shows the vacuum load-lock chamber used for loading two inch wafers and various other substrates.
1.4 Silicon based polymeric materials

1.4.1 Organosilane polymers

Organosilane (organosilicon) polymers have been known for nearly a century, the interest in these materials is motivated by the abundance of silicon on earth and also the distinctive and superior properties of these inorganic polymers as compared to organic polymers [44]. Organosilane polymers in their broadest definition are defined as polymers with silicon atoms in their backbone. They can only be obtained through chemical synthesis, as they do not occur naturally. Because the silicon can form bonds with most of other elements in the periodic table, this has lead to an explosion in the number of organosilicon polymers available today [31, 44, 45].

Organosilicon polymers can be subdivided into four major categories based on silicon coordination, which include polysiloxanes, polysilazanes, polycarbosilanes, and polysilanes [44, 46]. The global interest in polysiloxanes, polysilazanes, and polycarbosilanes polymers is primarily linked to their wide use in production of ceramic materials, such as silicon carbide, silicon nitride and silicon dioxide, which are commonly used for protective coatings, insulation, and reinforcement of nanocomposite materials [47]. The polysilanes on the other hand started to emerge in recent years as a potential material, which is very promising as a dielectric, semiconductor, and conductor in various applications [46-48]. As a result, the following sections will be mainly focused on polysilanes polymers.
1.4.2 Polysilane polymers

Polysilane polymers also called polysilylene, have received much attention in recent years because of their unusual electric and photoelectronic properties. The distinctive properties of these polymers were attributed to the delocalization of the $\sigma$-electron along the Si-Si backbone chain [48, 49]. The electrical and optical properties of polysilanes differ significantly from structurally analogous carbon-based $\sigma$-bound systems, like polystyrene and polyethylene, and rather resemble fully $\pi$-conjugated systems, like polyacetylenes. While polysilanes, in general, exhibit dielectric behavior, they can be made semiconductor with the addition of suitable dopants such as FeCl$_3$, SbF$_3$ or iodine (I$_2$) [50]. The conductivity of the polymer can be modulated in the range $10^{-15}$ to $10^{-3}$ S cm$^{-1}$ through a combination of organic substituents and dopants. The ability to modulate the conductivity of polysilanes over a broad range have made them very attractive both as a dielectric and as a semiconductor in a wide range of microelectronic and optoelectronic applications such as solar cells [51], light emitting diodes [52], integrated waveguides [53] and phototransistors [54].

1.5 Preparation of polysilanes polymer-based thin film

1.5.1 Synthesis and functionalization of polysilanes

Polysilanes have been widely prepared by the classic Wurtz-type coupling reaction of dichlorosilanes with its typical conditions of molten sodium in hot toluene [46]. However this preparation method is not convenient for incorporating many functional groups in polysilanes polymers. As a consequence, a number of new routes suitable for the synthesis of polysilanes, which allow more diversified functional groups and enable the control of the
polymer structure at the micro and macro level, have been developed. Some of these synthesis routes include anionic polymerization of masked disilenes, ring opening polymerization, dehydrocoupling polymerization, electrochemical polymerization, chemical vapor deposition polymerization, redistribution polymerization and disproportionation polymerization [46, 55].

The modification of the physical and chemical properties of the polysilanes polymers can be achieved through pre- and post-polymerization functionalization [56, 57]. The combination between the different synthesis routes and the functionalization processes, discussed above, provide unlimited possibilities to design and tune the properties of polysilanes polymers to satisfy the requirements of future microelectronic and nanoelectronic materials and devices.

1.5.2 Chemical vapor deposition of polysilanes thin films

The conventional method commonly utilised to prepare polysilanes based polymers films consist of dissolving a polymer precursor in an organic solvent to obtain a liquid solution with the required viscosity. The solution is then spin coated on the substrate and pyrolyzed at high temperature in oxygen-free atmosphere in order to evaporate the solvent. This method of preparation has been broadly used for ceramic coating and preparation of dielectric materials [58, 59]. The poor quality of polymer thin films obtained by this method and their porous nature and also the non availability of solvent for many polysilanes polymers such as polydimethylsilane (PDMS), have considerably limited the applications of polysilanes polymers.
Due to many attractive properties of polysilanes, they are very promising for wide range of nanoelectronic and nanophotonic applications. However, many of the new emerging applications require precise control of thin films thickness, morphology, atomic composition, and chemical structure which cannot be achieved by spin coating process. Therefore, over the past few years our research group have been focusing on the development of polymer-based chemical vapor deposition process of polysilanes materials [60, 61]. This process is expected to enable the growth of high quality thin film with a wide range of properties that can be easily customised through polymer synthesis and functionalization. One of the main objectives of this Ph.D. thesis is to design and optimize the chemical vapor deposition system and the deposition process of polysilanes polymer-based thin film and to explore their potential applications.

1.6 Polysilanes polymer-based thin films potential applications

In recent years a growing number of promising applications based on of polysilanes are under development. In the following section we will briefly present some of the most important and potential applications of polsilane polymers, which will be further investigated throughout this thesis.

1.6.1 Low-κ dielectrics materials

As the interlayer spacing in advanced integrated circuit manufacturing is continuously shrinking, low-κ dielectric materials are needed to reduce the interlayer dielectric capacitance, in order to minimize the interconnect propagation delay, cross talk noise and power dissipation [62]. In recent years, several spin coated organic and inorganic materials
with very low dielectric constant have been considered as an alternative to SiO₂ in the fabrication of CMOS devices, such as silsesquioxane (SSQ), siloxane (SOG), teflon (PTFE) and polyimides [62, 63]. While materials with dielectric constant values below 3 have been demonstrated, most of them are either not stable at processing temperature above 400 °C or are mechanically weak, and present integration challenges with Cu damascene processes. In order to solve these issues, several low-κ dielectric materials obtained by CVD have been recently investigated. Some of the most promising materials include hydrogenated amorphous silicon oxycarbide [64], parylene [65] and fluorinated amorphous carbon [66]. Silicon oxycarbide thin films are widely obtained by CVD using dimethylsilane, trimethylsilanes and tetramethyldisilanes as a source material [67]. Polysilanes polymers are very promising alternative to methylsilane molecules as a source material in CVD process. The ability to tune polysilanes polymers through polymer synthesis and functionalization is expected to enable the development of very low-κ dielectric materials.

1.6.2 High-κ dielectrics materials

The further increase of computing speed is a very difficult and complex problem, which includes the use of new materials, novel electronic devices, and maybe novel principles of computing and computer architecture. As we move toward nanodevices it is becoming obvious that the silicon CMOS technology is facing a very doubtful future. The scaling of conventional silicon based metal-oxide-semiconductor (MOS) transistors will soon require very thin gate dielectric films, below 1 nm. However, the increase of leakage current through thinner SiO₂ films puts a fundamental limit on the existing MOS technology [68].
High dielectric constant materials are therefore needed in order to reduce the MOS transistor gate leakage current and improve its performance.

In hope to extend the lifetime of Silicon CMOS technology for at least one or two more decades, a large number of new high-κ dielectric materials have been investigated as substitutes for SiO₂ in MOS devices, some of these high-κ dielectric materials include SiON, Al₂O₃, HfO₂, Ta₂O₅, ZrO₂, TiO₂ and La₂O₃ [69-70]. Significant progress has been achieved in the growth processes of these materials and in understanding their chemical, structural and electrical properties, as well as their integration into CMOS devices. After nearly a decade of intense research, the family of hafnium-oxide-based materials, such as HfO₂, and HfSiₓOᵧNₓ, has emerged as a leading candidate to replace SiO₂ gate dielectrics in advanced CMOS ULSI devices [71]. While hafnium-oxide based high-k dielectrics will probably remain attractive down to 32 nm node, a new high-k dielectric materials will be again required for 22 nm node and beyond.

Hybrid organic-inorganic polymer materials are expected to play a major role in the design of future high-κ dielectric materials. Several composite polymer materials with ultra high dielectric constant exceeding 100 have been reported in recent years [73, 74]. Although these materials are still not suitable for MOS application, their development has stimulated interest in the synthesis of new polymers with ultra-high dielectric constant for a wide range of application.

1.6.3 MOSFET passivation

It is well known that III-V semiconductors having high values of charge carrier mobility can offer much higher operational frequency than silicon devices. However, despite
obvious functional advantages of III-V semiconductor devices, 95% of the microelectronics market remains dominated by silicon technology. This is mainly attributed to the high quality of the interface between crystalline silicon and thermally grown silicon dioxide. However, as the silicon technology approach its limits, a shift towards III-V compounds semiconductor materials or other high mobility semiconductor materials will be inevitable in the near future [75]. As a result, research has intensified in recent years in order to identify the most promising high mobility channel materials as a substitute to silicon in CMOS technology, beyond the 22 nm node. Currently, compound semiconductors such as GaAs, InAs and InSb are receiving a great deal of attention as the most attractive high mobility materials for next generation MOSFET [76, 77].

The development of stable gate dielectric material for III-V compound semiconductors, which can achieve very low density of interface defects, comparable with that of silicon dioxide on silicon, remain one of the big hurdles facing the integration and the wide adoption of very high mobility materials. In recent years, tremendous efforts have been made to develop new passivation processes and new nanostructured materials, which have allowed better control and understanding of surface and interface properties of various dielectric thin films on III-V compound semiconductor [78, 79]. As a result, it is becoming clear that precise control of the atomic composition and the molecular structure of the passivation layer are very critical in order to achieve excellent passivation of high mobility compound semiconductors. Therefore, synthetic polymer materials with precise atomic configuration and chemical composition are expected to play a key role in the development of new passivation materials for high mobility compound semiconductor in future CMOS technology. Currently, organosilanes polymers such as polysilanes are starting to attract a lot
of attention as a source material in a wide range of surface passivation and surface functionalization processes [80]. The ability to tailor atomic composition and chemical structure of these polymers, via chemical synthesis and functionalization, make them very promising for passivation of high mobility compound semiconductors.

1.6.4 Silicon carbide

Silicon carbide (SiC) based semiconductor electronic devices and circuits are presently being developed for use in high-temperature, high-power, and high-radiation conditions under which conventional semiconductor materials cannot adequately perform [81]. Silicon carbide’s ability to function under such extreme conditions is expected to enable significant improvements in the performance of a variety of applications such as high-voltage switching, electric motor drives, and more powerful high speed communications systems. Silicon carbide exhibits many superior properties, such as high thermal conductivity (4.9 W/cmK), relatively high electron mobility (1000 cm²/Vs), high breakdown electric fields (4 × 10⁶ V/cm), wide bandgap (2 to 3.5 eV), and excellent physical and chemical stability. These characteristics make this material the ideal choice for high temperature, high power, and high voltage integrated electronic devices such as power MOSFET and rectifying diodes [82, 83]. The biggest problem with the commercialization of SiC devices is the high cost and limited availability of bulk substrate. Although 6H-SiC and 4H-SiC bulk substrates are now available from few suppliers, the wafers quality is still far from optimized. As a result, a lot of works have been focused on the development of high quality silicon carbide thin films on various substrates.
Chemical vapor deposition (CVD) is widely employed for epitaxial growth silicon carbide (β-SiC) thin films on crystalline silicon substrate. Highly crystalline β-SiC thin films are normally obtained at relatively high temperature, around 1300 °C, using a combination of gases precursors such as silane and hydrocarbons [84]. High growth temperatures usually result in high tensile stress and lattice defects in silicon carbide thin films, due to the differences in lattice constants and thermal expansion coefficients between silicon carbide and silicon. Furthermore, the very high deposition temperature makes the integration of silicon carbide thin film difficult and incompatible with many applications and fabrication processes.

In attempt to reduce the deposition temperature of β-SiC thin film, efforts have been focused in recent years on the synthesis of new precursor materials. Single source precursors of organosilanes molecules such as tetramethylsilane, trimethylsilane, dimethylsilane, monomethylsilane, and disilabutane have been extensively investigated, as an alternative to conventional silane and methane gases mixture in CVD process [85]. Ceramic SiC thin film is also widely prepared via spin coating and pyrolysis of organosilanes polymers such as polysilanes and polycarbosilanes [86].

In recent years, our research group has been focused on development of new CVD process for the deposition of ceramic silicon carbide thin film using polysilanes polymers as source materials [61]. This new approach has many advantages such as high deposition rate, hazard free environment; due to elimination of gases precursors, compatibility with batch processes, and overall low deposition cost of ceramic SiC thin films.
1.6.5 Integrated optical waveguides

The rapid growth of telecommunication market increasingly demands high speed processing and transmission of large-bandwidth data. In order to satisfy these demands, highly integrated low cost optical and photonic devices are required. During the last two decades, attention has been paid to silicon oxynitride (SiOxNy) as a potential material for planar integrated optics [87]. This attention has been mainly motivated by its excellent optical properties such as low absorption losses in the visible and near infrared. SiON combines the dielectric properties of SiO2 together with good chemical inertness and low permeability of Si3N4. In addition, the refractive index of SiON thin film can be easily adjusted over a wide range (1.45 to 2.0) by simply varying the concentration of oxygen in the film [88]. This attractive property allows fabrication of waveguides with desired characteristics of fiber match and compactness. Moreover, the growth of SiON layers on silicon substrate is done by well established standard silicon integrated circuit fabrication processes, which enable low cost and high integration of planar waveguides and several other optical devices.

