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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF SILICON DIOXIDE FILMS USING DIETHYL SILANE AND OXYGEN

by

Kiran Kumar

This study focuses on producing thin and thick silicon dioxide films towards the fabrication of integrated optical sensor capable of monitoring and determining in-situ, the concentration of numerous analyte species simultaneously. In this study, diethylsilane (DES) has been used as a precursor to produce silicon dioxide films by low pressure chemical vapor deposition. The films were synthesized with two different flow ratios of oxygen to DES in the temperature range of 550°C to 800°C at a constant pressure of 200mTorr. The films deposited with lower oxygen to DES flow ratio have very high growth rate but suffer from high tensile stress leading to cracks in the films. However the films deposited with higher oxygen to DES flow ratio were crack free. The stress was found to be very low and tensile in these films and tended towards compressive with increasing deposition temperature which is necessary in producing thick films. The films were uniform and amorphous. The growth rate followed an Arrhenius behavior with an apparent activation energy of 10.59Kcal/mol in case of lower oxygen to DES ratio. Also, depletion was observed with increase in the distance between the wafers. The refractive index of the films were found to be near 1.45 and the films were highly transparent. The thick silicon dioxide films showed excellent properties at a deposition temperature of 775°C, a pressure of 200mTorr and an oxygen to DES flow ratio of 10:1.

SYNTHESIS AND CHARACTERIZATION OF SILICON DIOXIDE FILMS USING DIETHYL SILANE AND OXYGEN

by
Kiran Kumar

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Master of Science in Materials Science and Engineering

Department of Materials Science and Engineering

August 1998

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APPROVAL PAGE

SYNTHESIS AND CHARACTERIZATION OF SILICON DIOXIDE FILMS USING DIETHYL SILANE AND OXYGEN

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This thesis is dedicated to
my beloved parents

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CHAPTER 1

INTRODUCTION

1.1 General

The successful growth of SiO_2 forms the basis in the fabrication of silicon integrated circuits. SiO_2 finds application in low packing density devices, large scale integrated circuits (LSI), very large scale integrated circuits (VLSI) and ultra large scale integrated circuits (ULSI). SiO_2 performs nearly all the requirements of passivation layers and a dielectric film for multilevel metalization [7].

In the manufacture of electronic components, especially solid state devices, a wide variety of physical and chemical processes are employed. Many of these processing steps serve the single function of forming a thin layer of a given material on a suitable substrate. This layer may play an active or passive role in the operation of the component, or alternatively, it may be employed only for processing purposes and may not be present in the complete device.[54]

Materials already in use as deposited thin films for electronic devices exhibit a tremendous range of physical phenomena. They may be superconductors, conductors, semiconductors or insulators composed of elements, compounds, or mixtures [14]. Some can be deposited by any of the several methods; others can be handled only by a single technique.

Because of the importance of these thin film materials, the electronic industry has invested heavily in the development of new deposition technology. Chemical vapor

deposition (CVD) is one of the most versatile of the deposition techniques employed in the electronics industry. In CVD, a gaseous chemical compound, or a mixture of compounds, reacts at a heated surface to form non-volatile coating on that surface. By a suitable choice of chemical reagents, it is possible to deposit an extraordinary variety of film materials on a wide range of substrates, often at rate higher than obtainable by other deposition methods such as vacuum evaporation, or sputtering. Until recently, most CVD operations were relatively simple and could be readily optimized experimentally by changing the reaction, the activation method or deposition variables until a satisfactory deposit was achieved. It is still possible and, indeed, in some cases it is the most efficient way to proceed. However, many of the CVD processes are becoming increasingly complicated with many more variables which could make the empirical method very cumbersome[28].

CVD is a very versatile and dynamic technology which is constantly expanding and improving as witnessed by the recent developments in Metal Organic CVD, plasma CVD, laser CVD and many others. As the technology is expanding, so is the scope of its applications. This expansion is the direct result of a large research effort carried out by many workers in the industry, the universities and government laboratories. Two major areas of application of CVD have rapidly developed, namely in the semiconductor industry and in the so-called metallurgical coating industry. CVD applications can be classified by product functions such as electrical, opto-electrical, optical, mechanical and chemical. CVD applications can also be classified by product form such as coatings, powders, fibers, monoliths and composites [54].CVD processes are often selected over competing deposition techniques because they offer the following advantages:[7]

1) High purity deposits can be achieved;

2) A great variety of chemical compositions can be deposited;

3) Some films cannot be deposited with adequate film properties by any other method;

4) Good economy and process control are possible for many films.

With CVD , it is almost possible to produce any metal and non-metallic element. This technology is now an essential factor in many optical and opto-electronic applications. An integrated-optic biosensor could monitor the concentration of liquid pollutants on the surface of a planar substrate comprising single-mode channel waveguides [50]. A silica based Mach Zehnder interferometer structure on silicon could be used to measure thickness or refractive changes on the wave guide surface. The fabrication of a channel waveguide device which integrates the splitting and combining portion of the interferometer on a glass substrate requires the fabrication of an optical waveguide. Thus, it more closely satisfies the definition of an integrated optic device.

Silicon films containing small amounts of phosphorus could be used to build the optical fiber for the integrated device since the difference between its refractive index and that of silicon dioxide is large enough for total internal reflection. Low Pressure Chemical Vapor Deposition of silicon dioxide is based on the reaction of an organic precursor, Diethylsilane (DES) and oxygen. The silicon dioxide thus deposited forms the cladding for the optic fiber. By a suitable injection technique, trimethylphosphite (TMP) can be injected into the reaction chamber to obtain the required amount of phosphorus in the phosphosilicate glass.[54]

1.2 Objective of the Thesis

A technology to develop the optic fiber with a very small difference in refractive index between the core and the cladding was the chief goal of this project. This work is focused on producing silicon dioxide films using diethylsilane (DES) and oxygen as precursors. The effects of deposition parameters on the growth rate and physical properties of the CVD SiO_2 films were investigated.

1.3 Silicon Dioxide Films

Chemical Vapor Deposited silicon dioxide films, and their binary and ternary alloys find wide use in VLSI processing. These materials are used as insulation between polysilicon and metal layers in multilevel metal systems, as getters, as diffusion sources, as diffusion and implantation masks, as capping layers to prevent outdiffusion, and as final passivation layers.

In general, the deposited oxide films must exhibit uniform thickness and composition, low particulate and chemical contamination, good adhesion to the substrate, low stress to prevent cracking, good integrity for high dielectric breakdown, conformal step coverage for multilayer systems, low pinhole density, and high throughput for manufacturing. Some of the properties obtained for thermal oxide are shown below.

Table 1.1: Properties of silica glass (Thermal Oxide) [51,52]

Boiling Point(°C)	~2950
Melting Point (°C)	~1700
Molecular Weight	60.08
Refractive Index	1.46
Specific Heat (J/g°C)	1.0
Stress in film on Si (dyne/cm^3)	2-4 x 10^9, compressive
Thermal Conductivity(W/cm°C)	0.014
Dc Resistivity (Ω-cm), 25°C	10^{14}-10^{16}
Density (gm/cm^3)	2.27
Dielectric constant	3.8-3.9
Dielectric Strength (V/cm)	5-10x10^6
Energy Gap (eV)	~8
Etch rate in buffered HF (Å/min)	1000
Linear Expansion Coefficient (cm/cm°C)	5x10^{-7}

In general, the deposited oxide films must exhibit uniform thickness and composition, low particulate and chemical contamination, good adhesion to the substrate, low stress to prevent cracking, good integrity for high dielectric breakdown, conformal step coverage for multilayer systems, low pinhole density, and high throughput for manufacturing. Some of the properties obtained for thermal oxide are shown above.

CVD silicon dioxide is an amorphous structure of SiO_4 tetrahedra with an empirical formula SiO_2. Depending on deposition conditions, CVD silicon dioxide may

have a lower density and slightly different stoichiometry from thermal silicon dioxide, causing changes in mechanical and electrical film properties (such as index of refraction, etch rate, stress, dielectric constant and high electric field breakdown strength). Deposition at higher temperatures, or use of a separate high temperature post-deposition anneal step (referred to as densification) can make the CVD films approach those of thermal oxide. [54]

Deviation of the CVD silicon dioxide film's refractive index, n, from that of the thermal SiO_2 value of 1.46 is often used as an indicator of film quality. A value of n greater than 1.46 indicates a silicon rich film, while smaller values indicate a low density, porous film. CVD SiO_2 is deposited with and without dopants, and each has unique properties and applications.[6]

Silicon dioxide was deposited using an organic precursor, diethylsilane (DES), and oxygen. DES, a colorless liquid with a boiling point of 56°C, has a chemical formula of $(C_2H_5)_2SiH_2$ and is a safe alternate precursor to SiH_4 with a flash point of -20°C (closed cup) [51],[52].

CHAPTER 2

REVIEW OF LITERATURE OF SiO_2 FILMS

2.1 Introduction

In this chapter, a review of deposition techniques of silicon dioxide films will be discussed. A brief review of the optical characteristics and the aim and scope of this work will be discussed.

