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## ABSTRACT

### SYNTHESIS AND CHARACTERIZATION OF SILICON DIOXIDE THIN FILMS BY LOW PRESSURE CHEMICAL VAPOR DEPOSITION USING DITERTIARYBUTYLSILANE AND OXYGEN

by  
Sung-Jun Lee

This study is focused on the synthesis and characterization of silicon dioxide thin films deposited on silicon wafers 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 was found to follow an Arrhenius curve with the variation in the temperature with an activation energy of 12.6 kcal/mol. The growth rate was found to be inversely proportional to the temperature in the range 550-750 °C. The refractive index and density were observed to be close to 1.47 and 2.71 g/cm<sup>3</sup> respectively with flow rate ratio O<sub>2</sub>/DTBS = 2/1. Producing crack-free thick oxide films were performed at two different conditions. One was at 850 °C with flow rate ratio O<sub>2</sub>/DTBS = 5/1 which produced compressive stress with lower growth rate, and the other was at 700 °C with flow rate ratio O<sub>2</sub>/DTBS = 10/1 which produced tensile stress with higher growth rate. Both conditions were able to produce about 10 μm oxide films with no sign of cracking.

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

by  
Sung-Jun Lee

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

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This thesis is dedicated to  
my dear parents

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## TABLE OF CONTENTS

Chapter	Page
1 INTRODUCTION.....	1
1.1 Applications of SiO <sub>2</sub> Thin Films.....	1
1.2 Chemical Vapor Deposition (CVD).....	3
1.2.1 Fundamentals of CVD.....	3
1.2.2 Categories of CVD.....	8
1.2.2.1 Plasma Enhanced CVD (PECVD).....	8
1.2.2.2 Atmospheric Pressure CVD (APCVD).....	9
1.2.2.3 Laser CVD.....	9
1.2.2.4 Photo CVD.....	10
1.2.2.5 Metallo-organic CVD (MOCVD).....	11
1.3 Low Pressure CVD (LPCVD).....	12
1.3.1 Introduction of LPCVD.....	12
1.3.2 Horizontal Tube LPCVD Reactors (hot wall).....	13
1.3.3 Diffusion Model of LPCVD Reactors.....	14
1.4 CVD of SiO <sub>2</sub> Films.....	15
1.4.1 Methods of Preparing CVD of SiO <sub>2</sub> Films.....	15
1.4.1.1 Low Temperature Deposition.....	16
1.4.1.2 Medium Temperature Deposition.....	17
1.4.1.3 High Temperature Deposition.....	18

**TABLE OF CONTENTS**  
**(Continued)**

<b>Chapter</b>	<b>Page</b>
1.4.2 Properties of SiO <sub>2</sub> Films Deposited by Various CVD Techniques.....	18
1.4.2.1 Conformal Coverage.....	18
1.4.2.2 Water Absorption.....	20
1.4.2.3 Stress.....	21
1.5 Objectives of this Thesis.....	22
2 EXPERIMENTAL.....	23
2.1 Set-up of LPCVD Reactor.....	23
2.2 Pre-experiments.....	25
2.2.1 Flow Rate Calibration.....	25
2.2.2 Leakage Check.....	26
2.3 Experimental Procedures.....	26
2.3.1 Wafer Loading.....	26
2.3.2 Setting Deposition Condition.....	27
2.3.3 Film Deposition.....	27
2.4 Characterization of SiO <sub>2</sub> Thin Films.....	27
2.4.1 Thickness.....	27
2.4.2 Film Density.....	28
2.4.3 Refractive Index.....	28
2.4.4 Infrared Spectra.....	29