Silicon oxynitride thin films are widely deposited by plasma enhanced chemical vapor deposition (PECVD) [88-90] and low pressure chemical vapor deposition (LPCVD) [90] using a mixture of gases precursor such as silane (SiH₄), ammonia (NH₃) and nitrous oxide (N₂O). SiON can also be prepared by several other CVD methods using a wide range of organosilanes molecules and polymers as a source material. Currently, polymer-based thin films materials, and particularly polysilanes are attracting a lot of attention as a low cost alternative for the fabrication of integrated optical waveguides [91, 92]. The discovery of photobleaching phenomenon in conjugated polymers has made polysilanes very promising
for the design and the fabrication of very complex planar waveguide structures for optical communication [93].
CHAPTER 2

CHARACTERIZATION OF SILICON CARBIDE THIN FILMS OBTAINED VIA SUBLIMATION OF A SOLID POLYMER SOURCE USING POLYMER-SOURCE CVD PROCESS

CARACTÉRISATION DES COUCHES MINCES DE CARBURE DE SILICIUM OBTENUES PAR SUBLIMATION D'UNE SOURCE POLYMÉRIQUE SOLIDE EN UTILISANT UN PROCÉDÉ CVD

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Abstract

Silicon carbide thin films have been deposited via sublimation of a solid organosilane polymer source using atmospheric pressure chemical vapour deposition process (PS-CVD). The advantages of this new process include high deposition rate, compatibility with batch process, hazard-free working environment and low deposition cost. The silicon carbide (SiC) thin films obtained through this process exhibit a highly uniform film thickness, highly conformal coating, and very high chemical resistance to acids and alkaline solutions. These characteristics make the SiC thin films obtained by PSCVD process very attractive as a structural material for micro-electro-mechanical systems (MEMS) and as a coating film in a wide range of other applications. These SiC thin films are also expected to be attractive as a semiconductor material provided that the defects, oxygen and nitrogen contaminations can be reduced and effectively controlled. In this work we have investigated the chemical, structural, electrical and optical properties of these films, using scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FT-IR), elastic recoil detection spectroscopy (ERD), ultraviolet-visible photospectroscopy (UV-Vis), ellipsometry, and capacitance-voltage measurements (C-V).
Résumé

Les couches minces de carbure de silicium ont été déposées par sublimation d'une source de polymère solide d'organosilane en utilisant un procédé de dépôt en phase vapeur, à pression atmosphérique (PS-CVD). Ce nouveau procédé a plusieurs avantages en particulier un taux de dépôt très élevé, la compatibilité avec le traitement par lots, un environnement de travail sans risque et un coût de dépôt relativement bas. Les couches minces de carbure de silicium (SiC) obtenues par ce procédé ont une épaisseur très uniforme, un revêtement conforme et une forte résistance chimique aux solutions acides et alcalines. Ces caractéristiques rendent les couches minces de SiC obtenues par le procédé de PSCVD très attrayantes comme un matériau de structure pour les systèmes micro-électro-mécaniques (MEMS) et comme une couche de revêtement pour un large éventail d'applications. Ces couches minces de SiC pourraient être également intéressantes comme matériau semiconducteur à condition que les défauts, et les contaminations d'oxygène et d'azote puissent être réduites et efficacement contrôlées. Dans ce travail nous avons étudié les propriétés de produit chimique, structurales, électriques et optiques des couches minces de SiC obtenues par le procédé PS-CVD en utilisant le microscope électronique à balayage (SEM), la spectroscopie infrarouge à transformée de Fourier (FT-IR), la spectroscopie élastique de détection de recul (ERD), la photospectroscopie ultra-violet-visible (UV-Vis), l'ellipsométrie, et la mesure de capacité-tension (C-V).
2.1 Introduction

Thin films of silicon carbide have been intensively investigated as an alternative to crystalline silicon carbide mainly because of their low preparation cost, simple processing and easy integration with other thin film materials. Nowadays they are commonly used in a wide range of semiconductor devices including window layer for solar cells [1], rectifying diode [2], photo-detector [3], MEMS pressure sensor [4], surface coating [5], membrane for X-ray lithography [6] and a variety of other applications.

Chemical vapour deposition (CVD) process has been widely used in semiconductor industry for several decades and it is commonly used to prepare both crystalline and amorphous thin films of silicon carbide [7-12]. However, high quality single crystal silicon carbide are usually obtained with this process at very high temperature. In recent years, thin film of 3C-SiC epitaxially grown on silicon at a relatively low temperature (800 °C -1300 °C) are being widely investigated as a promising alternative to bulk crystalline silicon carbide [8, 12]. However, these films can only be grown on silicon wafer and a carbonisation process is always required, to minimize film stress and to achieve epitaxial growth. Because the CVD process requires highly volatile precursors to achieve uniform and continuous vapour transport, the majority of CVD processes are designed for the utilization of gaseous or liquid sources with high vapour pressure at specific temperature. Most of these gases precursors are highly toxic, oxygen and moisture sensitive, and highly flammable, so that special handling precautions are always required.

The pyrolysis process on the other hand has received a great deal of attention as a promising low cost alternative method to deposit both bulk and thin films of silicon carbide.
Amorphous, nanocrystalline and polycrystalline silicon carbide films have been deposited as the ceramic residue obtained via spin-coating or dip-coating of various liquid and solid polymeric precursors, such as polycarbosilane or organo-polysilane species [13-16]. In contrast with the CVD process, the low volatility is a crucial property for the polymeric precursors in order to achieve a high ceramic yield. These silicon carbide ceramic films are sought due to their valuable intrinsic properties such as high tensile strength, high thermal conductivity and radiation resistance, and rarely for their electrical properties. Currently, many efforts are dedicated to the synthesis of high purity polymeric precursor, and to develop new methods for the deposition of silicon carbide thin films better adapted to the chemical and structural purity required by the semiconductor industry.

A CVD process using a polymeric source appeared to be an attractive method to deposit silicon carbide thin films at a relatively lower temperature and at a lower cost [17]. This idea has been rapidly accepted by various academic research groups and industrial players, covering the whole chart between fundamental research and new emerging commercial products. Currently, a handful of important players are in competition either for the design of various polymeric sources adapted to different applications, or for the optimization of CVD-parameters adapted to the utilization of polymeric sources. In this paper we present and discuss the chemical, electrical and optical characteristics of SiC thin films obtained by this method using polydimethylsilane (PDMS) solid polymer source.

### 2.2 Experimental

Silicon carbide thin films were obtained through the sublimation of polydimethylsilane (PDMS) polymer powder using Lindberg horizontal three-zone furnace.
The furnace is equipped with a 2.5 inch quartz tube attached to an argon tank, an oil bubbler, and a Fisher Maxima vacuum pump capable of achieving a vacuum down to $10^{-3}$ torr. The films were deposited on both polished N-type crystalline silicon wafer and on electronic grade quartz substrates. Prior to deposition of SiC thin films, silicon and quartz substrates were properly cleaned in an ultrasonic bath for several minutes using acetone, isopropyl alcohol (IPA) and deionized-water, and were dried using boiling isopropyl alcohol. The samples were introduced in the furnace together with a boat containing the PDMS polymer powder. In order to eliminate residual moisture and oxygen contamination, the reactor is pumped down for extended period of time and purged three times with the flow of ultra high purity argon before starting the polymer sublimation process. Argon was used as the carrier gas, with a constant flow during the deposition process. The deposition pressure is kept near atmospheric pressure while the deposition temperature is gradually increased up to 800 °C at a rate of 16 °C per minute. The samples were maintained at the maximum temperature for approximately 30 minutes, immediately after that the reactor is shut down to allow natural cooling of the samples, to avoid film cracking.

Fourier transform infrared spectroscopy (FT-IR) has been used to examine the deposited film on single crystal silicon wafers. The absorption spectra were acquired in the MID-IR range ($4000 \text{ cm}^{-1}$ to $400 \text{ cm}^{-1}$), using a Mattson Galaxy Series FTIR-6020 spectrophotometer. The atomic composition of the films was obtained by elastic recoil detection spectroscopy, using time-of-flight analysis (TOF-ERD). The films morphology was analyzed using high resolution scanning electron microscope (SEM). The dielectric constant was extracted from capacitance-voltage measurement obtained by Schlumberger impedance analyzer SI260 equipped with a mercury probe. The optical band gap was extracted from the
ultraviolet-visible absorption spectra measured using Hewlet-Packard HP8452 UV/Vis spectrophotometer. The films thickness and the refractive index were determined by J. A. Woollam Alpha-SE ellipsometer.

2.3 Results and discussion

2.3.1 Scanning electron microscope (SEM) analysis

The thin films obtained by polymer sources CVD process using PDMS powder are found to exhibit a very uniform film thickness over a relatively large area. Figure 2.1(a) show the cross section image of the film deposited on silicon substrate obtained by scanning electron microscope (SEM). Since the process is not conducted under continuous flow of polymer it was not possible to determine a deposition rate. Because the deposition process is conducted at near atmospheric pressure all the film obtained by this process are conformal; this is confirmed by the SEM cross section image of figure 2.1(c), which shows the deposition of the film on the edge of the wafer. The top view SEM image of the film obtained at high resolution shows very uniform film morphology with very small grain size, which suggests that these films are amorphous. The atomic concentration of oxygen in the samples was found to vary from sample to sample (from 2 at.% to 10 at.%) due to reactor leakage and residual contamination [18]. In this study we only focus on the samples with a low oxygen concentration (around 2 at.%).
Figure 2.1: High-resolution SEM of SiC film on silicon; (a, c) cross section view, (b) top view
2.3.2 Wet chemical etching analysis

The chemical resistance to acid and alkaline solutions was investigated by dipping a silicon substrate coated with 200 nm thick films in both HNA (C\textsubscript{2}O\textsubscript{2}H\textsubscript{4}:HNO\textsubscript{3}:HF; 8:3:1) and molten KOH (30 \%, 95 °C) solutions for 24 hours. During this experiment, the back sides of the silicon substrates were coated with polyimide and copper foil respectively. After this period of exposure, the film thickness was measured again by ellipsometry and did not show any noticeable change, which indicates that the etch rate in these solutions is extremely slow. These films are therefore highly resistant to both acids and alkaline solutions. The above characteristics make these films very attractive as a coating material and possibly as a thin film membrane for MEMS devices.

2.3.3 Fourier transform infrared spectroscopy (FT-IR) analysis

Immediately after the films deposition the chemical structure was analyzed using FT-IR spectroscopy. Figure 2.2 show the typical absorbance spectrum of the thin films deposited on silicon substrate under the experimental conditions described above. A preliminary look at the FT-IR spectrum shows a main peak around 780 cm\textsuperscript{-1} commonly associated with silicon carbide formation [16, 17, 19, 20]. The broad shoulder around 1250 cm\textsuperscript{-1} is generally associated with the bending mode of residual Si-CH\textsubscript{3} groups in silicon carbide thin film [16, 19, 20].

In order to better understand the structural composition of these films, we further analyzed their spectral decomposition using Peakfit software. The deconvolution of the FT-IR spectra was obtained assuming a Gaussian distribution. The deconvolution reveals several
hidden peaks as shown in figure 2.2. The association of each peak was determined by comparing the peak wavenumbers with those reported in the literature. The results are summarized in table 2.1.

![FTIR spectra of SiC thin film and the corresponding deconvolution peaks](image)

**Figure 2.2:** FTIR spectra of SiC thin film and the corresponding deconvolution peaks

The relatively high absorbance intensity of Si-C stretching mode observed at 787 cm\(^{-1}\) and the broad absorption band around 1280 cm\(^{-1}\) indicate that these films are very similar to amorphous silicon carbide thin films obtained by other deposition methods [20-22]. The presence of oxygen in this film was established with the weak absorption bands observed around 3770 cm\(^{-1}\) and 3885 cm\(^{-1}\) due to stretching mode of O-H bonds [16, 19]. Since the
PDMS polymer source in its purified form contains only silicon, carbon and hydrogen, the presence of oxygen in these films is likely due to the reactor or polymer contamination and film oxidation.

**Table 2.1:** Absorption peaks assignments of SiC thin film obtained by PS-CVD

<table>
<thead>
<tr>
<th>Wavenumber (/cm)</th>
<th>Peak Assignment and Vibration Mode</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>575</td>
<td>Si-H rocking and Si-Si stretching</td>
<td>21</td>
</tr>
<tr>
<td>787</td>
<td>Si-C stretching</td>
<td>16, 19-21</td>
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<td>995</td>
<td>Si-(CH$_2$)$_n$-Si, Si-C-C bending, Si-O-Si</td>
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<td>1540</td>
<td>Si-CH$_3$ asymmetric bending of CH$_3$</td>
<td>16, 19, 20</td>
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<td>Unassigned</td>
<td>-</td>
</tr>
<tr>
<td>2160</td>
<td>Si-H stretching</td>
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<td>3885</td>
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<td>16, 19</td>
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</tbody>
</table>

**2.3.4 Elastic recoil detection spectroscopy (ERD) analysis**

We have further analyzed the chemical composition of this film using elastic recoil detection spectroscopy. The concentration of chemical elements was determined from time-
of-flight analysis. Figure 2.3 show the percentage of the atomic concentration of chemical elements in the film as a function of the atomic depth. The ERD analysis shows that this film contain carbon, silicon, hydrogen, oxygen and nitrogen with very uniform depth profile except near the surface of the film. The very small and uniform atomic concentration of both oxygen and nitrogen in the bulk of these films suggest that these elements are due to polymer or reactor contamination. However, the increase of the oxygen near the surface of the film is obviously caused by the oxidation of the film probably during the cool-down process. These results appear to be in good agreement with the FT-IR analysis. Based on the ERD results we can conclude that the thin films synthesized in this series of experiments were carbon rich, non-stoichiometric SiC thin films.

![Graph showing atomic depth profile](image)

**Figure 2.3:** TOF-ERD analysis of the atomic depth profile of SiC thin film
The electrical properties of these films were investigated using capacitance-voltage measurements. Figure 2.4 shows the C-V characteristics of SiC/Si structure obtained by using a mercury probe as the metal contact. The silicon substrate is of an N-type with a doping concentration of 3×10^{15} \text{ cm}^{-3}. The SiC film thickness was approximately 405 nm. The C-V curve exhibits characteristics of a metal-insulator-semiconductor (MIS) structure, and the accumulation, depletion and inversion regions can be clearly distinguished. These results indicate that the SiC thin films are highly resistive. The film resistivity measured on quartz substrate was approximately 6×10^{5} \Omega \cdot \text{cm} (at about 2 \text{ at.\% of oxygen}). The shift of the C-V

![Image of C-V curve](image)

**Figure 2.4:** High frequency C-V characteristics of SiC/Si structure
characteristic toward the negative voltage is the result of the high density of positive fixed charge in this film, most likely due to the high concentration of dangling bonds in the bulk and near the interface of silicon carbide and silicon. The slow variation of the capacitance in the depletion region also indicates a high density of traps at the interface between silicon and silicon carbide thin film. The relative dielectric constant of SiC thin film extracted from the C-V characteristics at 1 MHz was found to be approximately 7.76 (at about 2 at. % of oxygen).