2.2 Deposition Techniques

There are various reactions that can be used to prepare CVD SiO_2. The reason for its promising applications lies in its versatility for depositing a very large materials at very low temperatures [1]. The choice of the reaction is dependent on the temperature requirements of the system, as well as the equipment available for the process. The deposition variables that are important for CVD SiO_2 include temperature, pressure, reactant concentrations and their ratios, presence of dopant gases, system configuration, total gas flow, and wafer spacing. There are three temperature ranges in which SiO_2 is formed by CVD, each with is own chemical reaction and reactor configurations. These are :

1) low temperature deposition (300-450°C);

2) medium temperature deposition (650-750°C);

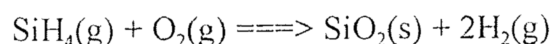
3) high temperature deposition (~900°C).

Table 2.1: Various techniques of CVD of silicon dioxide

Technique	Reactants	Remarks	References
APCVD	SiH_4, O_2	Deposition temp.: 450°C, atmospheric pressure. Phosphorus doping by adding PH_3.	30
PECVD	SiH_2Cl_2, N_2O	Deposition temp.: 200-350°C, $N_2O:SiCl_2H_2$ = 15:1 to 30:1.	30
PECVD	TEOS, O_2/N_2O	Deposition temp.: 400°C	22,23,24,25,26,27
LPCVD	$SiH_2(C_2H_5)_2$,(Diethylsilane), O_2	Deposition temp.: 475°C, 500 mTorr pressure	31
LPCVD	TEOS, N_2O	Medium temperature range 650-800°C	43
LPCVD	SiH_2Cl_2, N_2O	High temperatures (near 900°C), 500 mTorr pressure	42

Although excellent uniformity films and properties close to thermally grown oxide can be obtained by the reaction of dichlorosilane and nitrous oxide at 900°C [2,3], the high temperature probihits the application of such approaches for deposition over aluminum-based conductors.

In the lower temperature range most of the early processes were based on the silane chemistry:



$$SiH_4(g) + O_2(g) ===> SiO_2(s) + 2H_2(g)$$

The addition of PH_3 to the gas flow forms P_2O_5, which is incorporated in the SiO_2 film to produce a phospho silicate glass (PSG). The deposition can proceed in atmospheric pressure (APCVD) reactors [4-6], low pressure CVD (LPCVD) reactors [7-21], or plasma-enhanced CVD (PECVD)[22-29]. Table 2.1 shows CVD SiO_2 obtained by different techniques and using different precursors.

Various organosilicates have been used as chemical precursors in place of silane not only for generating good quality SiO_2 films and optimizing the deposition conditions, but also for safety purposes because silane is a toxic, pyrophoric and potentially explosive gas. Some of these precursors are listed in table 2.2.

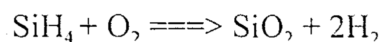
Table 2.2: New precursors for CVD silicon dioxide

Name	Formula	References
Tetraethoxysilane (TEOS)	$Si(OC_2H_5)_4$	7-10, 14, 15, 22-27, 32
Ethyltriethoxysilane(ETOS)	$C_2H_5Si(OC_2H_5)_3$	10-13, 16
Amyltriethoxysilane	$C_5H_{11}Si(OC_2H_5)_3$	10, 11
Vinyltriethoxysilane	$CH_2=CHSi(OC_2H_5)_3$	10, 11
Phenyldiethoxysilane	$C_6H_5Si(OC_2H_5)_3$	10, 11
Tetrapropoxysilane	$Si(OC_3H_7)_4$	13
Tetramethyicyclotetrasilane (TMCTS)	$Si_4(CH_3)_8$	20,21

Most of the work has been done with TEOS, using both LPCVD and PECVD techniques. Optimum deposition conditions and their effects on the deposit properties have been studied in detail. A rough kinetic mechanism has been proposed based on the experimental results [33].

Diethylsilane (DES), the precursor used in previous studies, has a vapor pressure as high as 200m Torr at room temperature (25°C). DES as a suitable chemical source for CVD SiO_2 film using LPCVD technique, has been studied earlier [12,13, 16-20, 28, 29]. These studies show conformal films below 400°C, further ensured by others [12-20]. The deposition rate as a function of temperature was found to follow an Arrhenius behavior between 375-475°C yielding an apparent activation energy of 10 Kcal/mol [16]. A few experiments were carried out with DES as the Si source. Using DES as a precursor, experiments have been carried out at medium to high temperatures between 550-800°C and varying gas flow ratios. Better results in terms of stress, uniformity, optical transmission and refractive index for the film to be used in the fabrication of Mach Zehnder interferometer have been obtained.

For the SiH_4 and O_2 reaction, the overall reaction can be summarized as [41]



$$SiH_4 + O_2 ===> SiO_2 + 2H_2$$

The reaction between silane and excess oxygen forms SiO_2 by heterogenous surface reaction. Homogenous gas-phase nucleation also occurs, leading to small SiO_2 particles that form a white powder on the reaction chamber walls which may potentially cause particulate contamination.

2.3 Properties and Applications

Thin films for use in VLSI fabrication must satisfy a large set of rigorous chemical, structural and electrical requirements. Deposited dielectric films should be conformal for

a number of reasons. Most important reason is that the films should maintain the integrity over side walls of the underlying topography so that subsequent film depositions and patterning of conductors can be easier. Step coverage gets worse with increasing aspect ratio (height/width) which can lead to the formation of voids[55]. The step coverage can be improved by flowing the dielectrics at temperatures higher than 900°C. SiO_2 has a flow temperature of about 1200°C, while the addition of impurities such as boron and phosphorous allows the flow temperature to be reduced[55]. It is important to keep the stresses in dielectric films to a minimum. High tensile stresses cause cracking of films and on the other hand, compressive stresses can generate tensile stresses in the underlying substrate and cause slipping. Stress present in deposited films are determined by the intrinsic stress of the film, and a component caused by the difference in thermal expansion coefficients of the film and the substrate[56],[57]. The intrinsic stress depends on the deposition techniques and the process parameters. APCVD oxide films tend to have tensile stresses, whereas LPCVD films are compressive[55]. PECVD oxides have compressive stresses, and the stress is a function of applied radio frequency, pressure, etc. Stress becomes more compressive as the pressure is reduced[55]. The deposited films should be uniform because a single wafer can produce many number of optical sensors and they should have similar properties. Uniform thickness leads to uniform refractive index. Also the films should be transparent in order for the light to pass through the waveguide of the sensor. In general, the deposited oxide films must exhibit uniform thickness and composition, low particulate and chemical contamination, good adhesion to the substrate, low stress to prevent cracking, good integrity for high dielectric breakdown,

conformal step coverage for multilayer systems, low pinhole density, and high throughput for manufacturing.

Table 2.3: Properties of silicon dioxide deposited by different methods.

FILM TYPE	THERMAL	PECVD	APCVD	$SiCl_2H_2 + N_2$	TEOS
Deposition Temp(°C)	800-1200	200	450	900	700
Step Coverage	conformal	good	poor	conformal	conformal
Stress (x 10^9 dynes/cm^2)	3C	3C-3T	3T	3T	1C
Dielectric Strength (10^6 V/cm)	3-6	8	10	10	
Etch Rate (Å/min); (100:1, H_2O:HF)		400	60	30	30

Properties of silicon dioxide [44] deposited by different methods are shown in table 2.3. Doping of SiO_2 can produce a variety of desirable film properties for some applications. Due to its poor interface qualities, CVD SiO_2 is a temporary structure if it is used in contact with single crystal silicon (e.g. as a capping layer over doped regions to prevent outdiffusion during thermal processes or as an ion-implantation mask). Its chief use, however, is a permanent structure, whose function is to increase the thickness of the field oxides, or to provide isolation between conductors. When the underlying conductor is able to withstand high temperature, one of the CVD methods may be employed due to their excellent uniformity, excellent step coverage, low particulate contamination, and high purity. The use of SiO_2 to mask against the diffusion of the common dopants is the cornerstone of planar technology. Devices are formed by etching windows in selected

areas of the SiO_2 grown on the silicon. Junctions are then formed by diffusing or ion-implanting impurities into these selected regions.

2.4 Silica-Based Single Mode Waveguides on Silicon

Low loss silica based single-mode waveguides and directional couplers have been fabricated on silicon substrates [50,51]. Silica based single-mode waveguides have a low propagation loss and an extremely low fiber coupling loss. Silica based single-mode wave guides can also be used for active optical devices such as optical switches, using temperature dependence of refractive index. Single mode channel waveguides were made from P-doped SiO_2 core layers [52]. The waveguides consisted of a 10-μm thick SiO_2 base layer by oxidizing the Si substrate in high pressure steam. A 2 μm thick phosphosiliicate glass (8 wt %) deposited using silane, oxygen and phosphene at temperature of 450°C was used a core layer. A 3 μm thick top layer of SiO_2 with 4 wt% P was deposited using tetraethylorthosilicate, oxygen and phosphene. The resulting difference in refractive index was made use of for the Mach Zehnder interferometer. The same principle was employed in building our proposed integrated optical device.

In our experiments, the thick oxide was deposited by chemical vapor deposition using diethylsilane and oxygen at a constant pressure, varying temperature and gas flow ratios.

