ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF SILICON DIOXIDE THIN FILMS BY LOW PRESSURE CHEMICAL VAPOR DEPOSITION

by
Sutham Niyomwas

Ditertiarybutylsilane (DTBS) and oxygen have been used as precursors to produce silicon dioxide films by low pressure chemical vapor deposition. These films were synthesized in the temperature range of 600°C to 800°C at constant pressure, and at different gas flow composition. The films were found to be uniform with a composition that varied with deposition temperature and gas flow ratio. The growth rate was found to follow an Arrhenius behavior with an apparent activation energy of 2.62 kcal/mol. The growth rate was seen to increase with higher distance between wafers and to vary as a function of square root of the O_2 flow rate. The refractive index of the films were found to be 1.462 at deposition temperature 600°C and increased with higher temperature. The stresses were very low tensile in the films and tended to be compressive with increasing deposition temperature.

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A Thesis
Submitted to the faculty of
New Jersey Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of
Master of Science in Engineering Science

Interdisciplinary Program in Materials Science and Engineering

January 1997

APPROVAL PAGE

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This thesis is dedicated to
my beloved family

ACKNOWLEDGMENT

I would like to express my sincere acknowledgments to my advisor, Professor Roland A. Levy, for his guidance, encouragement, inspiration throughout this research. Special thanks to Professor Lev N. Krasnoperov and Professor Vladimir B. Zaitsev for serving as a member of the committee.

I appreciates the timely help and suggestions from the CVD laboratory members, including: Vitaly Sigal, Krit Aryusook, Wiriya Thongruang, Hui Wu, Chenna Ravindranath, Justin Barone, and Roumiana Petrova.

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CHAPTER 1

INTRODUCTION

1.1 SiO_2 Thin Film

Deposited silicon dioxide [SiO_2] films have been an essential factor in the manufacture of integrated circuits from the earliest day of the semiconductor industry. The major application has been as an interlayer dielectric between conducting layers, i.e., as an insulator between Al layers and between Al and polysilicon or silicide layers [1]. They have been usually used as a final passivation film that protects the circuit from mechanical and chemical attack and provides the desired reliability that however upon films synthesized at low temperature(<300°C). Initially, most such films were deposited in atmospheric pressure systems. In recent years, low pressure process have assumed greater importance [2]. The successful growth and application of SiO_2 cause the success of silicon integrated circuits, from low packing density devices, through 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, which contain [3].

Requirement for intermetal dielectric films

1) low dielectric constant to keep the capacitance between metal lines at a minimum;

2) high dielectric break down field strengths;
3) low moisture absorption;
4) low compressive stress;
5) good adhesion to aluminum;
6) capability of being easily dry or wet etched;
7) being permeable to hydrogen to remove interface sites;
8) good conformal step coverage.

Requirement for passivation layers

1) capability of providing scratch protection to circuit below;
2) zero permeability to moisture;
3) low compressive stress;
4) good conformal step coverage;
5) being easily patterned;
6) good adhesion to conductors and interlayer dielectric.

The principal physical properties of SiO_2 are given in Table 1.1 [4][5].

Table 1.1 Physical Properties of Silicon Dioxide(Amorphous State)

melting point	1728°C
boiling point	2950°C
thermal expansion	$0.5x10^{-6}$ K^{-1} (0-150°C)
thermal conductivity	0.12 W/cm.°C (0-150°C)
hardness	600 - 1000 kg/mm^2
resistivity	$1x10^{15}$ Ω-cm (at 20°C)
refractive index	1.4584 (5893 Å)
heat capacity	0.185 cal/g (100°C)
Si-O bond distance	1.62 Å
density	2.1975 g/cm^3 (0°C)
Mohr's hardness	7.7 GPa
Young's modulus	$10.5x10^6$ psi

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 tetrahedral 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.

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.

In this study, silicon dioxide was deposited using an organic precursor, ditertiarybutylsilane (DTBS), and oxygen. DTBS has a chemical formula of $SiH_2(C_4H_9)_2$ and is a safe alternate precursor to SiH_4 with a flash point of 15°C. It is a colorless liquid with a boiling point of 120°C, vapor pressure of 20.5 torr at 20°C, and is commercially available from Olin Hunt as CONSi-4000 with a 99%+ chemical purity. This work addresses the use of this organosilane precursor for synthesizing amorphous silicon dioxide films.

1.2 Chemical Vapor Deposition

Chemical vapor deposition (CVD) is the process of chemically reacting a volatile compound of a material to be deposited, with other gases, to produce a nonvolatile solid that deposits atomistically on a suitably placed substrate. A wide variety of thin film utilized in VLSI fabrication is prepared by CVD. These materials comprise dielectric, elemental and compound semiconductors, electrical conductors, superconductor and magnetic. In addition to its unique versatility, this materials synthesis and vapor phase growth method can operate efficiently at relatively low temperature.

1.2.1 Basic Aspects of CVD

Chemical vapor deposition is defined as a process whereby constituents of the gas or vapor phase react chemically near or on the substrate surface to form a solid product. This product can be in the form of a thin film, a thick coating, or if allowed to grow, a massive bulk. It can have a single-crystalline, poly-crystalline, or amorphous structure. 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 means of creating thin films and coatings in solid state microelectronics where some of the most sophisticated purity and composition requirements must be met.

Chemical reaction type 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). 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. This film could be a thin film or a thick coating and should be less volatile to remain on the substrate.