**TABLE OF CONTENTS**  
(Continued)

Chapter	Page
2.4.5 Stress.....	29
3 RESULTS AND DISCUSSIONS.....	31
3.1 Temperature Effect.....	31
3.1.1 Film Growth Rate Analysis.....	31
3.1.2 Density Analysis.....	35
3.1.3 Refractive Index.....	38
3.2 Film Characterizations at Various Flow Rate Ratio.....	39
3.2.1 Densities at Various Flow Rate Ratio.....	39
3.2.2 Refractive Index at Various Flow Rate Ratio.....	41
3.2.3 Thickness.....	42
3.3 Deposition of Crack-free Thick Oxide Films.....	44
3.3.1 Flow Rate Ratio $O_2/DTBS = 5/1$ at $850\text{ }^\circ\text{C}$ .....	44
3.3.2 Flow Rate Ratio $O_2/DTBS = 10/1$ at $700\text{ }^\circ\text{C}$ .....	47
3.4 IR Spectroscopic Analysis.....	48
4 CONCLUSIONS.....	49
REFERENCES.....	50

## LIST OF TABLES

Table	Page
1.1 Physical Properties of Silicon Dioxide.....	3
1.2 Properties of Ditertiarybutylsilane (DTBS).....	22

## LIST OF FIGURES

Figure	Page
2. 1 A schematic Diagram of the LPCVD Reactor Modified for SiO <sub>2</sub> Deposition on Vycor tube and Permeability Measurements.....	24
3. 1 Variation of Growth Rate as a Function of Temperature at Fixed Flow Rate Ratio O <sub>2</sub> /DTBS = 2/1, Pressure = 200 mTorr.....	33
3. 2 Activation Energy, Effect of Temperature on the Growth Rate, showing Arrhenius Behavior between 600 and 750 °C, slope = -6.3172, Flow Rate Ratio O <sub>2</sub> /DTBS = 2/1, Pressure = 200 mTorr.....	34
3. 3 A plot of Thickness of the Film versus Mass Deposited on the Wafers at Various Temperatures, from 550 to 850 °C, slope = 470.68, Flow Rate Ratio O <sub>2</sub> /DTBS=2/1, Pressure = 200 mTorr.....	36
3. 4 Variation of Film Density as a Function of Various Temperature, Flow Rate Ratio O <sub>2</sub> /DTBS = 2/1, Pressure = 200 mTorr.....	37
3. 5 Variation of Refractive Index as a function of Various Temperatures, from 550 to 850 °C, Flow Rate Ratio O <sub>2</sub> /DTBS = 2/1, Pressure = 200 mTorr.....	38
3. 6 Densities at Various Flow Rate Ratio O <sub>2</sub> /DTBS = 2/1, 5/1, and 10/1 Pressure = 200 mTorr, Temperature = 750 °C.....	39
3. 7 Densities at Various Flow Rate Ratio O <sub>2</sub> /DTBS = 2/1, 5/1, and 10/1 Pressure = 200 mTorr, Temperature = 850 °C.....	40
3. 8 Refractive Index at Various Flow Rate Ratio O <sub>2</sub> /DTBS = 2/1, 5/1, and 10/1 Pressure = 200 mTorr, Temperature = 750 °C.....	41
3. 9 Refractive Index at Various Flow Rate Ratio O <sub>2</sub> /DTBS = 2/1, 5/1, and 10/1 Pressure = 200 mTorr, Temperature = 850 °C.....	42
3.10 Growth Rate at Various Flow Rate Ratio O <sub>2</sub> /DTBS = 2/1, 5/1, and 10/1 Pressure = 200 mTorr, Temperature = 850 °C.....	43
3.11 Growth Rate at Various Flow Rate Ratio O <sub>2</sub> /DTBS = 2/1, 5/1, and 10/1 Pressure = 200 mTorr, Temperature = 850 °C.....	44