CHAPTER 3

THIN FILM DEPOSITION TECHNIQUES

3.1 Introduction

Thin film technology has vastly improved in the modern era. Thin films are used in a host of different applications in VLSI fabrication, and can be prepared using a variety of techniques. Regardless of the type of the method by which they are formed, the process must be economical, and the resultant film must exhibit the following characteristics:[7]

1) good thickness uniformity;

2) high purity and density;

3) controlled composition and stoichiometries;

4) high degree of structural perfection;

5) good electrical properties;

6) excellent adhesion;

7) good step coverage.

For integrated optical sensors, following additional properties are required:

8) High transmission;

9) Low light scattering;

10) Good control of index of refraction.

Thin film fabrication is a complicated process which involves many controlled processing parameters. The time of processing, equipment cost, throughput and quality of films are important factors for a successful commercial production. Many techniques are available in the present technologies for film fabrication [7]. But, most common methods that are used for economical production are physical vapor deposition (PVD) and chemical vapor deposition (CVD). This chapter describes these two methods in detail.

3.2 Physical Vapor Deposition (PVD)

In this method, thin film material in gaseous form is allowed to deposit on the substrate directly. No chemical reaction is involved in this method. All the PVD process proceed according to the following sequence of steps [27]:

1. The material to be deposited (solid or liquid source) is physically converted into a vapor phase;
2. The vapor is transported across a region of reduced pressure (from source to substrate);
3. The vapor condenses on the substrate to form a thin film.

Depending upon the method of converting the deposition material to vapor phase, PVD is classified as: PVD by sputtering and PVD by evaporation.

3.2.1 PVD by Sputtering

Sputtering is a term used to describe the mechanism in which atoms are dislodged from the surface of a material by collision with high energy particles. Here, ions are generated and directed at a target, the ions sputter target atoms; the ejected (sputtered) atoms are transported to the substrate where they condense and form a thin film. The advantages of this method are [6]:

(i) Sputtering can be accomplished from large-area targets;

(ii) film thickness and its quality, like step coverage, grain structure can be controlled easily.

But, this method suffers from drawbacks such as:

(i) high equipment cost;

(ii) low deposition rate for some materials;

(iii) impurity incorporation in the film due to deposition in low-medium vacuum conditions;

(iv) inability of some materials to withstand ion bombardment resulting in degradation.

3.2.2 PVD by Evaporation

Thin films can be deposited by applying heat to the source of film material, thereby causing evaporation. If the heated source resides in a high-vacuum environment, the vaporized atoms or molecules are likely to strike the substrates (or chamber walls) without suffering any intervening collisions with other gas molecules. The advantages of this method are [12]:

(i) high deposition rate;

(ii) no substrate surface damage as the energy of the impinging atom is less;

(iii) high purity films can be achieved due to the deposition occurring in high vacuum.

The disadvantages are:

(i) accurately controlled alloy compositions are more difficult to achieve;

(ii) *in situ* cleaning of the substrate surface is not possible;

(iii) x-ray damage, caused by e-beam evaporation processes in sputter deposition, is avoided in this method.

3.3 Chemical Vapor Deposition (CVD)

CVD is a process where one or more gaseous species react on solid surface, forming a solid phase material as one of the reaction products, the others being mostly in gaseous form. The reactant gases are introduced into the reaction chamber and are decomposed and reacted at a heated surface to form the thin film. The solid product may form a film

or massive bulk on the substrate which enhances the reaction but does not undergo any chemical change. Many parameters like deposition temperature, pressure, flow rate, reactor geometry determine the nature and quality of the deposit thus produced [7].

Chemical and physical conditions during the deposition reaction can strongly affect the composition and structure of the product. This deposition technology has become one of the most important means of creating thin films and coatings in solid state microelectronics where some of the most sophisticated purity and composition requirements must be met [8].

Chemical reaction types basic to CVD include pyrolysis, oxidation, reduction, hydrolysis, nitride and carbide formation, synthesis reactions and chemical transport. A sequence of several reaction types may be involved to create a particular end product. The chemical reactions may take place not only on the substrate surface (heterogeneous reaction), but also in the gas phase (homogeneous reaction) [17]. Heterogeneous reactions are much more desirable, as such reactions selectively occur only on the heated surfaces, and produce good quality films. Homogeneous reactions, on the other hand are undesirable, as they form gas phase clusters of the depositing material, which will result in poor adherence, low density or defects in the film. Thus one important characteristic of CVD application is the degree to which heterogeneous reactions are favored over homogeneous reactions [34]. This film could be a thin film or a thick coating and should be less volatile to remain on the substrate.

3.3.1 Transport Phenomena of CVD

CVD of the film is almost always a heterogeneous reaction. The sequence of the steps in the usual heterogeneous processes can be described as follows [53]:

1. Arrival of the reactants

   a. bulk transport of reactants into the chamber,

   b. gaseous diffusion of reactants to the substrate surface,

   c. adsorption of reactants onto the substrate surface.

2. Surface chemistry

   a. surface diffusion of reactants,

   b. surface reaction.

3. Removal of by-products

   a. desorption of by-products from the substrate surface,

   b. gaseous diffusion of by-products away from the substrate surface,

   c. bulk transport of by-products out of the reaction chamber.

The steps are sequential and the slowest process is the rate determining step. The sequential steps of deposition process can be grouped into:

(i) mass transport-limited regime;

(ii) surface-reaction-limited regime.

If the deposition process is limited by the mass transfer, the transport process occurred by the gas-phase diffusion is proportional to the diffusivity of the gas and the concentration gradient. The mass transport process which limits the growth rate is only weakly dependent on temperature. On the other hand, it is very important that the same concentration of reactants be present in the bulk gas regions adjacent to all locations of a

wafer, as the arrival rate is directly proportional to the concentration in the bulk gas. Thus, to ensure films of uniform thickness, reactors which are operated in the mass-transport-limited regime must be designed so that all locations of wafer surfaces and all wafers in a run are supplied with an equal flux of reactant species.

If the deposition process is limited by the surface reaction, the growth rate, R, of the film deposited can be expressed as $R = R_o * \exp(-E_a/kT)$, where R_o is the frequency factor, E_a is the activation energy - usually 25-100 Kcal/mole for surface process, k is the Boltzmann's constant, and T, the absolute temperature. In the operating regime, the deposition rate is a strong function of the temperature and an excellent temperature control is required to achieve the film thickness uniformity that is necessary for controllable integrated circuit fabrication.

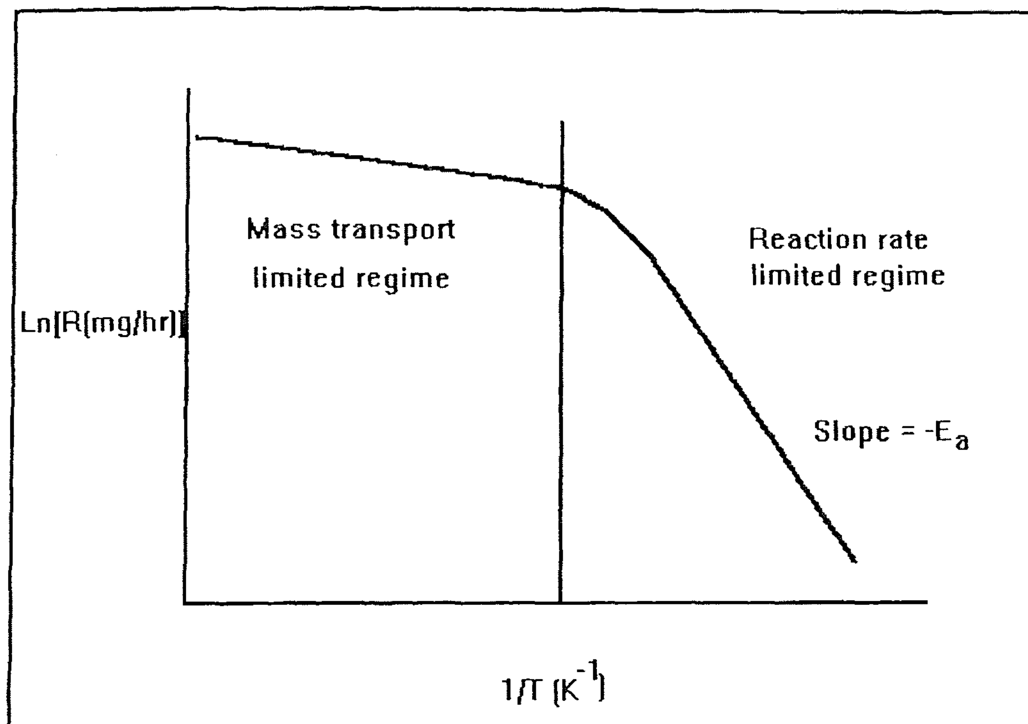


Figure 3.1: Deposition rate as a function of substrate temperature exemplifying diffusion controlled and surface-reaction controlled regimes

On the other hand, under such conditions the rate at which reactant species arrive at the surface is not as important. Thus, it is not as critical that the reactor be designed to supply an equal flux of reactants to all locations of the wafer surface. It will be seen that in horizontal low pressure CVD reactors, wafers can be stacked vertically and at very close spacing because such systems operate in a surface-reaction-rate limited regime. In deposition processes that are mass-transport limited, however, the temperature control is not nearly as critical. Figure 1.1 shows a relatively steep temperature dependence range and a milder temperature dependence range, indicating that the nature of the rate-controlling step changes with temperature[7].