1.2.2 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:

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 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 and (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 $R = R_o{}^* \exp(-E_a/RT)$, where R_o is the frequency factor, E_a is the activation energy - usually 25-100 kcal/mole for surface process, R is the gas 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.

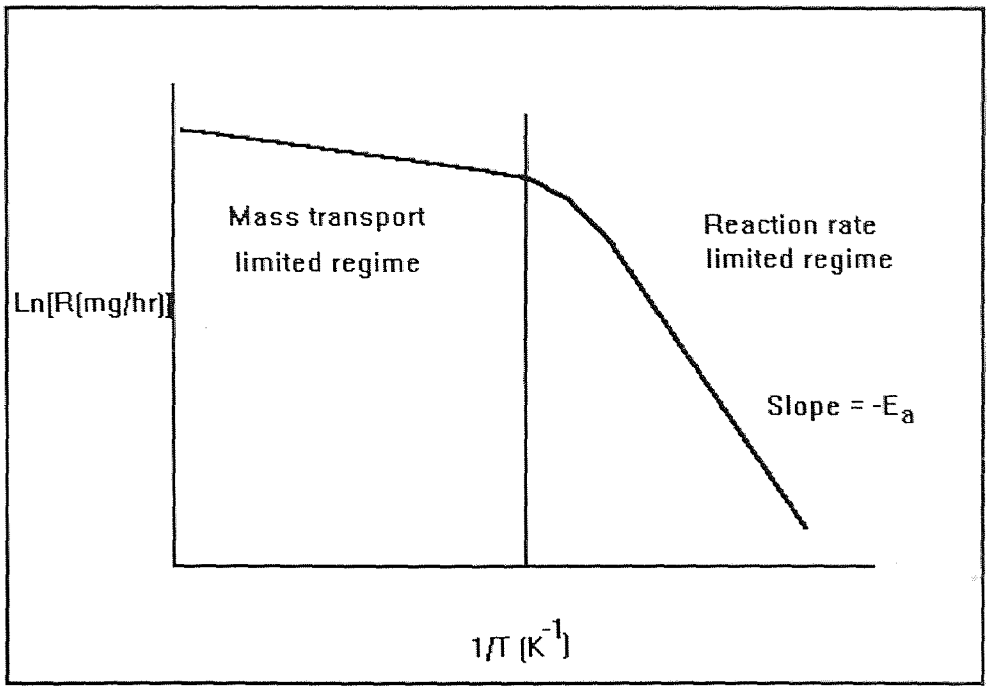

Figure 1.1 Deposition rate as a function of substrate temperature exemplifying diffusion controlled and surface-reaction controlled regimes

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. As shown in figure 1.1, a relatively steep temperature range, and a milder dependence in the upper range, indicating that the nature of the rate-controlling step changes with temperature.[3]

1.2.3 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 supersaturating 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.

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.

1.3 Types of CVD Process

Depending upon the type of energy that applied for the reaction to occur, CVD processes can be classified as: (i) Plasma enhanced CVD (ii) Photo induced CVD (iii) Thermally activated CVD. [6]

1.3.1 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 resulting in interaction between these species thus forming a solid thin film product on the substrate and electrode surfaces.

Glow discharge are usually created at low pressure in the .01 to 1 torr range. This causes breakdown of molecules into 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 to the ambient temperature but the breakdown electrons will be higher temperature causing the reaction. Thus this method can be employed at relatively low temperature and it is useful for temperature sensitive materials.

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 makes 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.[6]

1.3.2 Photo Induced CVD

Short wavelength UV radiation is used to activate the reactants in gaseous phase forming the product material. A selective absorption of photon 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 being 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.

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 of patterns on a substrate. In evaporation method, the laser simply acts as an energy source to vaporize atoms from a target to the 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.[6]

1.3.3 Thermally Activated CVD

This process uses direct thermal energy for the chemical reaction. The simplest type of this conventional atmospheric pressure CVD (APCVD) where, the reactant gases are allowed into the 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 the APCVD is its simplicity that it needs no vacuum pumps. The disadvantage is the tendency for homogeneous gas phase nucleation that leads to particle contamination, unless special optimized gas injection techniques are used.

The deposition rate and uniformity of films created by all CVD process 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 pressure CVD, these two rates of 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 low pressure CVD (LPCVD) is a widely used method in cost competitive semiconductor industry. Another advantage of this method is gas phase nucleation is very much reduced.

Depending on 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 wafer are not heated directly. The advantage of this system is a temperature gradient that can be provided to the chamber which results in uniform thickness. In the other type, the wafers are heated to high temperature directly. The reactants that are absorbed on the surface undergo chemical change due to the temperature of the wafer. But, controlling the wafer's temperature is difficult and hence uniform deposition is also difficult.

1.4 Low Pressure Chemical Vapor Deposition 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 or 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 2 basic parameters (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.

1.4.1 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, since 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.

1.4.2 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 particulate.

1.5 Advantages of CVD

Thin films are used in a host of applications in VLSI fabrication, and can be synthesized by a variety of techniques. Regardless of the method by which they are formed, however, the process must be economical, and the resultant films must exhibit uniform thickness, high purity and density, controllable composition and stoichiometries, high degree of structural perfection, excellent adhesion and good step coverage. CVD processes are often selected over competing deposition techniques because they offer the following advantages:

1. A variety of stoichiometric and non stoichiometric compositions can be deposited by accurate control of process parameters.
2. High purity films can be deposited that are free from radiation damage without further processing.
3. Results are reproducible.
4. Uniform thickness can be achieved by low pressure.
5. Conformal step coverage can be obtained.
6. Selective deposition can be obtained with proper design of the reactor.
7. The process is very economical because of its high throughput and low maintenance cost.