**LIST OF FIGURES**  
(Continued)

<b>Figure</b>	<b>Page</b>
3.12 Thickness as a Function of Deposition Time, Temperature = 850 °C Pressure = 200 mTorr, Flow Rate Ratio O <sub>2</sub> /DTBS = 5/1.....	45
3.13 Compressive Stress as a Function of deposition Time, Pressure = 200 mTorr Temperature = 850 °C, Flow Rate Ratio O <sub>2</sub> /DTBS = 5/1.....	46
3.14 Thickness as a Function of Deposition Time, Pressure = 200 mTorr Temperature = 700 °C, Flow Rate Ratio O <sub>2</sub> /DTBS = 10/1.....	47
3.15 FTIR Spectrum of LPCVD SiO <sub>2</sub> Film, Flow Rate Ratio O <sub>2</sub> /DTBS = 2/1 Pressure = 200 mTorr, Temperature = 700°C.....	48

# CHAPTER 1

## INTRODUCTION

### 1.1 Applications of SiO<sub>2</sub> Thin Films

Silicon dioxide (silica; SiO<sub>2</sub>) is a major industrial material with many applications in the semiconductor industry in the form of coatings which are mostly produced by CVD [1]. Silicon dioxide films have been an essential factor in the manufacture of integrated circuits from the earliest days of the industry. They have been used as a final passivation film to protect against scratches and to get mobile ion impurities (when doped with phosphorus). Another application has been an interlayer dielectric between the gate polysilicon and the aluminum metalization. Initially, most such films were deposited in atmospheric pressure systems. In recent years, low pressure process have assumed greater importance [2]. 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), lies in the successful growth and application of SiO<sub>2</sub> films on silicon. SiO<sub>2</sub> satisfies almost all the requirements of a dielectric film for multilevel metalization and passivation layers, which include [3]:

#### Intermetal dielectric

- 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;

#### 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 dielectrics.

The physical properties of  $\text{SiO}_2$  are given in Table 1.1 [1][4].

Recently, a new application of  $\text{SiO}_2$  as a composite/ceramic membrane for gas-separation has been developed by depositing the material on a microporous substrate to reduce the pore size and thus to achieve particular selectivity of the porous membranes. Silicon dioxide is a competitive material for this technology because of its inherent properties such as thermal stability, corrosion resistance, and also due to the fact that the difference in thermal expansion coefficients between the ceramic substrate and  $\text{SiO}_2$  deposit is very low.



**Table 1.1** Physical Properties of Silicon Dioxide

structure	hexagonal
melting point	1728°C
boiling point	2950°C
thermal expansion	0.5ppm/°C (0-150°C)
thermal conductivity	0.12w/cm.°C (0-150°)
hardness	600-1000kg/mm <sup>2</sup>
resistivity	1x10 <sup>21</sup> μohm-cm (at 20°C)
refractive index	1.4584 (5893Å)
heat capacity	0.185cal/g (100°C)
Si-O bond distance	1.62Å
density	2.1975g/cm <sup>3</sup> (0°C)
Mohr's hardness	7.7 GPa
Young's modulus	10.5x10 <sup>6</sup> psi

## 1.2 Chemical Vapor Deposition (CVD)

### 1.2.1 Fundamentals of CVD

Chemical vapor deposition (CVD) is a very versatile process used in the production of coatings, powders, fibers and monolithic components. With CVD, it is possible to produce almost any metal and non-metallic element, including carbon or silicon, as well as compounds such as carbides, nitrides, oxides, intermetallics and many others. This

technology is now an essential factor in the manufacture of semiconductors and other electronic components, in the coating of tools, bearings and other wear resistant parts and in many optical, opto-electronic and corrosion applications. Chemical vapor deposition may be defined as the deposition of a solid on a heated surface from a chemical reaction in the vapor phase. It belongs to the class of vapor transfer processes which are atomistic in nature; that is, the deposition species are atoms or molecules or a combination of these. Beside CVD, they also include the physical vapor deposition processes (PVD) such as evaporation, sputtering, molecular beam epitaxy, ion plating and ion implantation as well as peak cementation which is a hybrid process combining vapor phase transfer and solid state diffusion. In many respects, CVD competes directly with these processes, but it is also used in conjunction with them and many of the newer processes are actually hybrids of the two systems such as plasma enhanced CVD or activated sputtering. CVD has several important advantages which make it the preferred process in many cases. These can be summarized as follows:

- As generally used at pressures above the molecular flow region, it is not restricted to a line of sight deposition which is generally characteristic of sputtering, evaporation and other PVD processes, CVD has high throwing power. Deep recesses, holes and other difficult three-dimensional configurations can usually be coated with relative ease. For instance, integrated circuit via holes with an aspect ratio of 10/1 can be completely filled with CVD tungsten.
- The deposition rate is high and thick coatings can be readily obtained (in some cases centimeters thick) and the process is generally competitive and, in many cases, more economical than the PVD processes.

- The CVD equipment is relatively simple, does not require ultra-high vacuum, and generally can be adapted to many process variations. Its flexibility is such that it allows many changes in composition during deposition and codeposition of compounds is readily achieved.

CVD however is not the universal coating panacea. It has several disadvantages, a major one being that it is most versatile at temperatures of 600°C and above where the thermal stability of the substrate may limit its applicability. However the development of plasma CVD and metallo-organic CVD partially offsets this problem. Another disadvantage is the requirement of having chemical precursors (the starter materials) with high vapor pressure which are often hazardous and at times extremely toxic. The byproducts of these precursors are also toxic and corrosive and must be neutralized, which be a costly operation[1]. Chemical vapor deposition ( CVD) can be defined as a material synthesis method in which the constituents of the vapor phase react to form a solid film at some surface [5]. CVD of the film is a heterogeneous reaction consisting of at least the following steps:

### I. Arrival

- 1) bulk transport of the reactants into the processing chamber;
- 2) gaseous diffusion of the reactants to the surface;
- 3) adsorption of reactants onto the surface;

### II. Surface reaction

- 4) surface diffusion of the reactants;
- 5) surface reaction;

### III. Removal of reactant by-products

- 6) desorption of the reactant by-products;
- 7) gaseous diffusion of reactant by-products;
- 8) bulk transport of the by-products out of the chamber;

The rate at which these three steps are carried out controls the chemical vapor deposition. At low temperature the reaction is generally surface reaction controlled, while at a high temperature, it is usually limited by mass transfer. If the process is controlled by the surface reaction, i.e. reaction rate is limited by the rate of surface reaction, the deposition mechanism of the solid film follows the empirical Arrhenius behavior [6][7]:

$$D.R. = A \exp(-E_a/RT) \quad (1.1)$$

where,

D.R. is the deposition rate of the film;

$E_a$  is the apparent activation energy of the chemical reaction;

R is the gas constant;

T is absolute temperature (K);

A is constant.

According to this equation, the reaction rate increases with the increasing temperature. When the temperature rises high enough and the reaction rate approaches the rate of the reactant species arriving at the surface, the reaction rate cannot increase any more, unless there is an increase in the rate at which the reactant species are supplied to the surface by diffusion and mass transport. In this case, the reaction is mass transport controlled. The reaction rate can then be expressed as below:

$$D.R. = s k_D / RT (P - P_0) \quad (1.2)$$

where,

s is surface area of the substrate;

$k_D$  is mass transport coefficient;

P is partial pressure of the reactant;

$P_0$  is equilibrium partial pressure of the reactant at certain temperature;

Thus the chemical reaction is an essential characteristic of CVD. It strongly depends on the temperature, pressure, reactant flow rates etc. A good understanding of the effect of process variables is required in order to explain CVD processes. The reasons for the success of CVD are:

- CVD is a relatively uncomplicated and flexible technology which can accommodate many variations;
- With CVD, it is possible to coat almost any shape of almost any size;
- Unlike other thin film techniques such as sputtering, CVD can also be used to produce fibers, monoliths, forms and powders;
- CVD is economically competitive.

The deposition rate and the properties of the CVD film depend on the deposition conditions, such as reaction temperature, pressure, reactant flow rates, power density and so on. Studies on the effect of such variables will result in good understanding of CVD processes.