3.3.2 Film Growth Aspects of CVD

In general, lower temperature and higher gas phase concentration favor formation of polycrystalline deposits. Under these conditions, the arrival rate at the surface is high, but the surface mobility of adsorbed atoms is low. Many nuclei of different orientation are formed, which upon coalescence result in a film consisting of many differently oriented grains. Further decrease in temperature and increase in supersaturation result in even more nuclei, and consequently in finer-grained films, eventually leading to the formation of amorphous films when crystallization is completely prevented. Amorphous films include oxides, nitrides, carbides and glasses are of great technical importance for microelectronics applications [10].

Deposition variables such as temperature, pressure, input concentrations, gas flow rates, reactor geometry and reactor opening principle determine the deposition rate and the properties of the film deposit.

3.4 Types of CVD Processes

Depending upon the type of energy that is applied for the reaction to occur, CVD processes can be classified as:

(i) Plasma enhanced CVD;

(ii) Photo induced CVD;

(iii) Thermally activated CVD [53].

3.4.1 Plasma Enhanced CVD

In this method, gaseous reactants are allowed in a region of glow discharge created between two electrodes by electric supply. Highly reactive species are created in this region resulting in interaction between these species thus forming a solid thin film product on the substrate and electrode surfaces [7].

Glow discharges are usually created at low pressures in the 0.01 to 1 Torr range. This causes breakdown of molecules into the reactive species like ions, electrons. Electric field due to ac, dc or microwave sources across two electrodes creates plasma region between the electrodes. The molecules themselves can be near the ambient temperature but the breakdown electrons will be at higher temperature causing the reaction. Thus, this method can be employed at relatively low temperature and it is useful for temperature sensitive materials [7].

Film deposition rates are substantially higher in this method than in thermally activated LPCVD. Also, conformal step coverage can be achieved. But the disadvantage of this method is the complex process that occurs in the plasma state making the synthesis of stoichiometric films difficult. The low deposition temperature of film formation results in gases trapped in the film, which frequently causes thermal instability due to outgassing. In a newly developed method, high density plasma is created using electron cyclotron resonance ion source. The main feature of this method is low deposition temperature that is needed for high growth rate.[53]

3.4.2 Photo Induced CVD

Short wavelength UV radiation is used to activate the reactants in gaseous phase forming the product material. A selective absorption of photonic energy by the reactant molecules or atoms initiates the process. Typically, mercury vapor is added to the reactant gas mixture as a photosensitizer and is activated by the radiation from a high intensity quartz mercury resonance lamp (253.7 nm wavelength).

The advantage of this method is low deposition temperature needed for films like SiO_2 and absence of radiation damage like the previous method. The limitation of this method is unavailability of effective production equipment [7], [42].

In another type, laser beams are used for activating the reactants. In pyrolysis type reaction, a highly localized heating of the substrate that induces film deposition by CVD surface reactions, and can be exploited for the direct writing patterns on a substrate. In evaporation method, the laser simply acts as an energy source to vaporize atoms from a

target to a substrate. In yet another type, the reactant atoms or molecules absorb a specific wavelength of the laser energy applied resulting in chemical gas phase reaction that are very specific, leading to highly pure film deposits. But these methods are still in developing stages.[53]

3.4.3 Thermally Activated CVD

This process uses direct thermal energy for the chemical reaction. The simplest type of this method is conventional atmospheric pressure CVD, where the reactant gases are allowed into the reaction chamber at normal atmospheric pressure. Energy is supplied by heating the substrate directly. The temperature and reactant flow rate determine the film growth rate. The advantage of APCVD is that it needs no vacuum pumps. The disadvantage is the tendency for homogenous gas phase nucleation that leads to particle contamination, unless special optimized gas injection techniques are used [7].

The deposition rate and uniformity of films created by all CVD processes are governed by the rate of mass transfer of reactant gases to the substrate and the rate of surface reaction of the reactant gases. In atmospheric CVD, these two rates are of the same magnitude. Lowering the gas pressure enhances the mass transfer rate relative to the surface reaction rate. This makes it possible to deposit films uniformly in a highly economical close spaced positioning of the substrate wafers kept vertically inside the chamber. Thus, LPCVD is a widely used in cost competitive semiconductor industry. Another advantage of this method is that gas phase nucleation is very much reduced. This is a suitable method for SiO_2 deposition [7].

Depending upon the supply of energy, CVD can be further classified as hot wall and cold wall reactor system. In hot wall reactor system, the reactor is heated to high temperature and the gas molecules hitting the wall receive the thermal energy. Here the wafers are not heated directly. The advantage of this system is that a temperature gradient can be provided to the chamber which results in uniform thickness. In the other type, the wafers are heated to high temperatures directly. The reactants that are adsorbed on the surface undergo chemical change due to the temperature of the wafer. But, controlling the wafer temperature is difficult and hence uniform deposition is also difficult [36].

3.5 Low Pressure CVD Process

The most important and widely used CVD processes are atmospheric pressure CVD (APCVD), low pressure CVD (LPCVD) and plasma enhanced CVD (PECVD). Only LPCVD is discussed in detail below as this process is employed in this study.

Most low pressure CVD processes are conducted by resistance heating and less frequently infrared radiation heating techniques to attain isothermal conditions so that the substrate and the reactor walls are of similar temperature. The deposition rate and uniformity of the films created by all CVD processes are governed by two basic parameters [29]:

(i) the rate of mass transfer of reactant gases to the substrate surface; and

(ii) the rate of surface reaction of the reactant gases at the substrate surface.

Lowering the pressure to below atmospheric pressure enhances the mass transfer rate relative to the surface reaction rate thus making it possible to deposit films uniformly in a highly economical close spaced positioning of the substrate wafers in the standup position.

3.5.1 Mechanism

The mass transfer of the gases involve their diffusion across a slowly moving boundary layer adjacent to the substrate surface. The thinner this boundary layer and the higher the gas diffusion rate, the greater is the mass transport that results. Surface reaction rates, on the other hand, depend mainly upon reactant concentration and deposition temperature. High deposition rates are attainable with LPCVD despite the fact that the operating total pressure is usually two to four orders of magnitude lower than atmospheric CVD. This is due to the fact that the large mole fraction of reactive gases in LPCVD, and no or little diluent gas is required. Wafer spacing has a marked effect on the deposition rate of all types of films, the deposition rate increasing linearly with increasing spacing since the quantity of available reactant per wafer increases [28].

3.5.2 Factors Affecting Film Uniformity

Some of the main factors affecting the film thickness uniformity in LPCVD are the temperature profile in the reactor, the pressure level in the reactor and the reactant gas flow rates. To obtain a flat thickness profile across each substrate wafer throughout the reactor requires a judicious adjustments of these parameters. In tubular reactors, increase in temperature or pressure, increases the deposition rate upstream, thereby using up more

reactant gases and leaving less to react at the downstream end; the opposite effect takes place on lowering the temperature and pressure. Similar effects occur with variations of the reactant gas flow rates at constant gas partial pressure, or with changes in the size and number of the wafers processed per deposition run. The uniformity of thickness and step coverage of these films are very good. These films have fewer defects, such as particulate contaminants and pinholes, because of their inherently cleaner hot wall operations and the vertical wafer positioning that minimize the formation and codeposition of homogeneously gas phase nucleated particulates [54].

Most of these chemical reactions are endothermic and of different types such as pyrolysis, decomposition, oxidation, reduction, chemical transport reaction, etc. The process should have the following sequential steps for completion [54]:

1) Mass transport of reactants to substrate

2) Adsorption of reactants on substrate surface

3) Chemical reaction on the surface

4) Desorption of the product gases from the surface

5) Mass transport of product gases away from substrate

CVD processing has several advantages over other methods of film deposition. These advantages make it one of the popular methods adapted commercially. These are listed below [25]:

1) Conformal step coverage can be achieved by this method. It is an important factor for the fabrication of electrical devices.

2) Stoichiometric control of the film can be easily achieved by adjusting the processing parameters like deposition temperature, flow rates, etc.

3) High thıoughput is possible, especially by LPCVD, due to reactor structure and enhanced mass transfer of the reactant.

4) The quality of the film can be easily reproduced by this method because the processing parameters can be repeated without difficulty.

5) Since the whole area of the substrate is equally exposed to the reactants, good uniformity of film thickness can be achieved.

6) Selective deposition of film onto the substrate can be done by masking unwanted portions of the substrate.

7) Unlike in PVD, there is no radiation like e-beam involved, therefore, there is no possibility of damage of substrate or the film, by this method.

8) CVD offers an excellent opportunity of impurity doping in device fabrication. This is possible by simply mixing the required dopant along with the reactants.

9) Low maintenance cost of the equipment makes it an attractive method for large scale production.

3.6 Summary

The common methods of film deposition, namely PVD and CVD, were described. Their classification, advantages and disadvantages were mentioned. The LPCVD was found to be suitable method due to its advantages over APCVD. Therefore, in this study, hot wall pressure chemical vapor deposition system was employed.

CHAPTER 4

EXPERIMENTAL SETUP AND CHARACTERIZATION TECHNIQUES

4.1 Introduction

Silicon dioxide films were synthesized in a LPCVD reactor altering various parameters like temperature, gas composition and time of deposition. Refractive index and thickness of the films were measured by using ellipsometry and interferometry respectively. The optical transmission of the films was measured using a UV/visible spectrophotometer.