1.6 Limitations of CVD

Fundamental limitations of CVD are the chemical reaction feasibility and the reaction kinetics that govern the CVD processes. Technological limitations of CVD include the unwanted and possibly deleterious but necessary by-products of reaction that must be eliminated, and the ever present particle generation induced by homogeneous gas phase nucleation that must be minimized.

1.7 Objectives of this Thesis

In this study, ditertiarybutylsilane (DTBS) and oxygen have been used as a precursor to produce silicon dioxide films by low pressure chemical vapor deposition (LPCVD). These films were synthesized in the temperature range of 600 to 800°C at constant pressure of 0.2 Torr, a DTBS flow rate of 10 sccm, and a variable O_2 flow rate. The effects of deposition parameters on the growth rate and physical properties of the LPCVD SiO_2 films were investigated. Some properties of DTBS are listed in Table 1.2.

Table 1.2 Properties of ditertiarybutylsilane (DTBS)

formula	$SiH_2(C_4H_9)$
molecular weight	144 g/mol
vapor pressure	20.5 torr at 20°C
boiling point	120°C at 760 Torr

CHAPTER 2

REVIEW OF LITERATURE

Many research papers were published regarding the deposition techniques and the properties of silicon dioxide. In this chapter a review of research on silicon dioxide will be presented.

2.1 Deposition Techniques of SiO_2 Film

CVD SiO_2 can be prepared by various reactions. The choice of the reaction is dependent on the temperature requirements of the systems, as well as the equipment available for the process [3]. There are many important deposition variables for CVD SiO_2 include : temperature, pressure, reactant concentrations and their ratios, presence the 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 its own chemical reactions and reactor configurations. These are : 1) low temperature deposition (300 - 450°C) ; 2) medium temperature deposition (650 - 750°C) ; and 3) high temperature deposition (~ 900°C)

In the lower temperature range, most of the early processes were base on silane chemestry:

$$SiH_4\,(g) + O_2\,(g) \rightarrow SiO_2\,(s) + 2H_2\,(g) \qquad (2.1)$$

Table 2.1 Deposited Techniques of CVD Silicon Dioxide

Technique	Reactants	Remarks	References
LPCVD	TEOS;TMOS;TBOS, N_2O	Deposition temp.690 - 810°C, at 0.2-1.0 Torr	[1]
LPCVD	$SiH_2(C_2H_5)_2$,(Di-ethylsilane), O_2	Deposition temp. 475°C,at 0.5 Torr	[7]
LPCVD	TEOS , N_2O	Deposition temp. 650 - 800°C	[8]
LPCVD	SiH_2Cl_2, N_2O	Deposition temp.800 - 900°C,at 0.5 Torr	[9]
APCVD	SiH_4, O_2	Deposition temp. 450°C, at atmospheric pressure	[4]
APCVD	TEOS, Ozone	Deposition temp. 400°C, at atmospheric pressure	[10]
PECVD	SiH_2Cl_2 , N_2O	Deposition temp. 350°C, N_2O:SiH_2Cl_2 = 15:1 to 30:1	[4]
PECVD	TEOS , O_2/N_2O	Deposition temp. 400°C	[12],[13],[14]

The deposition can proceed in atmospheric pressure CVD (APCVD) reactors [15,30], low pressure CVD (LPCVD) reactors [7,11,18,26,29,31], plasma enhanced CVD (PECVD) [12,13,14,16,36,37]. Many researchers used different techniques and different precursors to obtain CVD SiO_2 (as shown in Table 2.1) APCVD is a simpler and less expensive system, which is the main advantage over other ones that required vacuum environment. Because rates as large as 100 nm/min were readily attained [15], such reactors achieved very good throughput. But operation at atmospheric pressure has a problem of gas phase nucleation which produced unacceptably high levels of defects, unless a high degree of inert diluent gas is used.

LPCVD produces cleaner films because of a reduction in gas phase nucleation. But the deposition rate based on the same chemistry (equation (2.1)) as found to be as low as 3 nm/min where the system throughput was not competitive though excellent uniformity of film thickness and composition were obtained.

Silicon dioxide film is usually based on the reaction of silane and oxygen. Various new precursors are coming up in the place of silane. The purposes are not only for generating good quality films and optimizing the deposition conditions, but also for the safety because silane is toxic, pyrophoric explosive gas. Some of these precursors are listed in the table 2.2.