2.3.6 Ultraviolet-visible photospectroscopy (UV-Vis) analysis

The optical characteristics of SiC thin film deposited on quartz were characterized by ellipsometry and the UV-Vis photospectroscopy in order to determine the refractive index and the optical band gap respectively. Figure 2.5 shows the plot of the square root of the absorption coefficient as a function of photon energy, calculated from the UV-Vis absorption data. The square root of the absorption coefficient shows a nearly linear variation at high photon energy. According to Tauc's law the optical band gap can be extracted from this graph by extrapolating the linear region of the curves as indicated by the dotted line. The value of the optical bandgap obtained for SiC carbide thin film with about 2 at. % of oxygen is approximately 2.1 eV and the value of the refractive index measured by ellipsometry at a wavelength of 632.8 nm is about 2.2. The values of the optical properties are in good agreement with the results reported for carbon rich amorphous SiC thin films obtained by other methods [23].
Figure 2.5: The square-root of the absorption coefficient of SiC thin film as a function of photon energy. The optical band gap is extracted by extrapolating the linear region of the curve as indicated by the dotted line.

2.4 Conclusions

Thin films of silicon carbide have been prepared via sublimation of polydimethylsilane polymer powder, using polymer-source CVD process. The structural analysis indicates that these films are very similar to amorphous silicon carbide thin films obtained by other deposition methods. The analysis of the bulk atomic concentration of chemical element showed that these thin films are carbon rich and non-stoichiometric with very uniform atomic depth profile.

The electrical and optical constants of these films were determined. Electrical characterization of SiC/Si junction showed a MIS structure behavior which suggests that
these silicon carbide thin films are highly resistive. The film resistivity was as high as $6 \times 10^5$ Ω cm, which is explained by the relatively high atomic concentrations of oxygen found in these films (about 2 at. %) due to both polymer and reactor contamination. By reducing the concentration of oxygen, through process optimization and polymer purification, electronic grade silicon carbide thin films could be obtained using PS-CVD process.

The strong chemical resistance to acid and alkaline solutions and the uniform thickness of these thin films make them very attractive as a conformal coating material and possibly as a structural material for MEMS devices. Some of the advantages of the polymer-source CVD process include low deposition cost, batch process compatibility, and hazard free working environment.
References


CHAPTER 3

CHEMICAL AND STRUCTURAL CHARACTERIZATION OF SiONC
DIELECTRIC THIN FILM DEPOSITED BY POLYMER SOURCE CVD

CARACTÉRISATION CHIMIQUE ET STRUCTURELLE DES COUCHES MINCES
DIÉLECTRIQUE DE SiONC DÉPOSÉES PAR PSCVD


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Abstract

Thin films of silicon oxynitrocarbide (SiONC) have been deposited on silicon by Polymer-Source Chemical Vapour Deposition (PSCVD) using poly(dimethylsilane) (PDMS). The chemical and structural composition of these films have been investigated using Fourier transform infrared spectroscopy (FTIR), elastic recoil detection spectroscopy (ERD) and X-ray photoelectron spectroscopy (XPS). ERD depth-profile analysis revealed a homogeneous film with uniform bulk concentrations for silicon, carbon, nitrogen and oxygen. XPS analysis showed that nitrogen, oxygen and carbon were all uniquely bonded to silicon. The oxygen nitrogen bonds were not observed in these films. The XPS analysis also revealed the presence of carbon-carbon bonds associated with graphite. It was evidenced that the graphitic phase is limited to the surface layer of these films, and is due to unintentional carbonization at the end of the deposition process. The relatively low bulk atomic concentration of carbon in the SiONC thin films (about 1 %) render these films a possible alternative to SiON, and could become very attractive for the fabrication of integrated optical waveguides, and as a dielectric material in variety of microelectronic and optoelectronic devices.
Résumé

Les couches minces d'oxynitrocarbure de silicium (SiONC) ont été déposées sur le silicium par le procédé de dépôt en phase vapeur de source polymère (PSCVD) en utilisant du poly(dimethylsilane) (PDMS) comme source. La composition chimique et structurale de ces films ont été étudiées par la spectroscopie infrarouge à transformée de Fourier (FTIR), la spectroscopie élastique de détection de recul (ERD) et la spectroscopie des photoélectrons par rayon X (XPS). Le profil en profondeur obtenu par l'analyse ERD montre que les couches obtenues par le procédé PSCVD sont homogènes avec des concentrations uniformes de silicium, carbone, azote et oxygène. L'analyse XPS indique que l'azote, l'oxygène et le carbone sont tous uniquement liés au silicium. Les liaisons azote-oxygène n'ont pas été observées dans ces films. L'analyse XPS indique également la présence des liaisons carbone-carbone qui sont associées au graphite. Les analyses montrent que la présence de la phase graphitique est limitée à la surface des couches, et due à la carbonisation involontaire des échantillons à la fin du procédé de dépôt. La concentration atomique relativement basse du carbone dans les couches de SiONC (environ 1 %) rend celles-ci utiles comme une alternative aux couches minces de SiON, et peuvent être très attrayantes pour la fabrication des guides d'ondes pour l'optique intégré, et aussi comme un matériau diélectrique dans plusieurs dispositifs microélectroniques et optoélectroniques.
3.1 Introduction

Silicon oxynitride has been widely investigated as a promising alternative high-k gate dielectric material for silicon dioxide due to its similar properties with SiO$_2$ and Si$_3$N$_3$, its ability to suppress boron penetration, to reduce leakage current, and to enhance semiconductor devices reliability [1]. Applications such as field effect transistor (FET) [4-5], memories devices (ROM) [6], and integrated optical waveguides [7-9] have been developed using this material. Silicon oxycarbide, on the other hand, is only starting to receive attention as a low-k dielectric material, for applications in advanced copper interconnects, due to its close chemistry to silicon dioxide and silicon carbide, its lower dielectric constant, better thermo-mechanical properties, and lower adsorption coefficients for moisture and chemical impurities [10-11].

Due to expected intermediate properties between silicon oxynitride and silicon oxycarbide, silicon oxinitrocarbide (SiONC) thin films became the focus of our research, as an attractive alternative material for both SiON and SiOC. In addition, a comparison with the properties of the thin films based on classic electronic ceramics, such as SiO$_2$, Si$_3$N$_4$ and SiC, may also be instructive. It is expected that by controlling the concentration of oxygen and nitrogen in the films, it may become possible to deposit a wide range of dielectric materials, designed to mimic the behaviour of homogeneous mixtures of, for example, SiOC, SiON and SiCN thin films. It should be possible, this way, to tailor a wide range of electro-optical properties of the SiONC thin films, including the dielectric constant, refractive index, and optical band gap, in order to meet the requirements of a broad range of microelectronic and optoelectronic applications.
In this paper, we report the synthesis and properties of SiONC thin films obtained by PS-CVD as an alternative to SiON. While a large number of papers have been published in recent years dealing with the synthesis and properties of SiON thin films obtained by a variety of deposition processes, the majority of these studies concern CVD processes using gaseous precursors. In this work we use Polymer source CVD (PS-CVD) which offers several advantages for SiONC thin films synthesis, including low setup cost, low thermal budget, hazard-free and chemical compatibility with standard semiconductor fabrication processes. The objective of this study is to investigate the influence of oxygen incorporation on the chemical and structural composition of SiONC thin films. To our knowledge this is the first time such a material, and deposition process have been reported.

3.2 Experimental

The thin films used in this work were obtained by reactive volatilization of poly(dimethylsilane) (PDMS), a polymer source existing as a solid powder, using a chemical vapour deposition process described elsewhere [12]. The deposition was carried out in 3 zone Thermco Mini-Brute furnace with 3-inch diameter quartz tube. The reactor is equipped with a rotary vacuum pump which can achieve a vacuum down to $10^{-3}$ Torr. To maintain the deposition pressure at a constant atmospheric pressure the gas escape line is closed by an oil bubbler. The vacuum manifold is connected to a vacuum pump, nitrogen tank, and anhydrous ammonia tank. To reduce the moisture-content in the commercial anhydrous ammonia provided by Air Liquide Inc., a drying procedure was designed, involving passing the flow of ammonia through a 20 cm column filled with potassium hydroxide, and a 60 cm column of 0.4 nm molecular sieves with silica gel witness. As a precautionary measure to limit residual
moisture and oxygen the quartz tube is flushed with UHP-nitrogen three times prior to deposition.

The films were deposited on two different types of substrates: polished, p-type silicon wafers purchased from Virginia Semiconductor Inc., and fused quartz plates supplied by GM Associates. The substrates were cleaned in an ultrasonic acetone bath for 5 minutes then dried with a nitrogen gun. The PDMS powder is weighted and introduced into the reactor chamber together with the substrates. During the deposition, the reactor is kept at atmospheric pressure while the deposition temperature is gradually increased and then maintained at 750 °C for one hour.

The identification of characteristic lattice modes of vibration used for the assignment of the ceramic materials was extracted from the spectral decomposition of FTIR absorption spectrum. FTIR spectra were recorded on a Galaxy Series 6020 instrument, at a resolution of 4 cm$^{-1}$ in the 400-4000 cm$^{-1}$ wavenumber range (MidIR). The atomic concentrations of all significant chemical elements were determined by Elastic Recoil Detection (ERD) analysis, using the upgraded EN-1 HVEC Tandem accelerator at Ecole Polytechnique de Montreal. The XPS measurements were performed with MgKα X-ray radiation source at 300 watts (I = 20 mA, V =15 kV). An area with a planar integration of 2 mm x 3 mm was analyzed, while the depth profiling was obtained by Ar+ sputtering calibrated with a PECVD SiON sample. The film thickness is obtained by ellipsometry measurement using Woollam alpha-SE ellipsometer.
3.3 Results and discussion

3.3.1 Fourier transform infrared spectroscopy (FTIR) analysis

As the first step of this study, we prepared several SiONC thin film samples under the same deposition condition as described in the previous section, with the nitrogen flow rate maintained constant. An unpredictable shift of the FTIR absorption band peak was observed from run to run, assigned to the incorporation of unintentional oxygen. The oxygen found in SiONC thin films is mainly due to the leakage in the vacuum chamber and to contamination of the reactor walls.

In order to understand the influence of oxygen on the chemical composition of these films we investigated three different samples within the FTIR peak shift range. Figure 3.1 shows the FTIR absorption spectra of three selected samples with different oxygen concentrations in the films. From these figures we can clearly see the influence of oxygen; as the oxygen concentration in these films increases the main absorption band peak shifts from about 860 cm\(^{-1}\) to around 1000 cm\(^{-1}\). In order to determine the structural bonding of chemical elements in these films, we have performed a spectral decomposition of the FTIR spectrum in the 400-4000 cm\(^{-1}\) wavenumber range, assuming a Gaussian distribution. The corresponding peaks are also shown in figure 3.1.

According to these figures, at a low concentration of oxygen (sample S1, \(\sim 5\%\) oxygen), the FTIR absorption spectrum shows a strong band centered around 877 cm\(^{-1}\), which has been associated with the stretching mode of Si-N bond-lattice, assignment supported by the weak absorption band observed at 484 cm\(^{-1}\), usually assigned to the
breathing mode of Si-N bond-lattice. The relatively weak absorption band at 1055 cm\(^{-1}\) has been assigned to the asymmetric stretching mode of Si-O bonds. We also observe weak absorption bands at 2200 cm\(^{-1}\) and 3300 cm\(^{-1}\), associated with the stretching mode of Si-H and N-H bonds, respectively.

![FTIR absorption spectrum](image_url)

**Figure 3.1:** FTIR absorption spectrum obtained at a resolution of 4 cm\(^{-1}\) in the wavenumber range between 400 cm\(^{-1}\) and 4000 cm\(^{-1}\) and the corresponding Gaussians spectral decomposition; (a) sample S1, (b) sample S2, and (c) sample S3.
At medium concentration of oxygen (sample S2, ~ 19 % oxygen), the FTIR spectral decomposition revealed several bands. The absorption bands observed at 858 cm\(^{-1}\) and 931 cm\(^{-1}\) were both associated with Si-N stretching modes. The breathing mode of Si-N bond previously seen at a low concentration of oxygen, around 484 cm\(^{-1}\) is no longer observed at a medium concentration of oxygen. The increase of oxygen in the film was obvious with the appearance of both symmetric and asymmetric stretching and also rocking modes of Si-O at 1010 cm\(^{-1}\), 1111 cm\(^{-1}\) and 447 cm\(^{-1}\) respectively. The absorption bands of Si-H and N-H showed little changes, however, the spectrum showed a new absorption band peak at around 657 cm\(^{-1}\) associated with Si-H rocking mode.

At a high concentration of oxygen (sample S3, ~34% oxygen), the absorption spectrum showed a further shift of the main absorption band. This shift is due to an increase of concentration of Si-O bonds. The spectral decomposition revealed a strong absorption peak at 1010 cm\(^{-1}\) which is associated with symmetric stretching mode of Si-O, and also a decrease in the amplitude of the absorption band associated with the stretching mode of Si-N. The absorption peaks observed between 2260 cm\(^{-1}\) and 2400 cm\(^{-1}\) are associated with carbon dioxide impurities found in the atmosphere around the sample during FTIR measurement. It is important to note that the concentration of hydrogen does not seem to be greatly influenced by the increase of oxygen concentration in these films. Despite the fact that the initial PDMS-source used for the deposition of our films contains only silicon-carbon and carbon-hydrogen bonds, no residual Si-C bonds have been observed in FTIR analysis. From these results it appears that thin films obtained from the sublimation of PDMS polymer source could be very similar to SiON obtained by other deposition methods.
Figure 3.2: Depth profile analysis of the relative atomic concentration of chemical elements in SiONC thin film obtained by Elastic Recoil Detection (ERD) technique using the upgraded EN-1 HVEC Tandem accelerator at Ecole Polytechnique de Montreal. (a) sample S1. (b) sample S2 and (c) sample S3
3.3.2 Elastic recoil detection spectroscopy (ERD) analysis

In order to correlate the results obtained from FTIR spectroscopy with the atomic composition of these samples, we further analyzed these samples using elastic recoil detection technique (ERD). Figure 3.2 shows ERD analysis of the above three samples. From these figures we can see that all three samples contain the same chemical elements (Si, O, N, C and H). The absorption peaks associated with these chemical elements have all been observed in the FTIR analysis with the exception of carbon due to its very small atomic concentration (approximately 1%) as expected. The presence of carbon in these films explains why we named our films SiONC instead of SiON, since SiONC combines a wider range of others materials which have been obtained by our research group using the PDMS polymer source [12-14]. The difference in the ERD depth profile of all three samples is due to films thickness variation, which is caused by a change in the mass of the polymer introduced into the reactor. The film thickness obtained by ellisometry is given in table 3.1.