4.2 LPCVD Reactor

The schematic for hot wall low pressure chemical vapor deposition reactor is shown in Fig 4.1. The reactor consists of fused quartz tube of 5 inches in diameter and about 50 inches in length. The tube is kept inside a Lindbergh three zone surface. The zone temperatures are controlled by manual settings. A maximum temperature of 1200°C can be reached using this furnace and a gradient of temperature can also be obtained inside the quartz tube. Heating is provided by Lindbergh silicon carbide heating elements. It is equipped with Plantinel II thermocouples which sense the temperature of the zone and the voltage developed which is used for automatic temperature control. The tube and the coils are surrounded with a ceramic enclosure. The tube is sealed on both the ends by end caps and metallic rings. During the heating process, thermal expansion of the O-rings may cause leakage in the system. To avoid this problem, water cooling is arranged by cold

water circulation. Apart from this, additional cooling is provided by fans. A MKS baraton gauge with a range of 10 Torr is used to monitor the pressure at the input end. The monitored pressure is displayed by the MKS display unit. The input seal consists of three provisions for gas inlet, so that if more than one precursor is used, they will mix together and diffuse inside.

The system is kept at low pressure by vacuum pumps. This system uses a booster pump and a mechanical backing pump. The Booster pump is used to enhance the flow of gases and thereby the pumping speed. Mechanical backup does the real pumping and the combination provides a vacuum as low as a milli Torr. The Booster pump is a *Ruvac* single stage roots pump operated at 220 V supply and the backing pump is a *Trivac* dual stage rotary vane pump. Nitrogen ballast gas is used in the pump to dilute any hazardous outgoing gas. An oil filtration system is also used to separate the micron size dust particles that are accumulated during the pumping process.

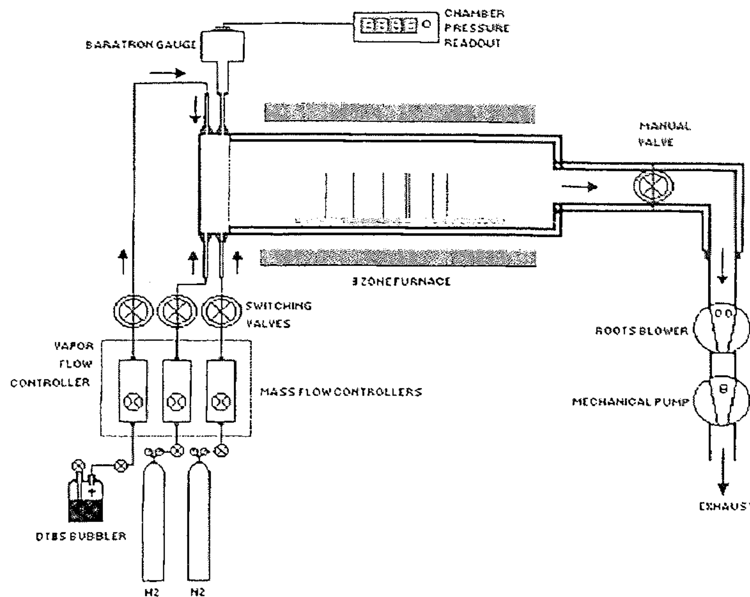


Figure 4.1: A schematic of the LPCVD reactor

Wafers are loaded inside the tube using a quartz carrier boat. Wafers are kept vertically in the slots provided in the boat. The boat is kept inside the quartz tube and the tube is sealed by the inlet lid. A manual control valve is provided at the output end to control the rate at which the gas is removed from the reactor. Precursors are allowed through a pneumatic control valve provided at the input end. Unloading of the wafers is done by bringing the reactor to atmospheric pressure. This is done by closing the valve and passing a controlled flow of nitrogen into the chamber.

4.3 Experimental Setup

4.3.1 Flow Rate Calibration

CVD reactors and other process systems require that the rates of introduction of the process gases into the process chambers be controlled. In some applications, this is achieved by adjusting the gas influx to maintain a constant chamber pressure. More commonly, the process gas flow is directly controlled. To do this, mass flow controllers are used. Mass flow controllers consist of a mass-flowmeter, a controller, and a valve. They are located between the gas source and the chamber, where they can monitor and dispense the gases at predetermined rates. The operation of a thermal mass flowmeter relies on the ability of a flowing gas to transfer heat. the mass flowmeter consists of a small sensor tube in parallel with the larger main gas flow tube. A heating coil is wrapped around the sensor tube midway along its length, and temperature sensors are located upstream and downstream of the heated point. When the gas is not flowing, and the heat input is constant, the temperatures at both sensors are equal. Flowing gas causes the temperature distribution to change. It can be shown that the mass flow, m_f, is given by:

$$m_f = (\kappa\ W_h\ \Delta T)^{1.25}$$

where W_h is the heater power, ΔT is the temperature difference between the points where the sensors are located, and κ is a constant that depends on the heat transfer coefficients, the specific heat of the gas, the density of the gas, and the thermal conductivity of the gas. Mass rate can be thus measured by the temperature difference.

Gas flows are controlled by Applied Materials model AFC 550 automatic N_2 mass flow controllers which are corrected for DES and O_2 flows. The pressure in the reactor is measured with a barratry gauge from MKS. The N_2 calibration of the AFC is checked by delivering a fixed volume of gas (product of the metered flow rate and time) into the known reaction chamber volume. The pressure increase is measured and used to calculate the volume of the gas corrected to the standard condition (0°C, 1 atm). According to the gas law, the flow rate corrected to STP (sccm) is given by the formula below:

$$\text{Flow Rate} = 60(\Delta P/\Delta t)(T_0 V/P_0 T)$$

where ΔP = pressure increase in Torr,

$T_0 = 273$ K

$P_0 = 760$ Torr

V = volume of the chamber, cm^3

Δt = time of delivering gas, sec.

Routine flow rate calibrations were conducted before every run.

4.4 Deposition Procedure

Wafers are loaded inside the tube using a quartz carrier boat. Wafers are kept vertically in the slots provided on the boat. The boat is kept inside the quartz tube and the tube is sealed by inlet lid. A manual control valve is provided at the output end to control the rate at which gas is removed from the reactor and therefore controls the pressure inside the

reactor. Precursor is allowed through a pneumatic control valve provided at the input end. Unloading of the wafer is done by bringing the reactor to atmospheric pressure. This is done by closing the output valve and passing a controlled flow of nitrogen into the chamber. Films deposited are on <100> oriented single sided polished wafers, and fused quartz wafers. Single side polished wafers are 10cm in diameter, 525 μm in thickness, labeled and weighed by electronic weighing balance. The wafers are placed at either 3 cm or 5 cm distance from each other. The boat is placed at a distance of 79 cm from the door.

After loading, the furnace is brought to low pressure by pumping down the chamber. The temperature is raised to the required level slowly in steps of about 250°C. The temperature is allowed to reach the set value in all the three zones before raising it further until the desired value is reached.

Once the required temperature is reached, the valves for oxygen flow are opened. When the flowmeter shows stabilized flow, the DES and TMP tanks are opened. The pressure is then set to the required value. Care must be taken not to let the organic precursors into the chamber before there is oxygen flow lest the films should have carbon in them. An oil filter is switched on for the safety of the pumps.

4.5 Characterization of Silicon Dioxide Films

4.5.1 Thickness

Film thickness is measured by Nanospec interferometer which bases its estimation on the monochromatic light interface fringes formed within a zone limited by sample surface

and a semi-transparent mirror. The device consists of Nanometrics Nanospec/AFT microarea gauge and SDP-2000T film thickness computer. The thickness of the film deposited on the wafer is measured at five different points. The refractive index provided is first estimated, as for silicon dioxide, 1.46 is the typical value. Thickness is measured at five different points on the wafer. Deposition rate is determined as the film thickness over the deposition time, and averaged over all the wafers in the run.

4.5.2 Refractive Index

The refractive index is determined by a Rudolph Research Auto EL ellipsometer, which consists of a polarizer and a compensator. Plane (45°) polarized light the polarizer is elliptically polarized when it passes through the compensator. It is then reflected by the sample surface, collected by a detector, analyzed for its intensity, and finally quantified by a set of delta psi values. The values are then fed to a computer which numerically solves an equation to give the refractive index of the film. The refractive index of the film deposited on the wafer is measured at five different points and then averaged out to the refractive index of the wafer.

4.5.3 Stress

The stress in the film is determined by a in-house developed device, employing laser beam equipment which measures change in radius of curvature of the wafer resulting from the film deposited on one side. Two fixed and parallel He-Ne laser beams are

incident on the wafer surface before and after deposition. The reflected beams from the two surfaces is then projected by an angled plane mirror as two points onto a scale in a certain distance, and thus, their separation can be measured more accurately. The change in separation of these two points is fed into Stony's Equation to obtain actual stress value. The calculation formula is:

$$\delta = 12.3\ D/T$$

where D = distance difference between two points before and after deposition (mm);

T = thickness of the films, (λm);

δ = stress of the film (Mpa), negative value indicates compressive stress

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Introduction

The results of silicon dioxide thin films synthesized on Si and quartz substrates at a constant pressure of 200mTorr, at different temperatures between 550°C and 850°C, and at different flow rates of DES and oxygen are presented in this chapter. Thick oxide (10μm thickness) film depositions were carried out to fabricate the buffer layer for the waveguide in the Mach Zehnder interferometer.