Table 2.2 New precursors of CVD SiO_2

Name	Formula	References
Tetraethoxysilane(TEOS)	$Si(OC_2H_5)_4$	[10,12-14,16,31,36,35-37]
Ethyltriethoxysilane(ETOS)	$C_2H_5Si(OC_2H_5)_3$	[7]
Amyltriethoxysilane	$C_5H_{11}Si(OC_2H_5)_3$	[39]
Vinyltriethoxysilane	CH_2=$CHSi(OC_2H_5)_3$	[39]
Phenyldiethoxysilane	$C_6H_5Si(OC_2H_5)_3$	[39]
Tetrapropoxysilane	$Si(OC_3H_7)_4$	[40]
Tetramethyicyclotetra-silane(TMCTS)	$Si_4(CH_3)_8$	[26]
Diethylsilane(DES)	$(C_2H_5)_2SiH_2$	[11]
Disilane	Si_2H_6	[23]
Dichlorosilane	SiH_2CL_2	[29]
Tetrametoxysilane(TMOS)	$Si[OCH_3]_4$	[1]
Tetrabutoxysilane(TBOS)	$Si[O(CH_2)_3CH_3]_4$	[1]

The most work has been done with TEOS, using both LPCVD and PECVD techniques. Optimum deposition conditions and there effects on the deposit properties have been studied in detail. A rough kinetic mechanism has been proposed based on the experimental results [13]

Levy et al.[7] used DES as a precursor to produce silicon dioxide films by LPCVD at various temperature ranging from 350°C to 475°C. The deposition rate as a function of temperature was found to follow an Arrhenius behavior yielding an apparent activation energy of 10 kcal/mol. They also varied pressure,O_2 flow rate, and O_2/DES ratio. They observed that at 400°C , there were points of abrupt cessation in deposition.

2.2 Properties and Applications

Thin films for use in VLSI fabrication must satisfy a large set of rigorous chemical, structural and electrical requirements. Very low densities of both particulate defects and film imperfections such as pinholes, become critical for small linewidths, high densities, and large areas necessary for VLSI. 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

Properties of silicon dioxide [17] deposited by different methods are shown in table 2.3:

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

SiO_2 film is easily deposited at low temperatures. 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 out diffusion 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.

CHAPTER 3

EXPERIMENTS

3.1 Introduction

Silicon dioxide thin film was synthesized in a LPCVD reactor altering various parameters including temperature, gas composition and time of deposition. Fourier Transform Infrared (FTIR) analyses were done on the synthesized films to examine the vibrational modes of the deposited films. Refractive Index and thickness of the films were measured by using ellipsometry and interferometry respectively. Stress on the films was measured and calculated by the principle of radius of curvature difference. The optical transmission of the films was measured using a UV spectrophotometer.

3.2 LPCVD Reactor

The schematic for hot wall low pressure chemical vapor deposition reactor is shown in Fig 3.1. 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 furnace. 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.

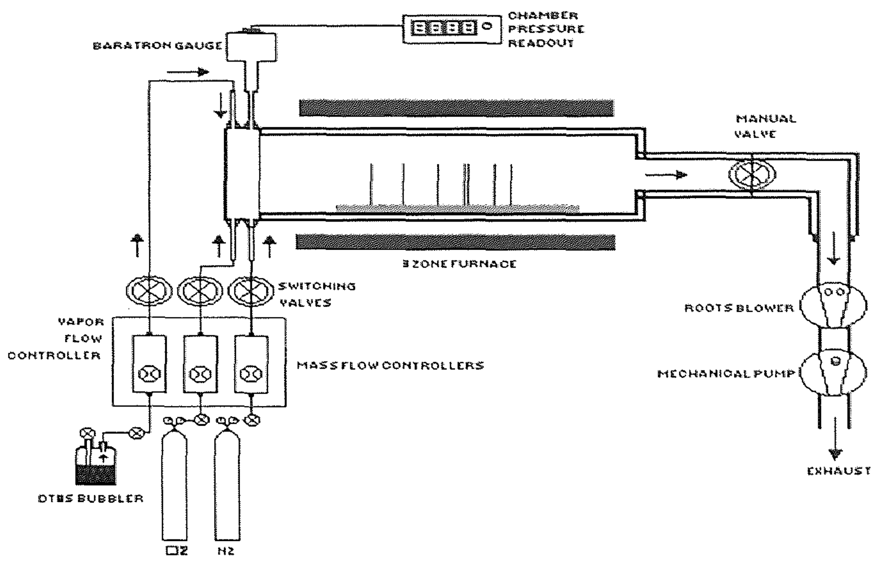

Figure 3.1 : A schematic of the LPCVD reactor

3.3 Deposition Procedure

3.3.1 Loading Wafers

Wafers were 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 were deposited 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 were placed at same distance from each other. The boat was placed at a distance of 64 cm from the door.

3.3.2 Leakage Check

A leak would result in a change in the deposit structure (due to oxygen) and could result in haze depending on the size of the leak, therefore the leakage check in the CVD is an important step before making an experiment. When carrying out leak check, all pneumatic controllers and gas regulators should be fully open to the gas cylinder main valve. The capillary is disconnected and the inlet is sealed with a plug because it is not possible to create vacuum in the capillary in the limited time period. After pumping the reaction system for a whole day, closing the outlet valve of the chamber, the pressure increasing rate was measured at a fix period of time in the chamber to obtain the leakage rate. For this LPCVD system, the leakage rate deviated from 0.13 to 2.0 mTorr/min. Depending on the chamber condition a very low leak rate for a new chamber and higher leak rate of a chamber after long time in service. However, the leakage rate in the system was basically good.

3.3.3 Calibration of Gas Flow System

Mass rate can be measured by the temperature difference. Gas flows were controlled by Applied Materials model AFC 550 automatic N_2 mass flow controllers which were corrected for DTBS and O_2 flows. The pressure in the reactor was measured with a barratry gauge from MKS. The N_2 calibration of the AFC was 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 was 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:

$$\text{Flow Rate} = 60(\Delta P/\Delta t)(T_0 V/P_0 T) \qquad (3.2)$$

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.