Table 3.1: Atomic concentration of chemical elements in SiONC thin films extracted from ERD analysis at a depth of 70 nm which approximately correspond to the average atomic concentration in the bulk of these samples. The table also shows the film thickness measured by ellipsometry.

<table>
<thead>
<tr>
<th>Sample</th>
<th>H (at.%)</th>
<th>C (at.%)</th>
<th>N (at.%)</th>
<th>O (at.%)</th>
<th>Si (at.%)</th>
<th>t_{ox} (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>9.09</td>
<td>1.13</td>
<td>52.26</td>
<td>5.33</td>
<td>32.19</td>
<td>167</td>
</tr>
<tr>
<td>S2</td>
<td>6.83</td>
<td>1.20</td>
<td>36.17</td>
<td>19.66</td>
<td>36.19</td>
<td>188</td>
</tr>
<tr>
<td>S3</td>
<td>8.30</td>
<td>0.98</td>
<td>21.07</td>
<td>34.13</td>
<td>35.52</td>
<td>125</td>
</tr>
</tbody>
</table>
Figure 3.3: The variation of relative atomic concentration of Silicon, Nitrogen, Carbon and Hydrogen as a function of the bulk atomic concentration of oxygen in SiONC thin films based on the results shown in table 3.1.

The atomic concentrations of chemical elements obtained from ERD analysis are in good agreement with the results obtained from FTIR spectroscopy and confirm the variation in the concentration of both oxygen and nitrogen in these samples. The ERD figures reveal that the atomic concentrations of all chemical elements remain uniform along the film.
thickness, which provide evidence that these films are homogenous. For the purpose of comparison, table 3.1 presents the bulk atomic concentrations of all samples at a depth of 70 nm. The atomic concentration of Si, C and H remain nearly constant for all three samples, despite the variation of the atomic concentration of oxygen and nitrogen in these films. The atomic concentration of nitrogen, however, showed a linear variation with the atomic concentration of oxygen as shown in figure 3.3.

It is important to note a slight increase of the atomic concentration of both oxygen and carbon near the surface of the film for all three samples. The increase of oxygen is believed to be mainly due to atmospheric oxidation during sample handling, after the deposition. The increase of the carbon concentration at the surface layer of the thin films obtained by PSCVD process was previously associated with the high-temperature decomposition of methane released from the samples at the end of the deposition process [13]. The surface carbonization of SiONC thin film is believed to occur during the dwelling time, after the polymer has been completely deposited on the substrate and on the walls of the reactor. The continuous generation of methane within the reactor at high temperature promotes the deposition of graphite on the surface of these films.

### 3.3.3 X-ray photoelectron spectroscopy (XPS) analysis

Based on the results obtained from FTIR and ERD analysis the bonding states of carbon in the films remain unclear and therefore further analysis are required to better understand the chemical structure of SiONC thin films. Figure 3.4 shows the results of XPS analysis conducted on sample S2. The relative atomic concentration of chemical elements in this sample is summarized in table 3.1. These results are very similar with those obtained by
ERD analysis. The high concentration of carbon and oxygen obtained from XPS analysis confirm the increase of the concentrations of these elements near the surface of the film as observed in ERD analysis. The concentration of chemical bonds extracted from

Figure 3.4: The X-ray photoelectron spectroscopy analysis of sample S2. The measurements were performed with MgKα X-ray radiation source at 300 watts. An area with a planar integration of 2 mm x 3 mm and a depth of
XPS analysis shown in table 3.2, reveals the presence of C-C bonds associated with graphite as well as Si-C bonds. The concentration of Si-C bonds obtained from XPS analysis (Approximately 1.1 %) is almost the same as the average atomic concentration of carbon in the bulk of the films extracted from ERD analysis (Approximately 1.2 %). As a consequence the C-C bonds are only expected to be found at the surface layer of these films. From table 3.2 we also notice that the concentration of oxygen O1s which corresponds to Si-O bonds (32.2 %) of sample S2, obtained from XPS is nearly equal to the atomic concentration of oxygen obtained from ERD analysis near the surface layer of this sample as shown in figure 3.2. This indicates that oxygen is uniquely bonded to silicon in SiONC thin films.

**Table 3.2: Relative atomic concentration percentage and identification of chemical bonding of sample S2 extracted from X-ray photoelectron spectroscopy analysis**

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak B.E. (eV)</th>
<th>Bonding</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar 2p</td>
<td>241.9</td>
<td>-</td>
<td>1.5</td>
</tr>
<tr>
<td>C1 1s</td>
<td>282.9</td>
<td>C-Si</td>
<td>1.1</td>
</tr>
<tr>
<td>C2 1s</td>
<td>284.0</td>
<td>C-H or C-C</td>
<td>3.2</td>
</tr>
<tr>
<td>C3 1s</td>
<td>285.0</td>
<td>C-C</td>
<td>2.5</td>
</tr>
<tr>
<td>N 1s</td>
<td>397.7</td>
<td>Si-N</td>
<td>22.5</td>
</tr>
<tr>
<td>O 1s</td>
<td>532.0</td>
<td>Si-O</td>
<td>32.2</td>
</tr>
<tr>
<td>Si 2p</td>
<td>101.3</td>
<td>Si$_5$O$_2$N$_2$</td>
<td>36.9</td>
</tr>
</tbody>
</table>

The high resolution XPS peaks analysis (Figure 3.5) revealed the presence of a single nitrogen and oxygen peaks at 397.7 eV and 532 eV respectively, which correspond to Si-N and Si-O bonds, as a result we conclude that there are no N-O bonds found in these SiONC
thin films. The structural composition of these films seems to be different from the SiON thin film obtained by other method [15-16], because of the absence of N-O bonds in these films they are expected to be more stable at high temperature.

Figure 3.5: High resolution X-ray photoelectron spectroscopy peaks analysis and the corresponding spectral decomposition for sample S2; (a) Silicon, (b) Nitrogen, (c) Carbon, and (d) Oxygen, The spectral decomposition of nitrogen and oxygen spectra showed a single peak corresponding to N1s and O1s respectively.
It is evident from the above chemical analysis that SiONC with a wide range of atomic concentration of oxygen and nitrogen can be deposited by the sublimation of PDMS polymer source using the conventional chemical vapour deposition process. By tightly controlling the incorporation of oxygen in the deposition chamber SiONC thin films with specific electro-optical properties suitable for a broad range of microelectronic and optoelectronic application can be prepared. The electro-optical properties of SiONC thin films are being investigated and the results will be released soon in future publication.

3.4 Conclusion

The influence of oxygen on the chemical composition of SiONC thin films obtained by chemical vapour deposition using a PDMS polymer powder source has been investigated. The results showed that the atomic concentration of nitrogen decrease linearly with an increase of the atomic concentration of oxygen in these films. The atomic concentrations of Si, C and H are not affected by the variation of oxygen concentration in SiONC thin films. The oxygen appears to have preference for nitrogen sites. All chemical elements are found to be uniquely bonded to silicon with the exception of carbon-carbon bond found at the surface layer of these films. The bulk composition of SiONC thin films appear to be uniform across all the film thickness, which indicate that these films are homogenous. The low atomic concentration of carbon in these films (about 1%) combined with the advantage of PSCVD process could make SiONC an attractive alternative to SiON.
References


CHAPTER 4

ELECTRICAL AND OPTICAL CHARACTERIZATION OF SiONC DIELECTRIC
THIN FILM DEPOSITED BY POLYMER-SOURCE CVD

CARACTÉRISATION ÉLECTRIQUE ET OPTIQUE DE COUCHES MINCES
DIÉLECTRIQUE DE SiONC DÉPOSÉES PAR PSCVD

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Abstract

The electro-optical properties of SiONC dielectric thin films deposited by polymer-source chemical vapour deposition (PS-CVD) using an organosilane precursor have been investigated as a function of oxygen concentration in the films. SiONC thin films were characterized using capacitance-voltage (C-V), conductance-voltage (G-V), ellipsometry and ultra-violet visible (UV-Vis) photospectroscopy. These measurements showed that the electro-optical properties of the films are greatly influenced by the atomic concentration of oxygen. The high frequency C-V measurement revealed a nearly ideal metal-oxide-semiconductor (MOS) structure behaviour at a high atomic concentration of oxygen (35 at.%). A relative dielectric constant as high as 6 is obtained at 10 kHz for samples with about 5 at.% of oxygen, which corresponds to high-k dielectric material. The interface trap density extracted from G-V measurement using Hill-Coleman method is as low as \(3.2 \times 10^{10} \text{ cm}^{-2}\text{eV}^{-1}\) making these films a viable high-k dielectric alternative to SiO\(_2\) and SiON in MOS devices. The refractive index measured by ellipsometry at a wavelength of 632.8 nm shows a linear variation with the atomic concentration of oxygen, from 1.58 to 1.69. The optical energy bandgap extracted from UV-Vis absorption spectra was found to vary between 4.40 eV and 5.25 eV.
Résumé

Les propriétés électro-optiques des couches minces diélectriques de SiONC obtenues par le procédé de dépôt en phase vapeur à source polymérique (PS-CVD) en utilisant un précurseur d'organosilane ont été étudiées en fonction de la concentration d'oxygène dans les couches. Les couches minces de SiONC ont été caractérisées par capacité-tension (C-V), conductance-tension (G-V), ellipsométrie et photospectroscopie ultraviolet-visible (UV-Vis). Ces méthodes d'analyse ont montré que les propriétés électro-optiques des couches minces sont considérablement influencées par la concentration atomique de l'oxygène. La caractéristique C-V obtenue à haute fréquence a révélé une structure de type métal-oxyde-semi-conducteur (MOS) avec un comportement quasiment idéal à haute concentration d'oxygène (35 at. %). Une constante diélectrique relative aussi haut que 6 a été obtenue à 10 kHz pour les échantillons avec environ 5 at.% d'oxygène, cette valeur correspond un matériau diélectrique haut-κ. La densité de pièges d'interface extraite à partir de la mesure de G-V, en utilisant la méthode de Hill-Coleman, est de l'ordre de $3.2 \times 10^{10}$ (cm$^{-2}$eV$^{-1}$). Par conséquent, les couches minces de SiONC sont très attractives comme une alternative au SiO$_2$ et SiON dans les dispositifs MOS conventionnelles. L'indice de réfraction mesuré par ellipsométrie, à une longueur d'onde de 632.8 nm, affiche une variation linéaire, entre 1.58 et 1.69, par rapport à la concentration atomique de l'oxygène. La bande interdite optique des couches minces de SiONC extraite à partir des spectres d'absorption UV-Vis varie entre 4.40 et 5.25 eV.
4.1 Introduction

For more than three decades, silicon dioxide (SiO$_2$) has been the versatile dielectric material of choice for the semiconductor industry, providing adequately high-k gate insulation for MOS devices and sufficiently low-k, crosstalk-free insulation between interconnect wiring. As the integrated circuits continue to shrink and become more densely packed, and with the continuous introduction of low resistance interconnect metal like copper to reduce power consumption, and increase operation speed of ultra large scale integrated (ULSI) devices, silicon dioxide dielectric (SiO$_2$) is no longer adequate for either application. Thus, in recent years a large number of new materials have been investigated with higher dielectric constants for gate or capacitor applications [1] and lower dielectric constants for interconnect applications [2]. However, integrating these materials in a device has brought many new challenges.

Silicon oxynitride thin films have been widely investigated as a promising high-k gate dielectric due to their low interface states density, ability to suppress boron penetration, reduce leakage current and enhance device reliability [3-5]. Applications such as metal oxide semiconductor field effect transistor (MOSFET) [6-7] and semiconductor memory devices [8] are being developed using this material. Integrated optical waveguides is another important application where SiON thin films are continuously receiving a great deal of attention [9-10].

Silicon oxycarbide on the other hand, is starting to receive great deal of attention as an interlayer dielectric for next generation advanced copper interconnects, due to it low
dielectric constant, close chemistry to silicon dioxide, better thermomechanical properties and lower absorption of moisture and chemicals [11-12].

SiON and SiOC thin films are widely deposited by a wide range of CVD processes and using a variety of precursors [1-12]. An approach to combine these two materials in a single material, and the development of an efficient deposition process adapted to this material may prove to be very attractive for easy integration of these dielectric materials in the fabrication process, due to significant simplification of device processing.

Silicon oxynitrocarbide (SiONC) thin film deposited using an organosilane polymeric source CVD process [13] is an attractive, alternative dielectric material to both SiON and SiOC. By simply varying the atomic concentration of oxygen and nitrogen in SiONC thin films, it is possible to tailor their electrical and optical properties within a wide range, in order to meet the requirements of a variety of microelectronic and optoelectronic applications. The polymer-source CVD process offers several advantages including relatively simple deposition process, compatibility with batch process, no physical damage to substrate during the deposition process and hazard-free working environment.

The objective of this work is to investigate the electrical and optical properties of SiONC thin films obtained by polymer-source CVD process as an alternative to SiON thin films obtained by other methods.