5.2 Silicon Dioxide Thin Films

Thin films of silicon dioxide were produced by carrying out deposition for shorter duration of time, the conditions remaining the same as used for thick films. Thin films are necessary as they provide useful data such as refractive index, stress, and also the growth rate. Refractive index data required that the films be lesser than 3000A thick due to the limitation of the ellipsometer which gives erratic results for films thicker than 3000A. It is necessary to measure stress at low deposition times because there are chances that the films might crack as they become thicker during longer runs .

5.2.1 Deposition Rate Analysis

One of the most important aspects of film growth is the rate of film growth with respect to the deposition temperature. Since a chemical reaction is involved in the formation of the film, the rate of the chemical reaction is a key factor for deposition rate. The rate of chemical reaction depends upon the deposition temperature if the reaction is endothermic. The purpose of this study is to evaluate the growth rate and characterize the silicon dioxide films deposited using diethylsilane. SiO_2 films were deposited at different temperatures from 550°C-700°C while the other parameters like pressure flow rate, deposition time and wafer spacing kept constant. Another study carried out between 700-800°C with pressure and wafer spacing constant, varied the flow rates of oxygen

The temperature dependence of the rate has been found to fit the expression proposed by Arrhenius:

$$\text{Growth Rate (G.R)} = A\exp(-E_a/RT)$$

where,

A is the pre-exponential factor (nearly independent of temperature);

E_a is the apparent activation energy of the chemical reactions;

R is the gas constant and is equal to 1.98717 cal $K^{-1}mol^{-1}$;

T is the absolute temperature of the reaction (K);

Taking natural logarithm (Ln) on both sides of the above equation, and plotting a graph of Ln growth rate versus reciprocal of temperature, leads to a straight line with a negative

slope. This type of curve is called Arrhenius plot. The negative slope of the curve gives the ratio between the activation energy and gas constant. By determining the slope of the curve, the activation energy for the reaction can be calculated. Figure 3.1 shows Ln of growth rate (in A per minute) plotted against the reciprocal of deposition temperature in Kelvin scale. The first set of experiments were carried out between temperatures of 550 and 700°C; DES flow rate of 50 sccm and O_2 flow rate of 100 sccm; pressure of 0.2 torr. In the case of oxygen/DES ratio of 2:1, the growth rate increased linearly with temperature as shown in fig5.1. With a oxygen/DES flow ratio of 10:1,the growth rate decreased with increase in temperature since the receding portion of the Arrhenius plot had been reached. Reducing the temperature below 700°C would yield the straight line portion of the plot. Since the films obtained at 775°C conformed to the films with properties necessary for the optical sensor fabrication, further film deposition at lower temperatures were not conducted. For the 2 to 1 flow ratio of oxygen and DES. The slope of the curve was found to be -5.33 giving an activation energy of 10.59Kcal/mol.The instrument used to measure the thickness of the films has an error which varies from ± 0.05% to 0.1%.

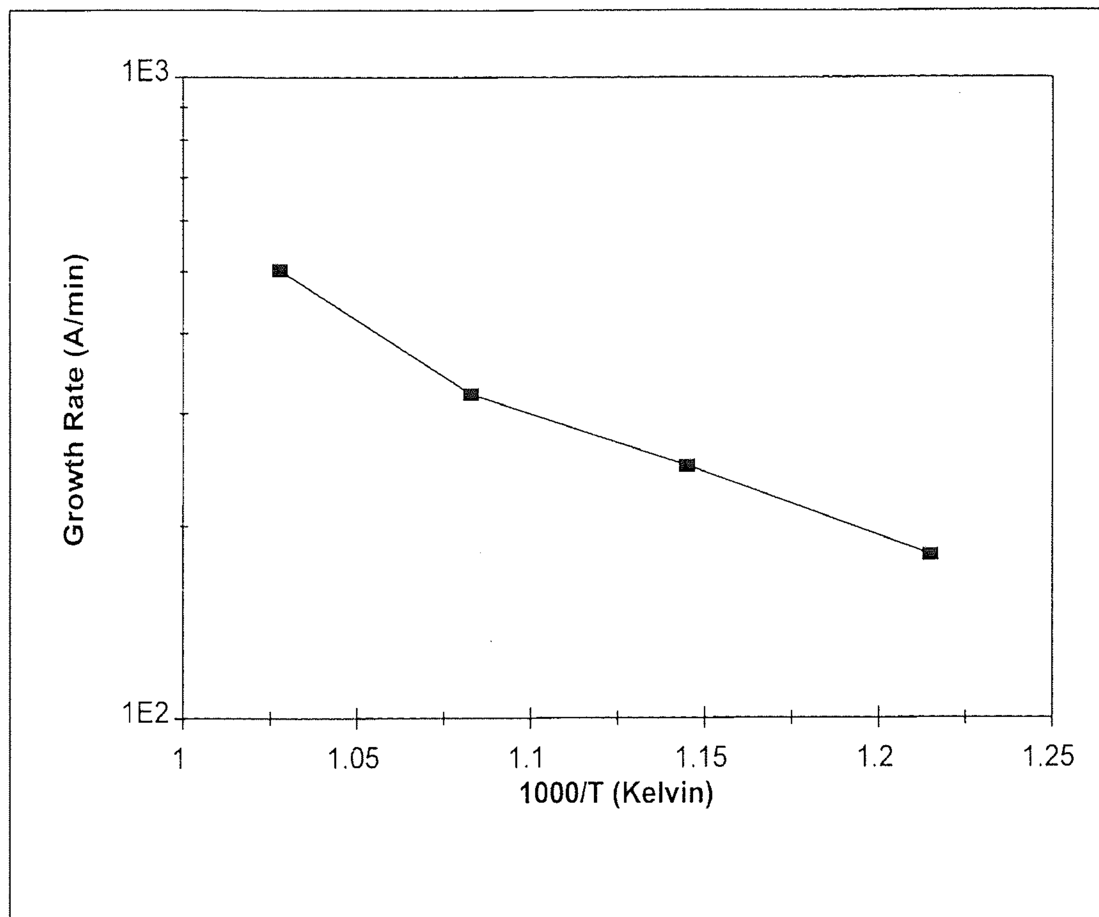


Figure 5.1: Growth rate as a function of Temperature at a O_2/DES flow ratio of 2:1

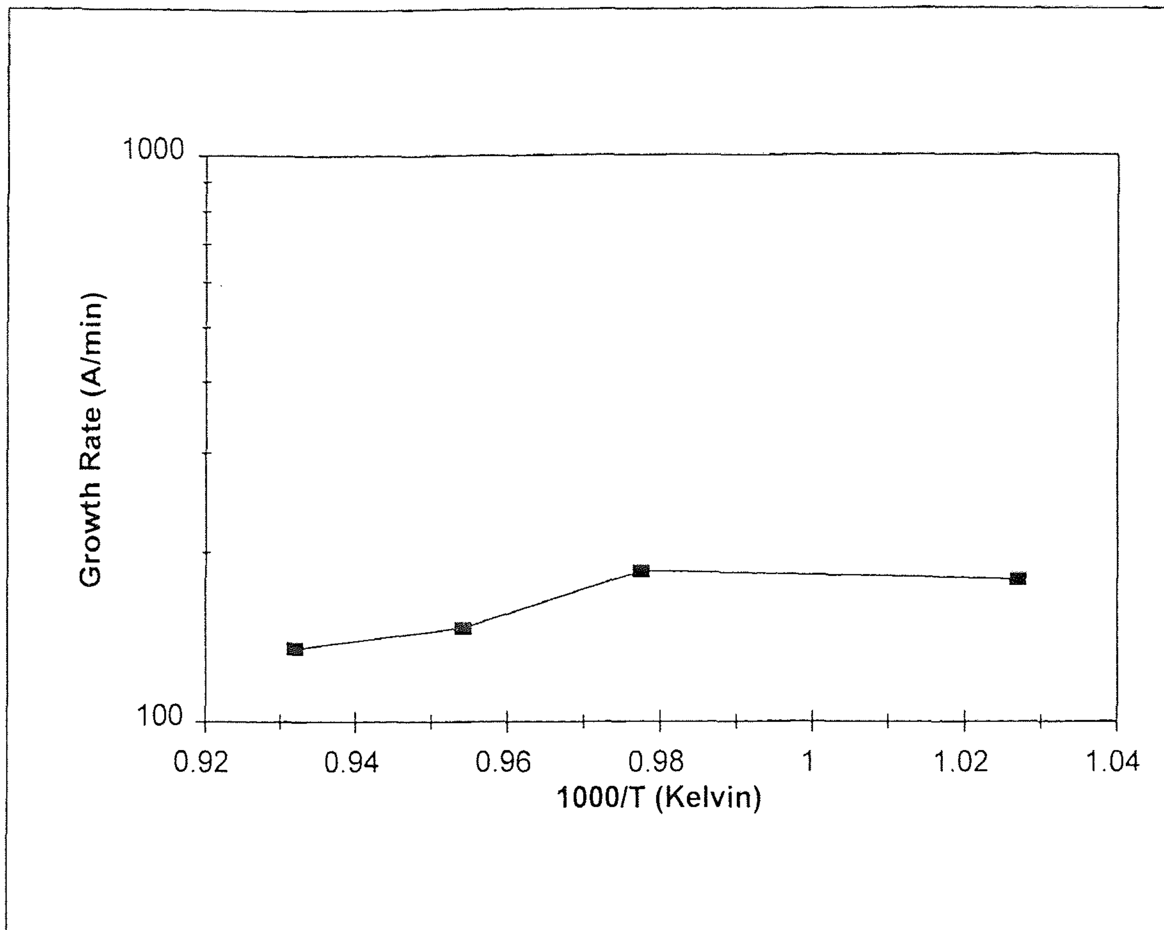


Figure 5.2: Growth rate as a function of Temperature at a O_2/DES flow ratio of 10:1

5.2.2 Refractive Index Analysis

Figure 5.4 shows the variation of refractive index as a function of various temperatures at flow ratios of oxygen to DES of 2 to 1 and 10 to 1 and at a fixed pressure. The refractive index of the deposits was determined by using a Rudolph Research Auto EL Ellipsometer at five different points which gives an indication of the uniformity of the film. The average was then taken for plotting.