3.3.4 Raising Temperature

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

3.3.5 Deposition

Once the required temperature was reached, waited about 30 min. for annealing, then opened oxygen valve to let it into the reactor. When the flowmeter showed stabilized value of flow, the DTBS was opened. The pressure was then set to the required value. Care was taken not to let the organic precursors into the chamber before there was oxygen flow lest the films should have carbon in them. Oil filter was switched on.

3.4 Characterization of SiO_2 Thin Films

3.4.1 Thickness

Film thickness was 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 was measured at five different points. The refractive index provided was first estimated, as for silicon dioxide, 1.46 is the typical value. Thickness was measured at five different points on the wafer. Deposition rate was determined as the film thickness over the deposition time, and averaged over all the wafers in the run.

3.4.2 Refractive Index

The refractive index was 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 were 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 was measured at five different points and then averaged out to the refractive index of the wafer.

3.4.3 Infrared Spectra

The levels of interstitial oxygen was determined by using infrared absorption spectroscopy. The analysis was done on a Perkin-Elmer 1600 series FTIR spectrophotometer to determine the characteristics of the deposits. A plot of energy level of the transmitted IR spectrum versus wave number (reciprocal of wavelength) can be used to detect the presence of vibrational mode of the particular molecule. IR spectroscopic analysis were carried out for various samples. The three absorption at 1080 cm^{-1},800 cm^{-1} and 460 cm^{-1} characterized SiO_2 films.

3.4.4 Stress

The stress in the film was determined by a house developed device, employing a 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 were incident on the wafer surface before and after deposition. The reflected beams from the two surfaces was 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 was fed into Stony's Equation to obtain actual stress value. The calculation formula is:

$$\sigma = 12.3\ D/T \qquad (3.3)$$

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

T = thickness of the films, (μm);

σ = stress of the film (MPa), negative value indicates compressive stress

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

The results of silicon dioxide thin film synthesized on Si and quartz substrates at a constant pressure 200 mTorr, at temperature 700°C, and at various flow rates of oxygen and DTBS are presented in this chapter. The distance between the wafers also varied to study the deposition rate as a function of distance and to get the high deposition rate with uniform films.

4.2 Deposition Rate Analysis

The purpose of this study is to evaluate the growth rate and characterize the silicon dioxide films deposited using detertiarybutylsilane (DTBS). Three important aspects of films growth are studied. They are the rate of growth with respect to the deposition temperature, O_2 flow rate, and wafer spacing.

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

$$\text{Growth Rate (G.R.)} = A\exp(-E_a/RT) \qquad (4.1)$$

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).

By 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. The negative slope of the curve give 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 4.1 shows Ln of growth rate (in Å per minute) plotted against the reciprocal of deposition temperature in Kelvin scale. The experiments were carried out between temperature of 600 and 800°C; DTBS flow rate of 10 sccm and O_2 flow rate of 100 sccm; pressure of 200 mTorr. The slope of the curve was found to be -1.32 giving an apparent activation energy of 2.62 kcal/mol.

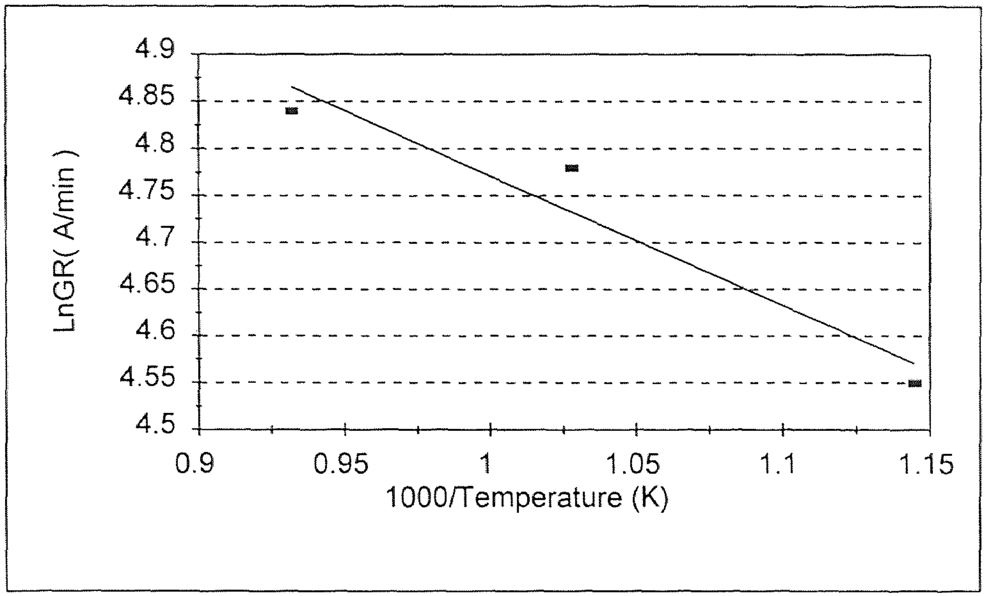

Figure 4.1 Variation of deposition rate as a function of temperature (at pressure 0.2Torr, O_2 to DTBS ratio 10:1, DTBS flow rate 10 sccm)