### 4.2 Experimental

Thin films of SiONC were deposited using Polymer-Source CVD process. The deposition was carried out in three zone Thermco Mini-Brute furnace, equipped with a quartz
tube. The films were deposited on two different types of substrates: single side polished p-type crystalline silicon substrates with a resistivity of about 1.5 to 3.5 Ωcm, and fused quartz substrates. The substrates were properly cleaned in an ultrasonic bath for several minutes then dried with a nitrogen gun. The solid organosilane precursor powder was then weighted and introduced in the reactor chamber together with the substrates. A vacuum down to $10^{-3}$ torr was obtained in the reactor using a rotary pump, where ultra high purity argon was used to purge the reactor several times prior to film deposition. The deposition pressure was maintained around the atmospheric pressure using an oil bubbler. The deposition temperature was gradually increased and then maintained constant at 750 °C for about one hour. The thickness of SiONC films varies slightly from sample to sample due to the small variation of polymer mass, substrate position and other deposition conditions. Precise control of the deposition parameters is required in order to achieve precise control of film thickness, especially for very thin films. The optimization of PS-CVD process is underway to address this problem. The polymer-source CVD process was discussed in more detail elsewhere [14].

Several samples with different atomic concentration of oxygen were prepared under the above experimental conditions. The chemical composition and the atomic concentrations of chemical elements were extracted using elastic recoil detection (ERD) technique. S1, S2 and S3 are used here to distinguish samples with approximately 5%, 20% and 35% atomic concentration of oxygen respectively. The atomic concentration of nitrogen in the films varies linearly with the atomic concentration of oxygen, whereas, the remaining chemical elements (Si, C, H) stay nearly constant. A detailed chemical and structural analysis of these films has been previously reported [15].
The electrical characterization was conducted by capacitance-voltage (C-V) and conductance-voltage (G-V) techniques using Solartron impedance-gain analyser SI260 equipped with a mercury probe. The films thickness and refractive index were extracted from ellipsometry measurement using Woollam alpha-SE ellipsometer. The optical energy bandgap was obtained by UV-Vis photospectroscopy using Hewlett Packard 8452A diode array spectrophotometer.

4.3 Results and discussion

4.3.1 Electrical characterization

Capacitance-voltage (C-V) characterization

The figure 4.1 and 4.2 show the C-V characteristic of SiONC/(p)Si structure obtained at 1 MHz and 10 kHz respectively for different concentration of oxygen in the films. The C-V characteristics of all the samples exhibit typical p-type MOS capacitor behaviour, as expected. The values of measured capacitance were corrected for series resistance according to the parallel capacitance conductance model [16], using the theoretical expressions (1) and (2), where \( C_{ma} \) and \( G_{ma} \) are respectively the capacitance and conductance in accumulation region, \( C_m \) and \( G_m \) are respectively the measured capacitance and conductance, and \( \omega \) is the angular frequency of measurement.

\[
R_s = \frac{G_{ma}}{G_{ma}^2 + \omega^2 C_{ma}^2} \quad (1)
\]
\[ C_s = \frac{(G_m^2 + \omega^2 C_m^2)C_m}{\left[ G_m - \left(G_m^2 + \omega^2 C_m^2\right)R_1 \right] + \omega^2 C_m^2} \]  

Figure 4.1: Capacitance-Voltage Characteristics of SiONC/(p)Si MOS structure measured at 1 MHz using an impedance analyzer equipped with a mercury probe.

At low concentration of oxygen (S1, \( \approx \) 5 at.%), we observe a positive voltage shift of the C-V characteristics which indicates the presence of relatively high concentration of
negative fixed charge in the bulk of the film. This result is in agreement with the result reported for nitrogen rich SiON thin film obtained by other deposition methods. The negatively charged defects in this case were explained by the electron trapping due to nitrogen defects [17].

Figure 4.2: Capacitance-Voltage Characteristics of SiONC/(p)Si MOS structure measured at 10 kHz using an impedance analyzer equipped with a mercury probe.
At intermediate concentration of oxygen (S2, \(\approx 20\) at.%), the C-V curve shows a negative voltage shift. This shift is explained by a relatively large concentration of positive fixed charges. The decrease of the concentration of nitrogen in the film has reduced the positively charged nitrogen defects. At the same time the increase of the concentration of oxygen induces a large increase of positively charged oxygen defects due to unsatisfied oxygen dangling bonds. The noticeable stretching of the C-V curve in the depletion region of this sample indicates a substantial increase of interface defects.

At a high atomic concentration of oxygen (S3, \(\approx 35\) at.%), The C-V characteristics show a nearly ideal C-V curve both at 1 MHz and 10 kHz which is similar to the C-V characteristics of thermally grown SiO₂ on silicon. This result indicates that there are no fixed charges in the bulk of this film or at least they are insignificant. The sharp transition from inversion to accumulation regions also suggests a very low concentration of density of states at the interface between Si and SiONC. The structural chemical analysis conducted at high concentration of oxygen has shown that the high concentration of oxygen promote the formation of symmetric Si-O-Si bonds [15], which saturate the oxygen defects due to dangling bonds. The excess of hydrogen released by silicon due to this new atomic rearrangement has contributed to the saturation of negatively charged nitrogen defect.

**Conductance-voltage (G-V) characterisation**

Conductance voltage (G-V) characteristic was used to investigate the density of states at the interface of Si and SiONC. Figure 4.3 shows the high frequency (1 MHz) G-V curves obtained for different atomic concentrations of oxygen in the film. The theoretical value of
corrected conductance based on the parallel capacitance conductance model [16], is given by expression (3).

\[
G_c = \frac{\left( G_m^2 + \omega^2 C_m^2 \right) \left[ G_m - \left( G_m^2 + \omega^2 C_m^2 \right) R_s \right]}{\left[ G_m - \left( G_m^2 + \omega^2 C_m^2 \right) R_s \right]^2 + \omega^2 C_m^2}
\]  

(3)

Figure 4.3: Conductance-Voltage Characteristics of SiONC/(p)Si MOS structure measured at 1 MHz using an impedance analyzer equipped with a mercury probe.
It is clear from figure 4.3 that all samples exhibit a peak conductance as the bias is swept through the depletion region. This peak conductance is due to interface trap loss [16]. The interface trap level density can be extracted from the maximum conductance [18] using expression (4).

$$D_{it} = \frac{2\omega C_{ox}^2 G_{\max}}{qA \left( G_{\max}^2 + \omega^2 \left[ C_{ox} - C_m \left( G_{\max} \right) \right]^2 \right)}$$

Table 4.1, show the calculated interface trap density extracted from G-V curves for different concentrations of oxygen. The density of interface states is relatively low particularly at high concentration of oxygen (35 at.%), interface states density as low as 3.24x10^{-10} cm^{-2}eV^{-1} is obtained. The correlation between defect density and oxygen concentration in SiONC thin films is in good agreement with the results recently reported for SiON thin films [19]. These results indicate that SiONC thin film obtained by polymer-source CVD could be a potential alternative to SiO_2 and SiON thin films obtained by other deposition methods.

**Table 4.1**: Electrical and optical properties of PS-CVD SiONC thin films obtained for different atomic concentrations of oxygen.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[O] (at.%)</th>
<th>t_{ox} (nm)</th>
<th>(\varepsilon_r) (10 kHz)</th>
<th>(D_{it}) (cm^{-2}eV^{-1})</th>
<th>n</th>
<th>(E_g) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>5</td>
<td>177</td>
<td>6.02</td>
<td>4.45 x 10^{10}</td>
<td>1.69</td>
<td>4.40</td>
</tr>
<tr>
<td>S2</td>
<td>20</td>
<td>146</td>
<td>5.46</td>
<td>1.26 x 10^{11}</td>
<td>1.63</td>
<td>5.08</td>
</tr>
<tr>
<td>S3</td>
<td>35</td>
<td>122</td>
<td>5.47</td>
<td>3.24 x 10^{10}</td>
<td>1.58</td>
<td>5.25</td>
</tr>
</tbody>
</table>
Figure 4.4 show the relative dielectric constant of SiONC as a function of the atomic concentration of oxygen in the films. The values of these dielectric constants are extracted from CV measurement at 10 kHz. The dielectric constants obtained vary between 5.4 and 6 which is much higher that the dielectric constant of SiO$_2$. Slightly higher dielectric constants are expected from the quasi-static C-V measurement. This result confirms that SiONC thin film can be considered as a high-k dielectric material. By reducing the atomic concentration of nitrogen and increasing the atomic concentration of carbon in SiONC thin films, a low-k dielectric material can be obtained [20]. Further studies are underway to demonstrate the capability of this process to deposit low-k dielectric material.

![Graph showing relative dielectric constant and refractive index vs. atomic concentration of oxygen](image)

**Figure 4.4**: Relative dielectric constant obtained by capacitance-voltage measurement at an angular frequency of 10 kHz. The refractive index is obtained by ellisometry at a wavelength of 632.8 nm.
4.3.2 Optical characterization

Ellipsometry analysis

We further investigated these samples by ellipsometry in order to correlate the refractive index with the atomic concentration of oxygen in the films. Figure 4.4 shows the refractive index, obtained by ellipsometry at a wavelength of 632.8 nm, as function of the atomic concentration of oxygen. The refractive index decreases monotonically and varies linearly as the atomic concentration of oxygen is increased. This linear correlation does not seem to remain valid at very low concentration of oxygen since the refractive index at zero concentration of oxygen, extracted from this graph, is approximately 1.73 while the refractive index of stoichiometric Si$_3$N$_4$ is approximately 2.1. On the contrary, at high concentration of oxygen, above 5 at.%, the linear variation of refractive index appears to remain valid since the projection shown by dotted line in figure 4.4 corresponds to the refractive index and the concentration of oxygen of stoichiometric SiO$_2$. The linear variation of refractive index with oxygen concentration confirms the results reported elsewhere [21-22]. Despite the increase of the interface density of states at medium concentration of oxygen we did not observe any discontinuous behaviour in the variation of refractive index. This indicates that the total density of states in the bulk of SiONC thin film did not noticeably change as the oxygen concentration increases. It has been reported that the majority of defects in SiON are linked to hydrogen [23], since the hydrogen concentration in SiONC thin films remains nearly constant, this may be a plausible explanation for the linearity of refractive index. The linear variation of refractive index with the atomic concentration of oxygen is an important characteristic for optical waveguide fabrication since it will allow us
to precisely adjust the refractive index by simply controlling the atomic concentration of oxygen in SiONC film. It will also be possible to determine the concentration of oxygen in SiONC thin films by simple measurement of refractive index.

![Graph](image)

**Figure 4.5**: Square root of the absorption coefficient as a function of incident photon energy calculated from the absorption spectra, which is obtained using an ultra-violet visible (UV-Vis) photo-spectrometer. The optical bandgap is extracted by extrapolation as indicated by dotted line in this figure.
Finally we investigated the influence of oxygen on the optical bandgap of SiONC thin films. The optical bandgap is extracted from the absorption coefficient measured by UV-Vis photospectroscopy. According to Tauc’s law [24] the absorption coefficient corresponding to the transition between extended states of both crystalline and amorphous materials satisfies the expression (5), where \(B\) is a constant, \(\alpha\) is the absorption coefficient, \(h\nu\) is the photon energy and \(E_g\) is the optical energy bandgap.

\[
\sqrt{\alpha h\nu} = B(h\nu - E_g) \quad (5)
\]

Figure 4.5 shows the variation of the square root of the absorption coefficient as function of photon energy. At high photon energy, the square root of the absorption coefficient shows a linear variation with photon energy. The optical bandgap can be extracted from figure 4.5 by simply extrapolating the linear region of the curves as shown by the dotted lines in this figure. The value of the optical bandgap obtained varies between 4.4 eV and 5.25 eV. The relatively small optical energy bandgap and its small variation with the atomic concentration of oxygen indicate the presence of a large density of localized states within the energy gap and particularly near the edges of the bandgap, due to the structural disorder in these films.

4.4 Conclusion

Electro-optical properties of SiONC dielectric thin films obtained by polymer-source CVD process were investigated. These thin films showed some important results:
• All SiONC/(p)Si samples showed a MOS capacitor behaviour, a nearly ideal MOS capacitor is demonstrated at a high concentration of oxygen (35 at.%).

• The interface trap density between SiONC and p type silicon is found to be very low. A trap density as low as $3.2 \times 10^{10}$ is obtained at a high concentration of oxygen.

• The dielectric constant of SiONC thin films extracted from C-V measurement at 10 kHz is found to vary between 5.4 and 6 which are much higher than the dielectric constant of SiO$_2$.

• The refractive index of SiONC thin film is found to vary linearly with the concentration of oxygen in these films. Optical waveguide with precise refractive index can be obtained by simply controlling the oxygen concentration in these films.

From these results we conclude that SiONC thin films deposited by polymer-source CVD process appear to be an attractive alternative to SiON thin films obtained by other methods. The simplicity of the deposition technique, the compatibility with batch process and the hazard-free working environment are some prominent advantages for considering SiONC dielectric thin films.
Reference


CHAPTER 5

GaAs SURFACE PASSIVATION WITH SiCON DIELECTRIC THIN FILMS GROWN BY CVD USING A POLYMERIC PRECURSOR


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Abstract

SiCON dielectric ceramic thin films grown by chemical vapor deposition process (CVD) using a polymeric precursor have been investigated as a passivation layer for gallium arsenide (GaAs) surface, and as a potential gate dielectric for GaAs metal-oxide-semiconductor field-effect-transistor (MOSFET). The properties of SiCON/GaAs MOS heterostructure were investigated using capacitance-voltage (C-V), conductance-voltage (G-V), time-of-flight elastic recoil detection spectroscopy (TOF-ERD), photoluminescence (PL) and X-ray photoelectron spectroscopy (XPS). The results obtained show an improvement in the interface quality at a low atomic concentration of oxygen, indicating a low density of interface traps. The mechanism of the passivation process appears to be linked to elimination of Ga$_2$O$_3$ and As$_2$O$_3$ from the interface, and their replacement with new chemical bonds based on silicon, carbon and nitrogen. The density of interface traps of SiCON/GaAs MOS structure estimated using Hill-Coleman method is as low as $6 \times 10^{11}$ cm$^{-2}$ eV$^{-1}$. 
Résumé

Les couches minces diélectriques de SiCON obtenues par le procédé de dépôt en phase vapeur (CVD) en utilisant un précurseur polymérique ont été étudiées comme couches de passivation de la surface de l'arséniure de gallium (GaAs), et comme un diélectrique de grille éventuel pour le transistor à effet de champ métal-oxyde-semiconducteur (MOSFET) à base de GaAs. Les propriétés de l'hétérostructure MOS de SiCON/GaAs ont été étudiées par la capacité-tension (C-V), la conductance-tension (G-V), la spectroscopie élastique de détection de recul à temps-de-vol (TOF-ERD), la photoluminescence (PL) et la spectroscopie de photoélectrons par rayons X (XPS). Les résultats obtenus montrent une amélioration notable de la qualité de l'interface à basse concentration d’oxygène dans les couches minces de SiCON, ce qui indique une faible densité de pièges d'interface. Le mécanisme du processus de passivation semble être lié à l'élimination de Ga₂O₃ et de As₂O₃ de l'interface, et leur remplacement par de nouvelles liaisons chimiques stables à base de silicium, de carbone d'azote. La densité de pièges d'interface de la structure MOS de SiCON/GaAs estimée à partir de la méthode de Hill-Coleman est de l’ordre de $6 \times 10^{11}$ cm$^{-2}$eV$^{-1}$.
5.1 Introduction

During the past few decades, there has been continued interest in GaAs-based metal-oxide-semiconductor field-effect-transistor (MOSFET) [1, 2]. GaAs based devices potentially have great advantages over silicon based devices for high-speed and high-power applications, in part from an electron mobility in GaAs that is many times greater than that in Si, the availability of semi-insulating GaAs substrates, and a higher breakdown field. Currently, the GaAs metal semiconductor field-effect transistor MESFET remains the dominant device for high-speed and microwave circuits [3, 4]. MOSFET features a larger maximum drain current, much lower gate leakage current, a better noise margin, and much greater flexibility in digital integrated circuits design due to large gate voltage range. The main obstacle to GaAs-based MOSFET devices is the lack of high-quality, thermodynamically stable gate dielectrics that match the performance of SiO₂ on silicon.