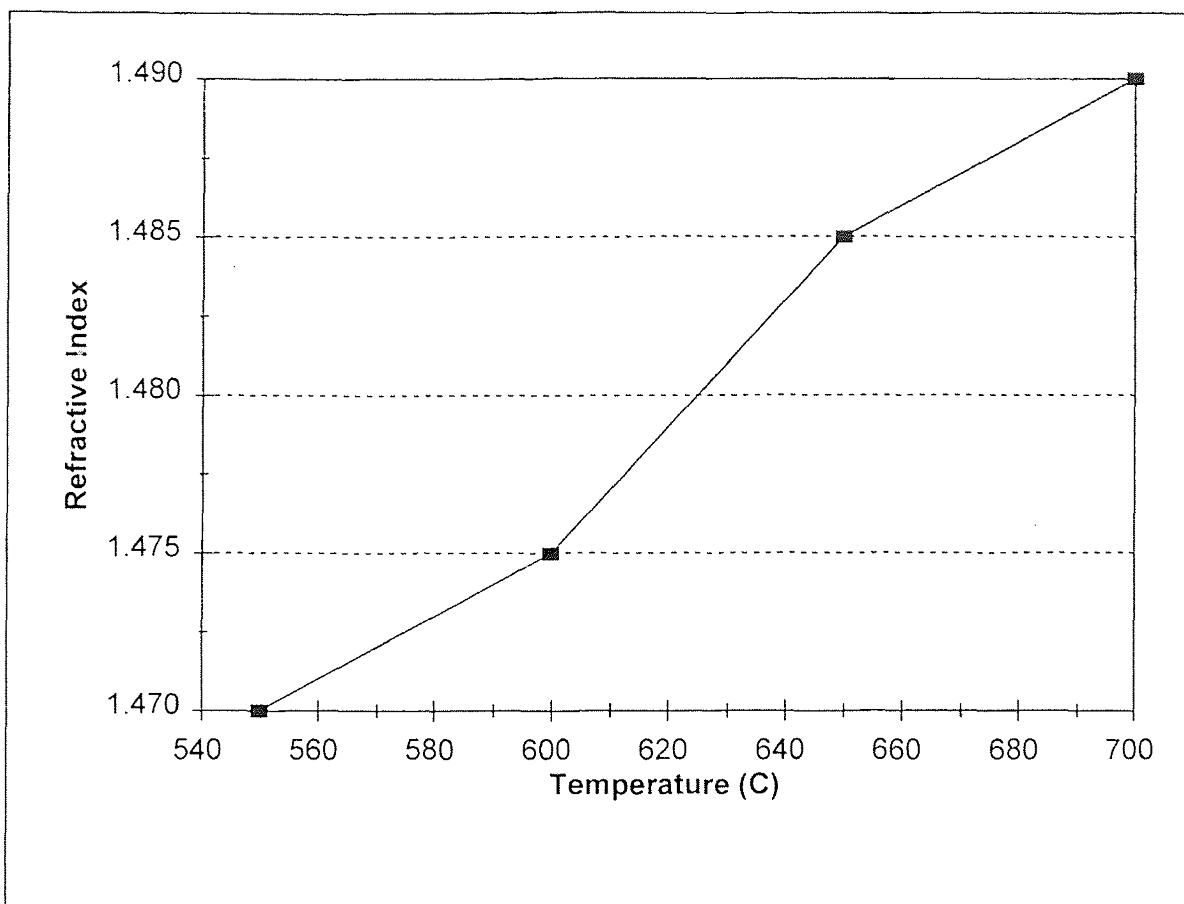


Figure 5.3: Variation of refractive index as a function of temperature for flow ratio of Oxygen to DES of 2:1

The refractive index for a flow ratio of 2:1 oxygen to DES increased with increase in temperature of deposition. It is suspected that at these higher temperatures a non stoichiometric silicon rich film was formed. At lower temperatures, comparison of the refractive index of the oxide with that of a thermal oxide shows that a stoichiometric oxide was formed. In the case of 10:1 oxygen to DES ratio, refractive index near 1.45 was obtained. But the refractive index data may not be accurate because the ellipsometer used also takes into account the thickness of the films. The error of the instrument varies from ±0.05% to 0.08% within a thickness of 3000A.

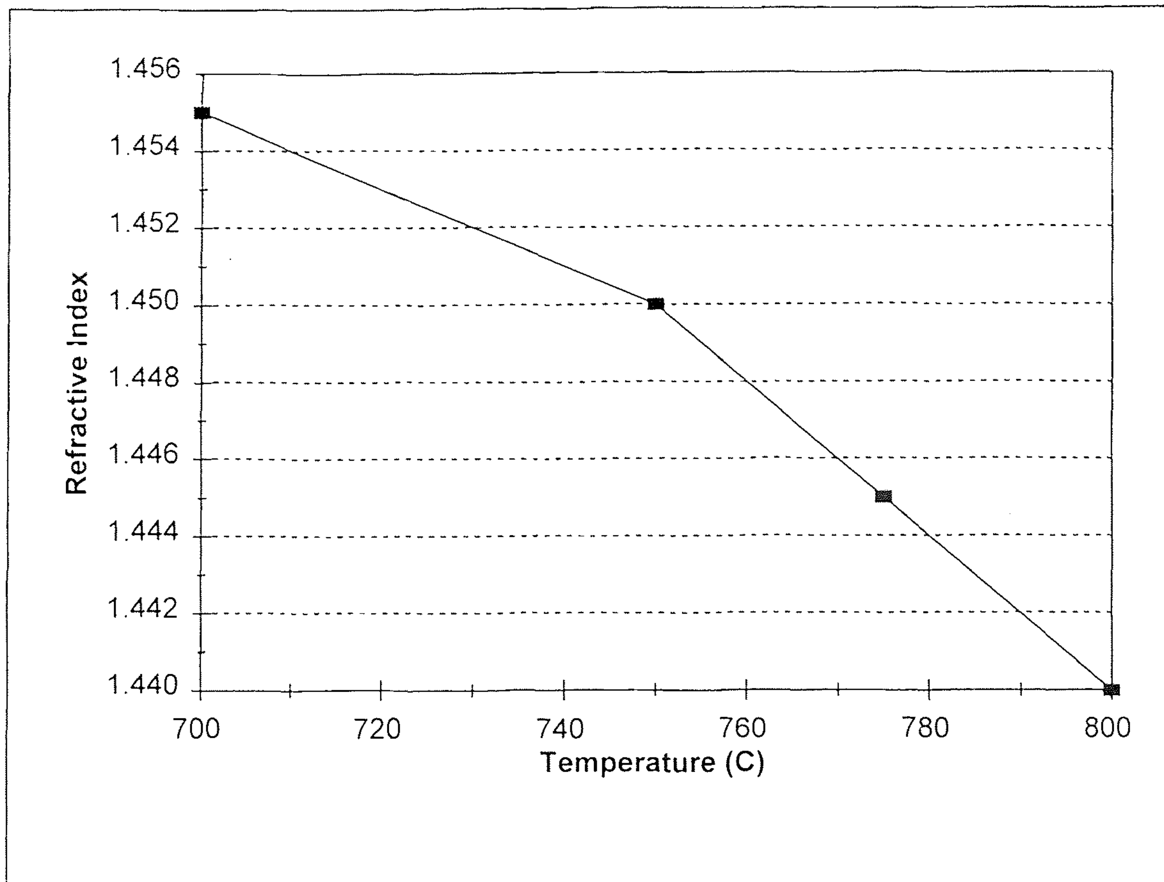


Figure 5.4: Variation of refractive index as a function of temperature for flow ratio of Oxygen to DES of 10:1

5.2.3 Stress Analysis

Stress was determined using a Laser Stress Analyser. Stress determined was plotted as a function of temperature as shown in figure 5.9. It was observed that the stress was highly tensile of the order of 70-90MPa in the case of 2:1 oxygen/DES flow ratio . Due to the high tensile stress, the films cracked for long runs, a serious problem in the deposition of thick films .