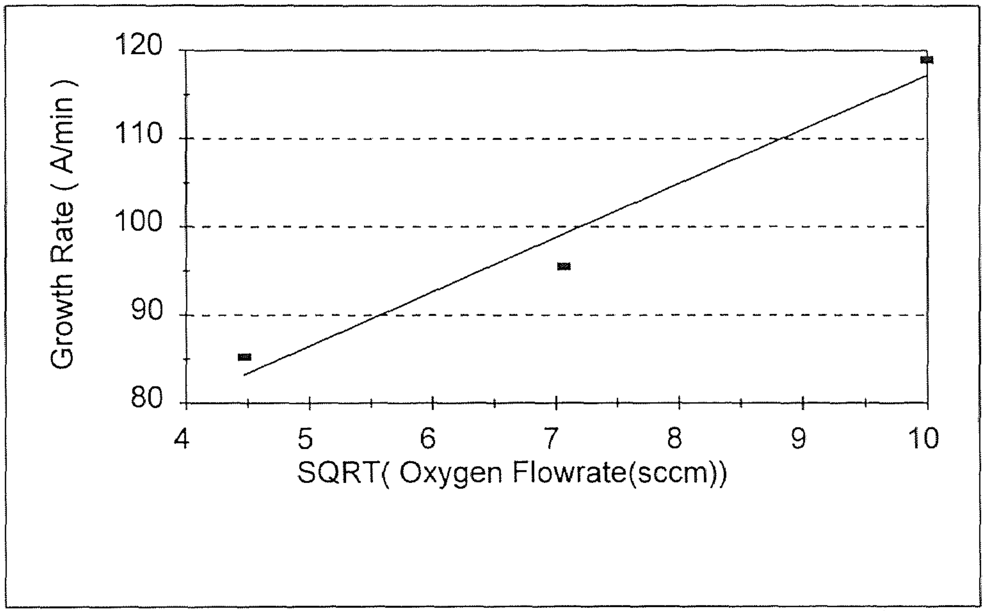

Figure 4.2 Variation of deposition rate versus square root of O_2 flow rate for constant DTBS flow rate(temperature 700°C, pressure 0.2 Torr. DTBS flow rate 10sccm)

Figure 4.2 shows a plot of deposition rate versus square root of O_2 flow rate for constant conditions of temperature (700°C), DTBS flow rate (10 sccm), and pressure (0.2 Torr). It is observed that at the O_2 flow rate range from 20 to 100 sccm the deposition rate is linearly increasing. It is indicated that the reaction rate is controlled by the amount of O_2 reaching the surface of wafers.

Figure 4.3 shows a plot of deposition rate as a function of distance between the wafers. It was observed that as the distance between the wafers was increased from 2 cm to 5 cm the deposition rate increased. This can be explained by the increase in distance exposed the wafers to the reactant gases to larger extent and thus, deposition and uniformity of the deposit were favored.

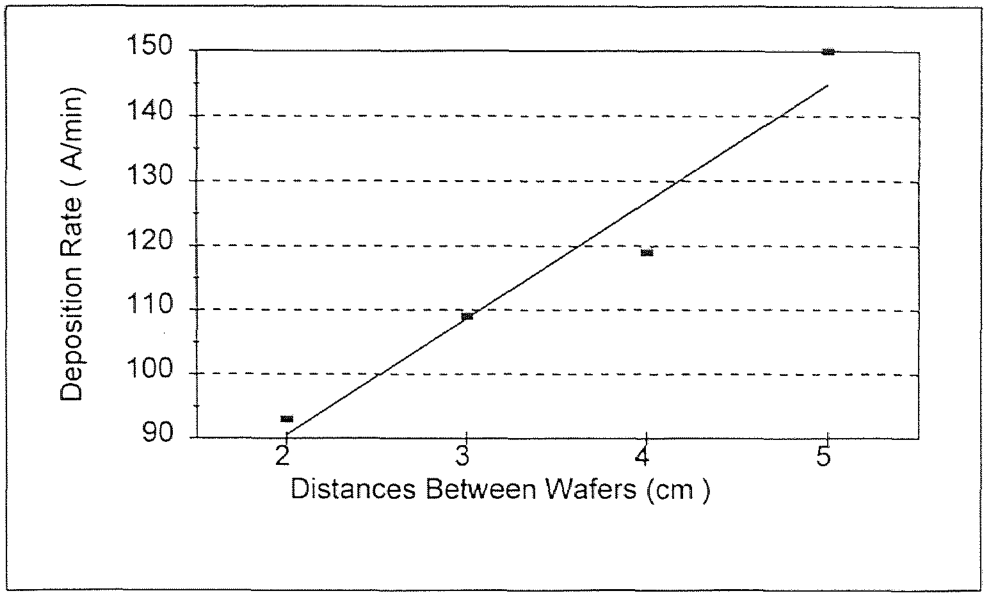

Figure 4.3 Variation of average deposition rate as a function of distance between thewafers (temperature 700°C, pressure 0.2 Torr, O_2 to DTBS ratio 10:1, DTBS flow rate 10 sccm)

4.3 Refractive Index Analysis

The variation of refractive index as a function of temperature is shown in Figure 4.4 for constant condition of pressure (0.2 Torr) ,and flow rate ratio of O_2 to DTBS of 10:1 (at DTBS flow rate 10 sccm). The refractive index of the deposits was determined by using a Rudolph Research Auto EL Ellipsometer at five different points. The average was then taken for plotting.