Extensive efforts have been devoted over the past two decades to passivate the GaAs surface to realize GaAs MOSFET and MISFETs [5-7]. Several processes have been developed to passivate GaAs surface, enabling important reduction of GaAs-Insulator interface defect. The majority of these processes are based on sulfur chemical passivation, and silicon interface control layer [6-8]. However, the devices stability and compatibility with high temperature processes remained a major challenge, limiting the wide adoption of these passivation techniques [9-12]. During the past few years a large number of dielectric materials have been investigated as alternative gate dielectrics for GaAs MOSFET devices, including Ga₂O₃, Gd₂O₃, HfO₂, Al₂O₃, InAlP and also stacked layers of many other dielectric materials [13-18]. Recently, the first enhancement mode GaAs MOSFET using
(GdGa)$_2$O$_3$/Ga$_2$O$_3$ dielectrics stack grown by molecular beam epitaxy (MBE) has been reported [19, 21]. Despite this achievement, the continuous scaling of the devices and the move toward nanodevices require a new approach to dielectric materials.

Polymers are expected to play a major role in the development of nanodielectric materials for both silicon and GaAs based nanodevices, beyond the 22 nm technology node. The reason for this expectation is that polymeric materials with a variety of chemical, structural, electrical and optical properties can be chemically synthesized from atomic or molecular elements. This will enable the development of nanodielectric materials that could meet the specific requirements of the gate dielectric such as very high dielectric constant, very low interface defects, very high breakdown voltage, and very low leakage current [22, 23]. The importance of the combination between CVD process and polymeric precursors lies in the infinite possibilities offered by organic and inorganic polymers synthesis. This approach is very appealing for the development of both high-k and low-k dielectric materials, as well as for new generation of semiconductor materials.

The dielectric properties of polymer based thin films grown by chemical vapor deposition (CVD) process have been intensively investigated by our research group. Recently, we demonstrated the suitability of polymer based thin films as a high-k gate dielectric for silicon MOS devices [24]. In this work we investigate the passivation of gallium arsenide using SiCON thin films obtained through similar deposition process using an organosilicon polymeric precursor. The viability of polymer based thin films as gate dielectrics for GaAs MOSFET is being considered.
5.2 Experimental

The dielectric thin films of SiCON were grown on GaAs wafers by chemical vapor deposition process (CVD) using a Thermco Mini-Brute horizontal furnace. The gallium arsenide wafers were (100) oriented, double-face polished, p-type, zinc doped, with doping concentration in the range of $1-5 \times 10^{17} \text{cm}^{-3}$. The wafers were properly cleaned three times in an ultrasonic bath using acetone, isopropanol and deionised water. The GaAs wafers were then immediately introduced in the reactor together with a boat containing the organosilicon polymer powder. The reactor is pumped down to a vacuum pressure of about 1 mtorr and then purged five times using ultra high purity nitrogen. The vacuum pump is then turned off and a constant flow of nitrogen is fed through the reactor and adjusted to maintain the deposition pressure near atmospheric pressure. The temperature is then gradually increased up to 700 °C at a rate of 25°C/min and then maintained at this temperature for 10 minutes before allowing natural cooling under vacuum.

The chemical compositions of the thin films obtained were investigated by time-of-flight elastic recoil detection spectroscopy (TOF-ERD) using a EN-1 Tandem accelerator. A 40 MeV cobalt ions beam was used for the depth profiling of the samples. The chemical structure at the interface between SiCON thin films and GaAs substrates was analyzed by X-ray photoelectron spectroscopy (XPS). The analyses were performed with Kratos AXIS-HS system using a non-monochromatic MgKα X-ray source with a power of 120 W. Argon ions beam with a power of 80 W (4 kV, 20 mA) was used to sputter the samples during XPS depth profile analysis.
The electrical characteristics of SiCON/GaAs metal-oxide-semiconductor (MOS) heterostructure were investigated by capacitance-voltage (C-V) and conductance-voltage (G-V) using Solartron impedance/gain-phase analyser equipped with an MDC mercury probe station. The measurements data were automatically acquired and processed using a LabVIEW control program developed in-house. The samples were also analyzed by photoluminescence spectroscopy (PL). Photoluminescence spectra were recorded using SPEX-1680 double-monochromator spectrophotometer. The PL experiments were performed under vacuum (15 mtorr) at a temperature of 20 °K. The measurements were carried out with argon ions laser beam, with a wavelength of 532 nm, a source power of 30 mW, and a beam spot diameter of approximately 2 mm. The film thickness, refractive index and extinction coefficient were measured by ellipsometry at a wavelength of 632.8 nm, using Woollam α-SE spectroscopic ellipsometer.

5.3 Results and discussion

Chemical vapor deposition process using synthetic polymer precursors has been developed by our research group. Previously, we demonstrated the viability of this process to deposit high-k gate dielectric for silicon MOSFET [24]. In this paper we investigate the passivation of GaAs using dielectric thin films obtained using an organosilicon polymer. We particularly focused on the influence of oxygen on the characteristics and interface properties of SiCON/GaAs MOS heterostructure.

5.3.1 Elastic Recoil detection spectroscopy (ERD) analysis

Figure 5.1 shows the atomic depth profile of three different SiCON/GaAs samples,
Figure 5.1: Atomic chemical composition of SiCON thin films obtained by Time-Of-Flight Elastic Recoil Detection spectroscopy (TOF-ERD), using EN-1 Tandem accelerator. A 40 MeV cobalt ions beam was used for depth profiling of the samples. The graphs correspond to three samples with different atomic concentrations of oxygen: (a) sample S1, (b) sample S2 and (c) sample S3.
obtained by TOF-ERD analysis. The samples were prepared under the same conditions as described above, but with different atomic concentrations of oxygen in the film. The depth profiles of the atomic concentrations of carbon, silicon, nitrogen and hydrogen are nearly constant for all three samples, whereas the atomic concentrations of oxygen measured near the interface are 12 at.%, 17 at.% and 23 at.%. The thickness of SiCON thin films was relatively uniform, but varies from run to run, especially for very thin films. It appears that there is no correlation between polymer mass and film thickness. This is probably due to the excessive amount of polymer available during the deposition process, which resulted in significant variation of the atomic depth observed in TOF-ERD analysis. The development of high vacuum CVD reactor equipped with a micro-dispensing system for polymer powder is expected to solve this problem.

5.3.2 Capacitance-voltage (C-V) and conductance-voltage (G-V) characterization

The influence of the atomic concentration of oxygen in SiCON thin films on electrical characteristics of SiCON/GaAs heterostructure was investigated by capacitance-voltage and conductance-voltage techniques using a mercury probe as a gate electrode. Figure 5.2 shows the capacitance and conductance characteristics obtained as function of sweep voltage at high frequency (1 MHz). It is clear from this figure that the C-V characteristics of all samples exhibit MOS capacitors behaviour. The G-V characteristics, on the other hand, show clear conductance peaks as the voltage is swept through the depletion region at a slow rate of 50 mV/s.

Figure 5.2(a) shows the C-V and G-V characteristics obtained at a high atomic
Figure 5.2: High-frequency capacitance-voltage (C-V) and conductance-voltage (G-V) characteristics of Mg/SiCON/p-GaAs MOS structure obtained at 1 MHz. The graphs correspond to three samples with different atomic concentrations of oxygen: (a) sample S1, (b) sample S2 and (c) sample S3
concentration of oxygen (S1, ≈ 23 at. %). The C-V characteristics exhibit well-defined accumulation, depletion and inversion regions. A relatively large hysteresis is observed, indicating the presence of a large concentration of mobile charges. The shift of the C-V curve toward negative voltage suggests the presence of positive oxide charges, due to positively charged hydrogen protons [25]. The density of interface traps of SiCON/GaAs MOS structure was estimated from the conductance peak using the Hill-Coleman method [26]. A relatively high interface trap density of approximately $6 \times 10^{12} \text{ cm}^{-2}\text{eV}^{-1}$ was obtained.

As the atomic concentration of oxygen in the film is decreased, the density of mobile charges previously observed at high concentration of oxygen is significantly reduced. This is clearly obvious from figure 5.2(b) which shows the C-V characteristics obtained at a medium concentration of oxygen (S2, ≈ 17 at. %) with almost no hysteresis. The C-V characteristics exhibit well defined accumulation and depletion regions. As the voltage is swept through the inversion region, the charges inversion process appears to be very sluggish even at a very slow sweeping rate. The slow inversion behaviour appears to be caused by the slow trapping and detrapping process due to positively charged slow oxide traps, also called oxide border traps. The presence of these traps is evident from the large value of the capacitance observed in accumulation region. The charging and discharging mechanism of the oxides border traps is explained by electron tunnelling effect [27]. The C-V characteristics showed a steeper depletion region compared to the samples with a high concentration of oxygen, indicating a lower density of interface traps. The interface trap density calculated from the conductance-voltage characteristics is approximately $9 \times 10^{11} \text{ cm}^{-2}\text{eV}^{-1}$.

Figure 5.2(c) shows the C-V and, G-V characteristics obtained at a low concentration of oxygen (S3, ≈ 12 at. %). It is clear from this figure that by further reducing the oxygen
concentration in the film, the influence of oxide border traps on the C-V characteristics, previously seen at a medium concentration of oxygen, is no longer visible. The C-V characteristics of the samples obtained at a low concentration of oxygen exhibit similar behaviour as the samples obtained at a high concentration of oxygen, but with relatively small hysteresis. The mechanism of the variation of the concentration of mobile and fixed oxide charges could be explained by the capture and release of hydrogen protons due to change in bonding configuration of silicon, carbon and oxygen atoms [25]. The interface traps density calculated from the peak of conductance-voltage characteristics is about $6 \times 10^{11}$ cm$^{-2}$ eV$^{-1}$. The decrease in the density of interface defects appears to be linked to an increase in carbon to oxygen ratio near the interface. A summary of electrical and optical properties of SiCON/GaAs MOS heterostructure is given in table 5.1.

**Table 5.1:** Summary of electrical, optical and chemical properties of SiCON thin films deposited on GaAs by chemical vapor deposition (CVD) process using a polymeric precursor.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[O] (at. %)</th>
<th>$t_{ox}$ (nm)</th>
<th>$\varepsilon_r$ (1 MHz)</th>
<th>$D_{it}$ (cm$^{-2}$eV$^{-1}$)</th>
<th>$n$ (632.8nm)</th>
<th>$k$ (632.8nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>23</td>
<td>134</td>
<td>3.37</td>
<td>$6 \times 10^{12}$</td>
<td>2.073</td>
<td>0.045</td>
</tr>
<tr>
<td>S2</td>
<td>17</td>
<td>184</td>
<td>9.71</td>
<td>$9 \times 10^{11}$</td>
<td>1.834</td>
<td>0.285</td>
</tr>
<tr>
<td>S3</td>
<td>12</td>
<td>195</td>
<td>4.90</td>
<td>$6 \times 10^{11}$</td>
<td>1.903</td>
<td>0.164</td>
</tr>
</tbody>
</table>
5.3.3 Photoluminescence spectroscopy (PL) analysis

The interface properties of SiCON/GaAs were further analyzed by photoluminescence spectroscopy in order to evaluate the interface quality. Figure 5.3 shows low temperature PL spectra of the samples obtained at different concentrations of oxygen, together with the spectrum of unpassivated GaAs substrate. It is obvious from this figure that

![Graph showing PL spectra](image)

**Figure 5.3**: Low temperature photoluminescence (PL) spectra acquired before and after the passivation of p-GaAs using SiCON thin films with different atomic concentrations of oxygen. The PL measurements were carried in vacuum using a 532 nm argon laser source, with a power of approximately 1W/cm²
the sample with a low concentration of oxygen exhibits the highest emission intensity; nearly 5 times stronger than that of unpassivated GaAs sample. This indicates that the sample with a low concentration of oxygen has the lowest density of interface defects. These results are in good agreement with the values of interface traps density previously estimated from conductance-voltage measurements using the Hill-Coleman method.

5.3.4 X-ray photoelectron spectroscopy (XPS) analysis

![XPS spectrum](image)

**Figure 5.4:** Low resolution X-ray photoelectron spectroscopy (XPS) spectrum obtained from the analysis of the interface between SiCON thin films and p-GaAs substrate. The analysis was performed with Kratos AXIS-HS system using a 120 W MgKα X-ray source
In order to understand the influence of the atomic bonding structure on the interface properties of SiCON/GaAs structure, we investigated the samples using X-Ray photoelectron spectroscopy (XPS). Figure 5.4 shows low resolution XPS spectra obtained from the interface. The analysis of the peaks confirms the presence of all chemical elements previously observed in ERD depth profile analysis, with the exception of hydrogen to which XPS is not sensitive.