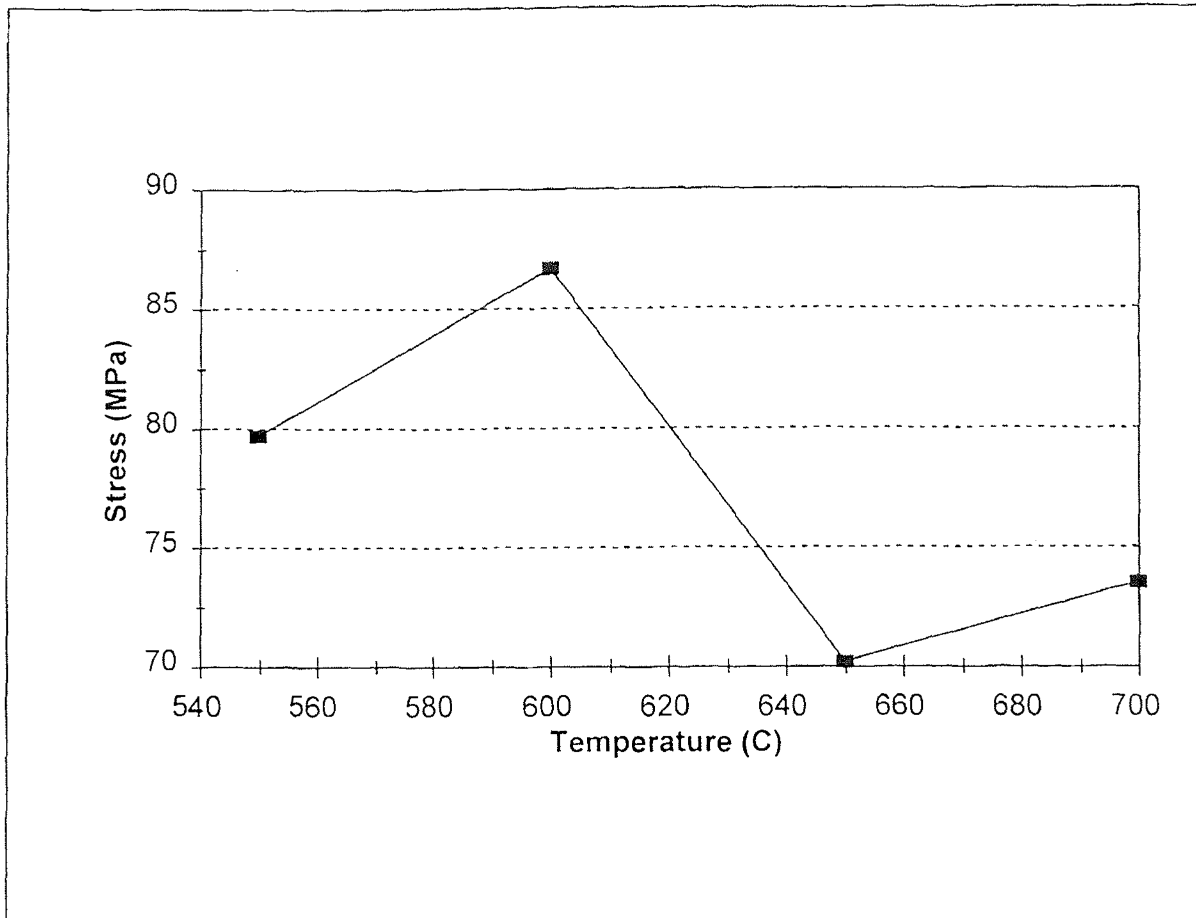


Figure 5.5: Stress as a function of temperature for flow ratio of oxygen to DES of 2:1

When the process was shifted to 10:1 oxygen to DES flow ratio, in the temperature range of 700-800°C, stress varied from low tensile at 700°C to low compressive at 800°C which is highly desirable in the synthesis of thick films. At 775°C, the stress was as low as 3.88MPa and was compressive. Hence this temperature has been chosen as ideal in the synthesis of thick silicon dioxide films at the oxygen to DES flow ratio of 10:1.It should be noted however that the error associated with the instrument varies from ±0.05% to 0.09%.

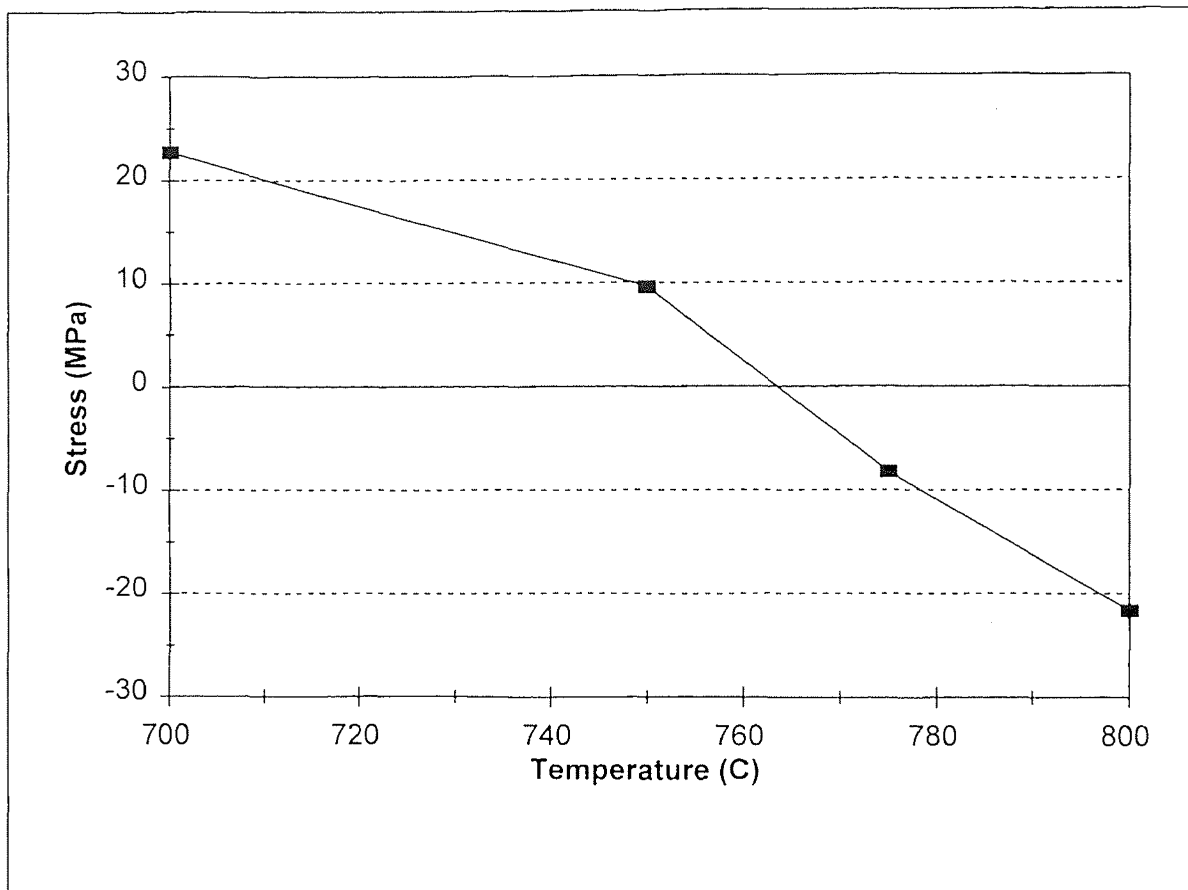


Figure 5.6: Stress as a function of temperature for flow ratio of oxygen to DES of 10:1

Table 5.1: Summary of results for CVD silicon dioxide thin films using DES and O_2

Deposition Temperature (°C)	Flow Ratio (O_2:DES)	Deposition Rate (Å/min)	Stress (Mpa)	Refractive Index
550	100:50	180	79.7	1.47
600	100:50	248.2	86.72	1.475
650	100:50	321	70.22	1.485
700	100:50	502	73.55	1.49
700	100:10	181	22.77	1.455
750	100:10	185	4.65	1.45
775	100:10	141	-3.88	1.445
800	100:10	135	-21.61	1.44

CHAPTER 6

CONCLUSIONS

Silicon dioxide films processed in this study were amorphous and uniform. The operating pressure was maintained at 200mTorr throughout. In the case of films deposited using oxygen to DES flow ratio of 2:1, the growth rate was observed to be as high as 500A/min which is necessary in the synthesis of thick films. The activation energy was found to be 10.59Kcal/mol, which is low and hence is desirable. However the stress was found to be very high (85MPa) and tensile which is not suitable for the synthesis of thick films. The oxide showed increasing refractive index with increasing deposition temperature and was probably carbon rich at these higher deposition temperatures. In the case of oxygen to DES flow ratio of 10:1, the growth rate was observed to be around 150A/min which is optimum. The stresses varied from low tensile at 700^0C to low compressive at 800°C. At 775°C, very low compressive stress of 3.88MPa has been observed. The refractive index has been found out to be near 1.45 which agrees with the expected values. The films have exhibited very high transmission as observed on the quartz substrate and by being transmissive to laser. So at 775°C, an operating pressure of 200mTorr and an oxygen to DES flow ratio of 10:1, SiO_2 films with superior physical and optical properties were obtained. At these conditions, the thick and thin silicon dioxide films are found to be suitable to be used as cladding and buffer layers respectively in the fabrication of Mach Zehnder interferometer.

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