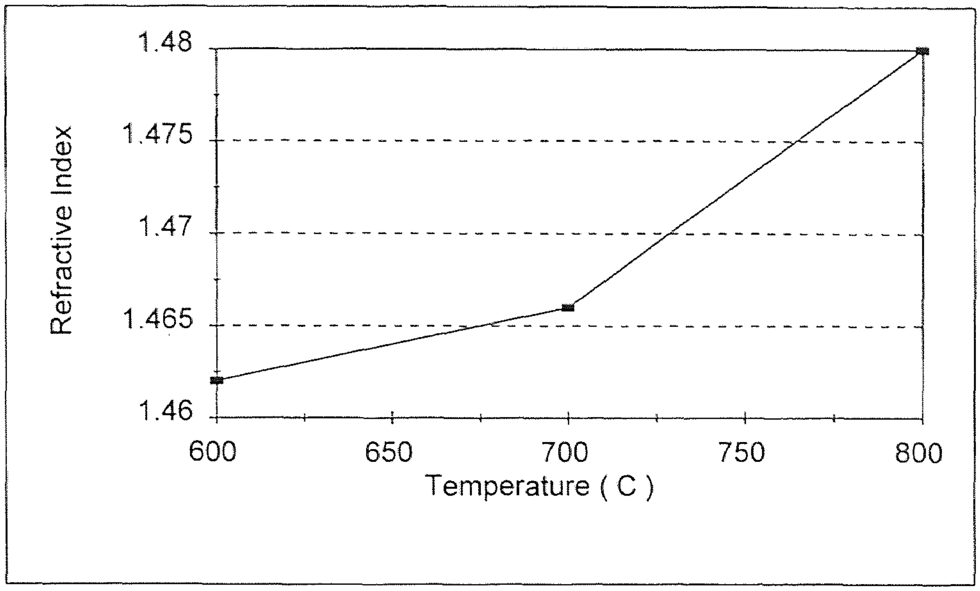

Figure 4.4 Refractive index at different deposition temperature for constant flow ratio of O_2 to DTBS at 10:1 (DTBS flow rate 10 sccm , pressure 0.2 Torr)

The refractive index showed increase with increase in temperature of deposition. It should be explained that the higher temperature, the composition of the deposits changed to carbon rich. A carbon rich film shows increase in refractive index due to the high inherent refractive index of carbon.

4.4 Stress Analysis

Analysis of stress with respect to temperature showed that the stresses were very low through the entire regime of deposition temperature. The stresses were tensile at low temperature and decreased as increased temperature from 600° to about 750°C, beyond that they tended to be increasingly compressive.

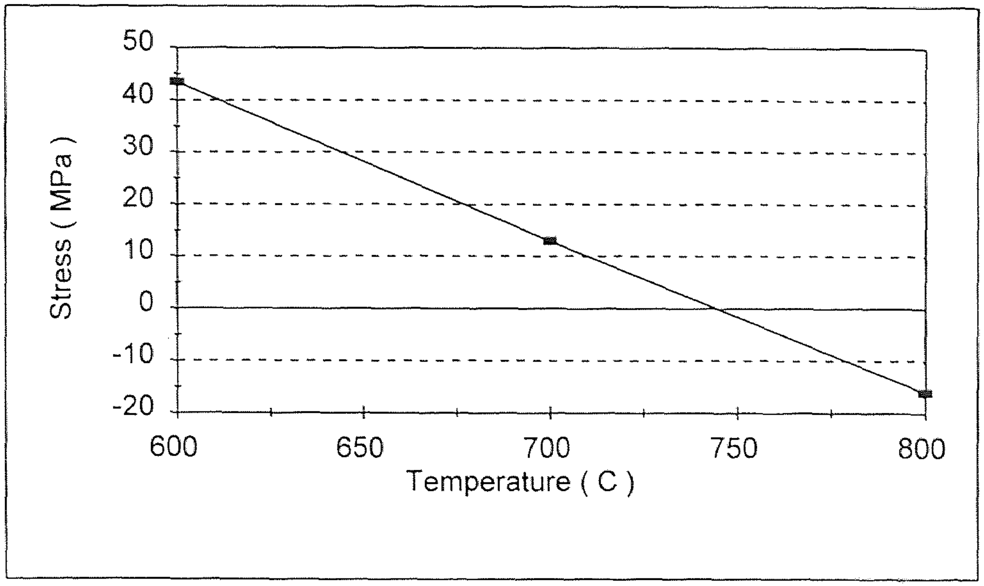

Figure 4.5 Stress as a function of temperature at constant flow ratio of O_2 to DTBS at 10:1 (DTBS flow rate 10 sccm , pressure 0.2 Torr)

Stress can result from differences in thermal expansion coefficients (α) of the film and the substrate. The presence of carbon ($\alpha=3.8\times10^{-6}$ cm/cmK) in film causes a positive difference in the thermal expansion coefficients resulting in stresses being compressive. Also, at higher temperature result in some stress relief and the stress tend to be more compressive.

4.5 FTIR Analysis

For all deposits, the Si-O stretching, bending, and rocking modes were identified at 1080, 800, and 460 cm^{-1} respectively by FTIR spectroscopy. Figure 4.6 illustrates a typical FTIR spectrum of silicon dioxide films at 700°C, 0.2 Torr pressure and a flow ratio of O_2 to DTBS at 10:1(DTBS flow rate 10 sccm).