To further clarify the bonding structure of gallium and arsenic we conducted a high resolution XPS analysis of Ga-3d and As-3d peaks both before and after passivation of the samples. Despite the variation of the atomic concentration of oxygen at the interface, all samples displayed similar results. Figure 5.5 shows the high resolution Ga-3d and As-3d spectra obtained at a low atomic concentration of oxygen. It is clear from the deconvolution results of Ga-3d and As-3d peaks that before passivation, the samples showed strong GaAs bonding peaks as well as both Ga$_2$O$_3$ and As$_2$O$_3$ related bonding peaks. The oxide peaks were expected and are well known to be the result of GaAs surface oxidation, due to air exposure. After the deposition of SiCON thin films, the results of XPS interface analyses did not show any gallium-oxide or arsenic-oxide related bonding peaks. However, new bonding peaks have emerged at different binding energies which indicate that both gallium and arsenic have formed new chemical bonds.

After comparing these results with the works previously reported in literature, we concluded that the shoulder doublet peaks obtained from the deconvolution of Ga-3d peak should be related to Ga-Si or Ga-C bonds [28-30]. On the other hand, the origin of the weak doublet peaks observed in the deconvolution of As-3d peak is assigned to As-N bonds [31,32].
Figure 5.5: High resolution X-ray photoelectron spectroscopy (XPS) analysis of As-3d and Ga-3d peaks, and the corresponding deconvolution peaks, obtained both before and after the passivation of p-GaAs with SiCON thin films.
Based on these results, it is obvious that the low interface defect observed at a low atomic concentration of oxygen is mainly due to elimination of Ga$_2$O$_3$ and As$_2$O$_3$ from the interface and the replacement of oxygen bonds by a more stable atomic structure based on silicon, carbon and nitrogen. More in-depth analyses are still required to elucidate the bonding structure at the interface and to understand the mechanism of this passivation process.

5.4 Conclusion

SiCON thin films obtained by chemical vapor deposition process using a polymeric precursor have been investigated as a passivation layer and a gate dielectric for GaAs MOSFET. SiCON/GaAs MOS structure with low density of interface traps was obtained at a low atomic concentration of oxygen; without any prior chemical treatment of GaAs surface. The interface traps density extracted from conductance-voltage characteristics was found to be as low as $6 \times 10^{11}$ cm$^{-2}$ eV$^{-1}$. This low density of interface defects was in good correlation with photoluminescence measurements. The results of XPS analysis suggest that the passivation of a GaAs surface, and the low density of interface traps obtained are linked to elimination of Ga$_2$O$_3$ and As$_2$O$_3$ from the interface and their replacement with new bonding structures based on silicon carbon and nitrogen. Further improvements are expected through optimization of the deposition process as well as through the chemical synthesis of the polymeric precursors.
References


CHAPTER 6

FABRICATION AND CHARACTERIZATION OF GaAs MOS CAPACITOR WITH CVD GROWN POLYMER-BASED THIN FILM AS A GATE DIELECTRIC


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Abstract

GaAs Metal-Oxide-Semiconductor (MOS) capacitor using polymer-based thin film as a gate dielectric has been fabricated and electrically characterized. The influence of the atomic concentration of oxygen in the dielectric films on the capacitance-voltage (C-V) and current-voltage characteristics of the MOS capacitors has been thoroughly investigated. The GaAs MOS capacitor obtained at low concentration of oxygen showed an almost ideal MOS capacitor behavior. The density of interface traps extracted from conductance-frequency measurement was found to be as low as $9.7 \times 10^9 \text{eV}^{-1}\text{cm}^{-2}$. In addition, the MOS capacitor exhibits very low leakage current ($6.6 \times 10^{-9} \text{A/cm}^2@-1\text{V}$) and relatively high breakdown voltage (2.05 MV/cm). These characteristics make polymer-based thin films very attractive as a passivation layer and a gate dielectric for GaAs MOSFET. The ability to tune the polymer through chemical synthesis and polymer functionalization makes CVD grown polymer-based thin films very promising for the passivation of virtually any semiconductor surface.
Résumé

Un condensateur en GaAs de type métal-oxide-semiconducteur (MOS) utilisant une couche mince à base de polymères comme diélectrique de grille a été fabriqué et électriquement caractérisé. L'influence de la concentration atomique d'oxygène dans les couches diélectriques sur les caractéristiques de capacité-tension (C-V) et de courant-tension des condensateurs MOS a été profondément étudiée. Les condensateurs MOS de GaAs fabriqués avec des diélectriques à basse concentration d'oxygène ont montré un comportement quasiment idéal. La densité des pièges d'interface extraite à partir de la mesure de la conductance en fonction de la fréquence est aussi basse que $9.7 \times 10^9 \text{ eV}^{-1}\text{cm}^2$. En outre, le condensateur MOS a démontré un courant de fuite très bas ($6.6 \times 10^9 \text{ A/cm}^2 @ -1\text{V}$) et une tension de claquage relativement élevée (2.05 MV/cm). Ces caractéristiques rendent les couches minces à base de polymères très intéressantes comme couche de passivation et aussi comme un diélectrique de grille dans le transistor MOSFET de GaAs. La possibilité d'adapter le polymère aux spécificités de la surface à travers la fonctionnalisation chimique et la synthèse des polymères rend les couches minces à base de polymères, obtenues par CVD, très prometteuses pour la passivation de la surface de pratiquement n'importe quel matériau semiconducteur.
6.1 Introduction

Metal-oxide-semiconductor field-effect-transistor (MOSFET) has been the workhorse of semiconductor technology for several decades. As the silicon CMOS technology is approaching its fundamental limits there is a growing interest in high mobility materials particularly GaAs. However, the lack of gallium arsenide (GaAs) MOSFET has limited its functionality, scalability, and performance; consequently, market acceptance of GaAs has been restricted. The development of GaAs MISFET and MOSFET has been an active field of research for many decades. Recently, GaAs surface passivation with very low interface defects has been reported by several research groups using a stack of dielectric thin films grown by atomic layer deposition (ALD) and molecular beam epitaxy (MBE) such as Al$_2$O$_3$ [1,2], HfO$_2$ [3], and Ga$_2$O$_3$ [4,5,6]. These results have enabled the development of the first enhancement mode GaAs MOSFETs [7, 8]. This achievement has again stimulated interest in GaAs as a possible future alternative to silicon in CMOS beyond the 22 nm technology node [9].

While ALD and MBE processes are very advantageous for the growth of high quality thin films with precise control of film composition and thickness, their significantly slow growth rate and relatively high sensitivity to contamination make them less attractive for high volume fabrication. As the semiconductor industry is gradually moving toward nanodevices, there are pressing needs to explore and develop new deposition processes and new dielectric materials to solve the growing number of problems related to devices scaling, processes integration, materials compatibility, and cross contamination issues.
In attempt to solve some of these problems, our research group has been focused on the development of a different approach to deposit thin films in batch process that provides better control of the intrinsic properties of thin films, and at the same time enables to customize the source materials to meet the specific requirements of devices and processes integration [10-12]. The process consists of the combination between the conventional batch CVD process and synthetic polymers as source materials. The benefit of this process beside its fast deposition rate is the ability to tailor the polymer source material prior to film deposition, through chemical synthesis, and polymer functionalization. In previous works we investigated the electrical optical and structural characteristics of polysilanes polymer–based dielectric thin films obtained by this process and demonstrated their suitability as a passivation layer for both silicon and GaAs [13, 14].

In this paper, we report the fabrication and characterization of GaAs metal-oxide-semiconductor (MOS) capacitor, using polymer-based thin films obtained by CVD process as a gate dielectric. The electrical characteristics of GaAs MOS capacitor are investigated using capacitance-voltage, conductance-frequency and current-voltage techniques.

6.2 Device fabrication and characterization

The first step in the fabrication process of GaAs MOS capacitor consists of the deposition of polymer-based thin films on GaAs wafer using CVD process. The deposition process had been discussed in great details in previous publications [12-14]. The GaAs wafer used in this study are double faces polished, p-type (100) oriented, zinc doped with a doping
concentration of $1-5 \times 10^{17}$ cm$^{-3}$. Prior to metallization the samples were first cleaned using opticlear, acetone, ethanol, and DI water. Immediately, the samples were dipped in (H$_2$O:NH$_4$OH:H$_2$O$_2$,50:1:1) solution for 20 seconds, followed by a rinse in DI water and then dipped again in (H$_2$O:H$_2$O$_2$:HCl,30:1:1) solution for 2 min, to remove native oxide and other organic and metal contaminants. Next the samples are then quickly rinsed in DI water, dried with nitrogen gun and right away introduced in the Sloan electron beam evaporator to deposit the back metal contact consisting of Au/Pt/Ti/Pt (100nm/10nm/40nm/10nm). To

Figure 6.1: MOS capacitor structure on GaAs substrate with SiCON polymer-based thin film as a gate dielectric.
achieve low resistivity of the back ohmic contact, the samples were subjected to rapid thermal annealing (RTA) at 400 °C for 60 seconds using Jipelec RTA system. The front metal gate electrodes (1 mm in diameter) were obtained by lithography using a lift-off process of Au/Ni (100nm/50nm) deposited using Edwards electron beam evaporator. The complete structure of the GaAs MOS capacitor is shown in figure 6.1.

The electrical characteristics of the fabricated GaAs MOS capacitors were analyzed by capacitance-voltage (C-V) and current-voltage (I-V) techniques. The C-V measurements were acquired using Solartron S1260 impedance/gain-phase analyzer directly connected to a probe station through coaxial cables. The I-V measurements were conducted using Hewlett Packard HP4145A semiconductor parameter analyzer. The atomic concentrations of oxygen were previously obtained by time-of-flight elastic recoil detection spectroscopy (TOF-ERD) using EN-1 Tandem accelerator. The film thickness was measured by ellipsometry at a wavelength of 632.8 nm, using Woollam α-SE spectroscopic ellipsometer.

6.3 Results and discussion

The chemical and structural composition of SiCON polymer-based dielectric thin films obtained by CVD were previously investigated [14]. The influence of the atomic concentration of oxygen in SiCON thin films on the electrical characteristics of SiCON/GaAs heterostructure was preliminarily studied by a non-destructive C-V analysis technique using a mercury probe. The initial results indicated that polymer-based dielectrics are very promising for the passivation of GaAs surface and as a gate dielectric for GaAs MOS devices. In order to further confirm the results previously obtained, SiCON/GaAs MOS capacitors have been fabricated and electrically characterized.
6.3.1 Capacitance-voltage (C-V) and conductance-voltage (G-V) characterization

Figure 6.2 shows the high frequency C-V and G-V characteristics of SiCON/GaAs MOS capacitors fabricated with SiCON dielectric thin films at three different atomic concentration of oxygen. The C-V characteristics of all samples exhibit a p-type MOS capacitor behavior with clear accumulation depletion and inversion regions which indicate that the Fermi level was unpinned. The C-V curves display almost no hysteresis subsequent to post-metallization rapid thermal annealing at 450 °C for 60 seconds. The important reduction in C-V hysteresis after thermal annealing is linked to desorption of hydrogen which is considered to be the main source of mobile charges in SiCON thin films.

At a high atomic concentration of oxygen (Figure 6.2(a)) the C-V characteristics shows a small shift toward the negative voltages which is an indication of the presence of fixed positive charges in the bulk of the gate dielectric. As the sample is forced through inversion the silicon majority holes are drawn from the surface toward the bulk of silicon at the same time the minority electrons start to accumulate at the SiCON/Si interface. As we continue to increase the voltage the C-V characteristics show a little kink at about 2 V, due to generation of extra positive charges, which can be explained by the exchange of charges between silicon and SiCON via positively charged slow border traps [15, 16]. The G-V characteristics of the sample obtained at 1 MHz is shown in figure 6.2(a). The interface traps density extracted from peak conductance using Hill-Coleman single frequency approximation [17] is about $5.3 \times 10^{11}$ eV/cm$^2$. 

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Figure 6.2: Capacitance-voltage and conductance-voltage characteristics of SiCON/GaAs MOS capacitors obtained at 1 MHz after correction for series resistance assuming a parallel capacitance conductance model. The measurements were obtained at different atomic concentrations of oxygen in polymer-based thin films: (a) sample S1, 23 at.%; (b) sample S2, 17 at.%; (c) sample S3, 12 at.%;
As the atomic concentration of oxygen in SiCON thin film is reduced to about 17 at.\%, (Figure 6.1(b)) the sample obtained at this concentration did not exhibit any noticeable shift in its C-V characteristics, however, an important increase in the capacitance is observed in the accumulation region. This large capacitance is the result of the accumulation of a large concentration of positive charges near the interface originating from both silicon majority holes and a large density of positively charged border traps in SiCON. As the voltage is swept from accumulation toward inversion, the C-V characteristics exhibit a behavior similar to that of the sample obtained at a high concentration of oxygen. The sluggish inversion process observed is explained by the large concentration of border traps and their slow response. The interface traps density calculated from the G-V characteristics in Figure 6.2(b) is approximately $9.7 \times 10^{11}$ eV/cm$^2$.

By further reducing the atomic concentration of oxygen in SiCON thin film to about 12 at.\%, an MOS capacitors with nearly ideal C-V characteristics is obtained. The relatively sharp transition from accumulation to inversion indicates a low density of interface defect. The interface traps density estimated from G-V characteristics in Figure 6.1(c) is found to be as low as $4.5 \times 10^{11}$ eV/cm$^2$. The small kink observed in the inversion region suggests the presence of few positively charged slow border traps in SiCON thin film. The complete elimination of border traps requires a more precise control of the atomic composition of the dielectric thin film as well as further optimization of the fabrication process of MOS capacitor.
6.3.2 Conductance-frequency (G-ω) characterization

The SiCON/GaAs interface traps density was further investigated using conductance-frequency method [18]. Figure 6.3 shows the MOS capacitors conductance as function of frequency and at different voltage, measured in the depletion region. The values of conductance were extracted assuming a parallel capacitance conductance model and using expression (1) where \( C_m \) and \( G_m \) are the measured capacitance and conductance respectively. \( C_{ox} \) is the oxide capacitance measured in strong accumulation.

\[
\frac{G_p}{\omega} = \frac{\omega C_{ox}^2 G_m}{G_m^2 + \omega^2 (C_{ox} - C_m)^2} \quad (1)
\]

The interface traps density is calculated from the peak of conductance versus frequency characteristics assuming a distributed interface trap levels throughout the band gap, in this case the peak frequency and the interface trap time constant are correlated by \( \omega \tau_n = 1.98 \). Under these conditions, the theoretical expression relating interface traps density and conductance is given by expression (2).

\[
D_{it} = \frac{2\omega \tau_n}{q} \cdot \frac{G_p/\omega}{\ln\left[1+(\omega \tau_n)^2\right]} \quad (2)
\]

The conductance-frequency characteristics obtained exhibit negligible frequency dispersion particularly at a low atomic concentration of oxygen. The interface traps density calculated from peak conductance was found to be as low as \( 9.7 \times 10^9 \) eV\(^{-1}\)cm\(^2\), which is remarkably low compared to the value obtained using Hill-Coleman method. The Hill-Coleman method is well known to overestimate the density of interface traps.
Figure 6.3: Conductance versus frequency characteristics measured in the depletion region, at different atomic concentrations of oxygen in polymer-based thin films: (a) sample S1, 23 at.%; (b) sample S2, 17 at.%; (c) sample S3, 12 at.%; assuming a parallel capacitance conductance model
6.3.3 Current-voltage (I-V) characterization

The leakage current and breakdown voltage of SiCON/GaAs MOS capacitors were investigated using current-voltage measurement. Figure 6.4 shows the J-V characteristics of the MOS capacitors obtained at different atomic concentrations of oxygen. The leakage current mechanism was analyzed using three different theoretical models including direct tunneling, Fowler-Nordheim tunneling, Frenkel-Poole tunneling and space charge limited tunneling. The results obtained indicate that only Frenkel-Poole tunneling model showed satisfactory fitting results. Figure 5 shows the \( \ln(J/E) \) versus \( E^{1/2} \) characteristics of the samples, which, exhibit a linear behavior as expected from Frenkel-Poole tunneling current model, according to expression (3), where \( E \) is the electric field, \( \Phi_B \) the barrier height, \( \varepsilon \) the dielectric permittivity, and \( \alpha \) a constant. The Frenkel-Poole emission model appears to be valid for both forward and reverse biased MOS diode at high electric field exceeding 1 MV/cm. At low electric field (below 1 MV/cm), the J-V characteristics display an almost linear behavior.

\[
J = \alpha E \exp \left[ \frac{q}{kT} \left( \frac{q}{\varepsilon \varepsilon_0} \right)^{1/2} E^{1/2} - \Phi_B \right] \tag{3}
\]

The breakdown voltage of SiCON thin film is found to vary in the range of 1.6 to 2.6 MV/cm, with the largest value obtained at a high atomic concentration of oxygen. The dielectric leakage current density obtained from the J-V characteristics at -1 V is as low as \( 7.7 \times 10^9 \) A/cm\(^2\). The large leakage current and the low breakdown voltage obtained at a medium concentration of oxygen are the result of a relatively high density of interface traps.
Figure 6.4: Current-voltage characteristics of forward and reverse biased SiCON/GaAs MOS diodes measured at different atomic concentrations of oxygen in polymer-based thin films: (a) sample S1, 23 at.%; (b) sample S2, 17 at.%; (c) sample S3, 12 at.\%
Figure 6.5: Linear fitting of the forward and reverse leakage current of SiCON/GaAs MOS diodes to Frenkel-Poole emission model, obtained at different atomic concentrations of oxygen in polymer-based thin films: (a) sample S1, 23 at.%; (b) sample S2, 17 at.%; (c) sample S3, 12 at. %
and the dielectric border traps found in sample 2. A summary of the results obtained is given in table 6.1.

Table 6.1: Summary of the properties of SiCON/GaAs MOS capacitors

<table>
<thead>
<tr>
<th>Sample</th>
<th>[O] (at. %)</th>
<th>( t_{ox} ) (nm)</th>
<th>( \varepsilon_{ox} ) (1MHz)</th>
<th>( D_{it} ) (G-V) ( \times 10^{11} )</th>
<th>( D_{it} ) (G-( \omega )) ( \times 10^{10} )</th>
<th>Breakdown (MV/cm)</th>
<th>Leakage (A/cm²) @-1V</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>23</td>
<td>134</td>
<td>2.7</td>
<td>5.3 \times 10^{11}</td>
<td>2.6 \times 10^{10}</td>
<td>2.61</td>
<td>7.7 \times 10^{-9}</td>
</tr>
<tr>
<td>S2</td>
<td>17</td>
<td>184</td>
<td>9.0</td>
<td>9.7 \times 10^{11}</td>
<td>3.1 \times 10^{10}</td>
<td>1.58</td>
<td>3.5 \times 10^{-5}</td>
</tr>
<tr>
<td>S3</td>
<td>12</td>
<td>195</td>
<td>3.7</td>
<td>4.5 \times 10^{11}</td>
<td>9.8 \times 10^{9}</td>
<td>2.05</td>
<td>6.6 \times 10^{-9}</td>
</tr>
</tbody>
</table>

6.4 Conclusion

CVD grown polymer-based thin films have been successfully used to passivate GaAs without any chemical treatment of the substrate surface. GaAs MOS capacitor with polymer-based thin film has been demonstrated. The Au/Ni/SiCON/GaAs/Pt/Ti/Pt/Au heterostructure with nearly ideal MOS capacitor behavior is obtained at a low concentration of oxygen. The interface traps density extracted from conductance-frequency measurements was found to be very low, in the range of \( 10^{-10} \) eV\(^{-1}\) cm\(^{-2}\). In addition, the polymer-based thin films exhibit very low leakage current. These characteristics make these thin films very attractive for the passivation of GaAs surface. The relatively low dielectric constant of SiCON thin films, however, makes them inadequate for very thin gate dielectric film. Therefore, a high dielectric material will be required on the top of SiCON to achieve high performance.
MOSFET. The ability to customize the chemical composition of the polymer through chemical synthesis and polymer functionalization, makes this polymer-based CVD process very attractive for passivation of virtually any semiconductor surface, and is expected enable the development of new generation of high-κ and low-κ dielectric materials.
References


CHAPTER 7

CONCLUSION

7.1 Summary

A new chemical vapor deposition process of thin film materials using polysilanes polymer as source material has been developed as a very attractive alternative to conventional CVD process based on gases precursors. The ability to tailor the polymer source material through chemical synthesis and polymer functionalization enable the development of very complex thin film materials with a wide range of chemical, mechanical, electrical and optical properties. In this work we demonstrated that this process can be used to deposit a broad range of conventional materials which can be tuned to meet the requirement of many applications.

Using this process we have successfully deposited silicon carbide thin films. The structural analysis indicates that these films are very similar to amorphous silicon carbide obtained by other deposition methods such as PECVD. The analysis of the bulk atomic concentration of chemical elements showed that these thin films are carbon rich and non-stoichiometric, with very uniform atomic depth profile. The film resistivity was as high as $6 \times 10^5 \ \Omega\cdot\text{cm}$, which is explained by the relatively high atomic concentrations of oxygen found in these films (about 2 at. %). By eliminating the oxygen, through process optimization and polymer purification, electronic grade silicon carbide thin films could be obtained. The
strong chemical resistance to acid and alkaline solutions makes these films very attractive as a conformal coating material in a wide range of application and as a structural material in MEMS devices.

The influence of the atomic concentration of oxygen on poly(dimethylsilane) polymer-based thin films has been investigated. The results showed that the chemical composition and the structure of these films can be easily adjusted by controlling the atomic concentration of oxygen and nitrogen. SiONC thin films with a wide range of chemical composition and physical properties were obtained. The bulk atomic composition of these thin films is found to be uniform across all the film thickness, which indicates that these films are homogenous.

The electro-optical properties of SiONC dielectric thin films deposited on silicon by polymer-source CVD process were thoroughly investigated. The results obtained show that SiONC/(p)Si diode exhibit a nearly ideal MOS capacitor behaviour at a concentration of oxygen of approximately 35 at.%. The density of traps at the interface between SiONC and silicon extracted from conductance-voltage measurements was found to be as low as $3.2 \times 10^{10}$ cm$^{-2}$ eV$^{-1}$, which is comparable to the density of thermally grown SiO$_2$ on crystalline silicon. The relative dielectric constant of SiONC thin films extracted from capacitance-voltage measurements is found to vary between 5.4 and 6, which is much higher than the dielectric constant of SiO$_2$. The refractive index showed a linear variation between 1.45 and 1.70 as a function of the atomic concentration of oxygen in the films. These results demonstrate that SiONC thin film obtained by polymer-source CVD process is a very attractive substitute to SiON thin films obtained by other conventional methods, and which is
widely used both as a gate dielectric in CMOS devices and as a waveguide in integrated optical devices.

Poly(dimethylsilane) polymer-based thin films grown on gallium arsenide wafer at various concentrations of silicon, carbon, oxygen and nitrogen were extensively investigated. By optimizing the deposition parameters we discovered that thin films of SiCON obtained by chemical vapor deposition process are very attractive for the passivation of GaAs surface. SiCON/GaAs MOS structure with low density of interface traps was obtained at a low atomic concentration of oxygen of about 12 at.%. These results were obtained without any prior chemical treatment of GaAs surface. The interface traps density extracted from conductance-voltage characteristics was found to be as low as $6 \times 10^{11}$ cm$^{-2}$ eV$^{-1}$, without any chemical treatment of the surface. This low density of interface defects was in good correlation with the results of photoluminescence measurements. The results of XPS analysis suggest that the passivation of GaAs surface, and the low density of interface traps obtained are linked to the elimination of Ga$_2$O$_3$ and As$_2$O$_3$ from the interface, and their replacement with new bonding structures based on silicon carbon and nitrogen. The exact mechanism of the passivation process of GaAs is still unclear, however we believed that the release of the methyl radical at the beginning of the sublimation process of the polymer source may have contributed to the removal of the defects associated with the formation of native oxide on GaAs wafer.

In order to confirm these results the GaAs MOS capacitor with SiCON thin film as a gate dielectric was fabricated and electrically characterized. The Au/Ni/SiCON/GaAs/Pt/Ti/Pt/Au heterostructure with nearly ideal MOS capacitor behavior was obtained at low concentration of oxygen. The interface traps density extracted from conductance-frequency measurements was found to be very low, in the range of $10^{10}$ cm$^{-2}$eV$^{-1}$.
which is comparable to MBE deposited Ga$_2$O$_3$(Gd$_2$O$_3$) on GaAs. The very low density of interface traps obtained is explained by the thermal activation and in-situ cleaning of GaAs surface at the early stage of the polymer sublimation process. Furthermore, the polymer-based thin films were found to exhibit very low leakage current. These characteristics make these thin films very attractive for the fabrication of GaAs MOSFET. The relatively low dielectric constant of SiCON thin films, however, makes them inadequate for very thin gate dielectric. Therefore, a high dielectric material will be required on the top of SiCON to achieve high performance GaAs MOSFET. The ability to customize the chemical composition of the polymer through chemical synthesis and polymer functionalization makes polymer-based CVD process very attractive for the passivation of virtually any semiconductor surface, and could enable the development of next generation high mobility compound semiconductors based CMOS devices.

In conclusion, throughout this work, I have demonstrated that polymer-based thin film materials obtained by polymer-based CVD process are very attractive for a wide range of microelectronic and optoelectronic applications including MOSFET, integrated optical waveguides and MEMS. The capability of polymer-based CVD process to passivate GaAs surface, in particular, is of enormous importance. This very promising passivation process is expected to enable the development of new generation of high speed and low power GaAs based MOSFET, which could eventually replace silicon based MOSFET in future CMOS technology for ultra large scale integrated (ULSI) circuits. The development of GaAs MOSFET will also enable the fabrication of high density and low power monolithic microwave integrated circuits (MMIC). In addition, the ability to deposit waveguide thin film materials using polymer-based CVD process will simplify the development and integration
of optical waveguides and other photonic integrated devices. Consequently, polymer-based CVD process is very promising for large scale integration of microelectronic, photonic and microwaves circuits.

7.2 Future Works

There is no doubt that the development of next generation semiconductor nanodevices will greatly depend on the ability to design new complex materials, with precisely tuned chemical composition and structure as well as physical and electrical properties. Polymer-based CVD process, offers a huge potential for achieving this objective. Future works should therefore continue to focus on the development of this process in order to enable the deposition of various polymeric materials including both inorganic and hybrid organic-inorganic polymers.

Meticulous attention should be paid to the design and setup of the deposition reactor. It is very important to develop an independent process which will allow to control and monitor the various parameters of the sublimation process of the polymer source, such as the polymer sublimation temperature, the precursor’s pressure and flow rate as well as the chemical evolution of precursors. In order to make this process more versatile and more commercially attractive it is very important to make the deposition setup compatible with both solid and liquid polymer sources. The development of an in-situ functionalization and polymerization process could also make this process very powerful. Another aspect of the process which requires special attention is the purification and doping processes of polymer source materials, which are very critical for the deposition of semiconductor thin film materials.
The preliminary results obtained in this study indicate that polymer-based CVD process is very attractive for the development of passivation process of compound semiconductors, as well as the fabrication of integrated optical waveguides and MEMS structures coating. Therefore, future work should equally focus on furthering the development of each of these very important applications. Attention should also be paid in future studies to the synthesis and preparation of new class of high-κ and low-κ dielectric thin film materials which are very crucial for the development and fabrication of high performance semiconductor nanodevices.

Last but not least, the intrinsic property of polymer materials which consist of the natural self-assembly of monomers and block copolymers is an important characteristic that could make polymer-based CVD process very promising for the development of self-assembled nanostructures. The ability to control the molecular composition and the structure of polymer precursors during the sublimation process of the polymer source and also the capacity to manipulate their orientation on the substrate are some important research directions that could open the way to a whole new era of molecular nanoelectronics.
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