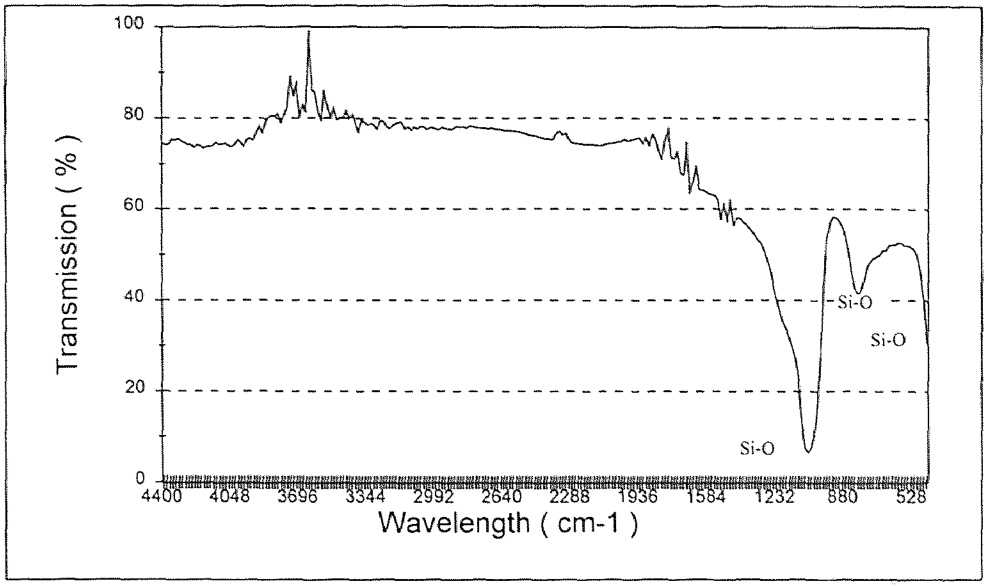

Figure 4.6 Typical FTIR spectrum of SiO_2 films at deposition temperature 700°C

4.6 Optical Transmission

The optical transmission of the silicon dioxide film deposited on quartz wafers were studied using a UV/Visible spectrophotometer. Typical optical transmission curve is shown in Figure 4.7. The thickness of this film was 9550 Å, and deposited at 700°C, 0.2 Torr and flow ratio of O_2 to DTBS at 10:1 (DTBS flow rate 10 sccm) The result shown that the optimal transmission was about 95% at visible wavelength.

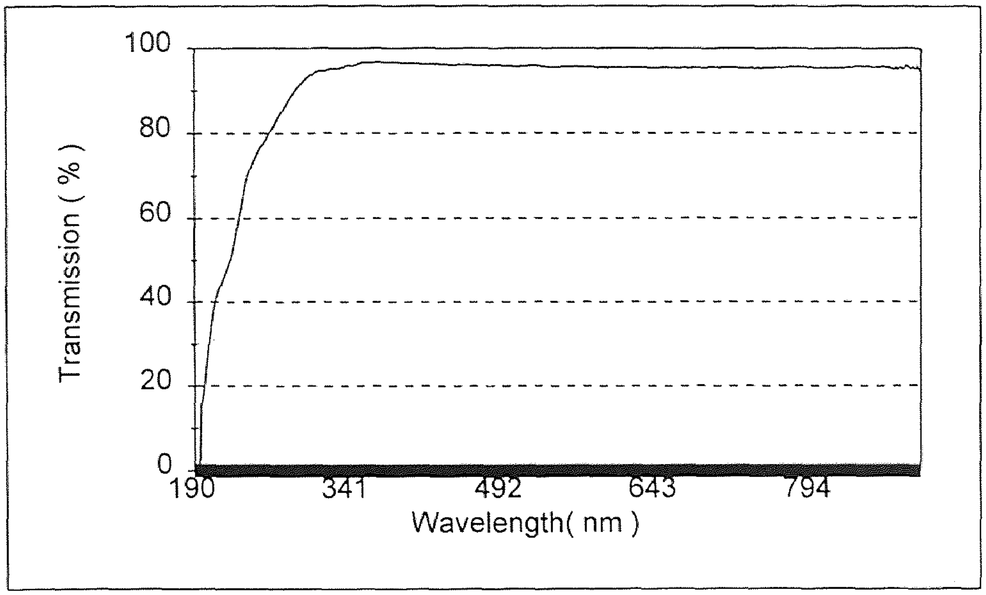

Figure 4.7 Optical transmission of SiO_2 thin films

CHAPTER 5

CONCLUSIONS

Silicon dioxide thin films were deposited on silicon substrates by Low Pressure Chemical Vapor Deposition (LPCVD) using ditertiarybutylsilane (DTBS) as a precursor and oxygen as the oxidant. The dependence of film growth rate on various process parameters were studied. The growth rate as a function of temperature was found to follow an Arrhenius behavior yielding an apparent activation energy of 2.62 kcal/mol. The growth rate was observed to increase with higher distance between wafers and to vary as a function of the square root of O_2 flow rate. The refractive index was observed to be close to 1.46 (1.462, 1.466 at deposited temperature 600,and 700°C respectively) which in good agreement with corresponding values of thermal oxide. The stresses were very low tensile (43.5 MPa at deposited temperature 600°C) and became compressive as the deposition temperature increased (- 16 MPa at 800°C). The FTIR spectroscopic analysis were carried out, the three maximal absorption at 1080, 800, and 460 cm^{-1} characterized the SiO_2 films. The optimal transmission was about 95 % at visible wavelength (for SiO_2 film at thickness 9550 Å.)

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