### 1.2.2 Categories of CVD

The energy to activate and drive the chemical processes can be thermal, supplied by an electric glow discharge plasma, or attained by electromagnetic radiation (usually ultraviolet or laser radiation). According to the type of energy supplied to initiate and sustain the reaction, CVD processes can be classified into following categories [8]:

- 1) Thermally activated reactions at various pressure ranges, which comprise the vast majority of CVD processes. Heat is applied by resistance heating, rf inducting heating, or infrared radiation heating techniques.
- 2) Plasma promoted reactions, where an rf or dc induced glow discharge is the source for most of the energy that initiates and enhances the rate of reaction, usually called plasma enhanced CVD (PECVD).
- 3) Photo induced reactions, where a specific wavelength radiation triggers and sustains the reaction by direct photolysis or by an energy transfer agent.

**1.2.2.1 Plasma Enhanced CVD (PECVD):** 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. Glow discharge are usually created at low pressures in the 0.01 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 electrode. The molecules themselves can be near to 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. 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 [9].

**1.2.2.2 Atmospheric Pressure CVD (APCVD):** Much of the early CVD development work was done by APCVD. It offered such advantages as operation without the need for a vacuum system, high dilution of toxic or flammable gases, and the potential for operation as continuous-feed belt systems. Disadvantages of APCVD operation included the need for large volumes of carrier gas, large size, and high levels of particulate contamination. In recent years, atmospheric operation have faded from popularity, with most significant developments occurring in LPCVD and PECVD.

**1.2.2.3 Laser CVD:** Thermal laser CVD (also known as laser pyrolysis) occurs as a result of the thermal energy from the laser coming in contact with and heating an absorbing substrate. The wavelength of the laser is such that little or no energy is absorbed by the gas molecules. The substrate is locally heated in a manner analogous to the local heating in a cold-wall reactor and deposition is restricted to the heated areas.

The major use so far of thermal laser CVD has been in the direct writing of thin films in semiconductor applications, using holographic methods to deposit complete patterns in a single step with a width as small as 0.5 micron. Laser CVD is also used on a development basis to produce rods and coreless boron and silicon carbide fibers.

**1.2.2.4 Photo CVD:** In photolytic CVD (photo CVD), the chemical reaction is induced by the reaction of light (single photon absorption), specifically ultraviolet (UV) radiation, which has sufficient photon energy to break the chemical bonds in the reactant molecules. In many cases, these molecules have a broad electronic absorption band and they are readily excited by UV radiation. Although UV lamps have been used, more energy can be obtained from UV lasers such as the excimer lasers which have photon energy ranging from 3.4 eV (XeF laser) to 6.4 eV (ArF laser). Photo CVD differs from thermal laser CVD in that, since the reaction is photon activated, no heat is required and the deposition may occur essentially at room temperature. Moreover, there is no constraint on the type of substrate, which can be opaque, absorbent or transparent. Materials deposited include  $\text{SiO}_2$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{Al}_2\text{O}_3$ , non-silicon oxides, aluminum, tungsten and other materials. A limitation of photo CVD is the slow rate of deposition which has so far restricted its applications. If higher power excimer lasers can be made available economically, the process could well compete with thermal CVD and thermal laser CVD, particularly in very critical semiconductor applications where low temperature is essential.

**1.2.2.5 Metallo-organic CVD (MOCVD):** MOCVD is a specialized area of CVD which utilizes metallo-organic compounds as precursors usually in combination with hydrides or



other reactants. The thermodynamic and kinetic principles of CVD and its general chemistry apply to MOCVD as well. A wide variety of materials can be deposited by MOCVD, either as single crystal, polycrystalline or amorphous films [10]. The most important application is for the deposition of the group III-V semiconductor compounds such as gallium arsenide (GaAs), indium arsenide (InAs), indium phosphide (InP) and gallium aluminum phosphide (GaAlP), particularly for epitaxial deposition. The most commonly used precursors are trimethyl gallium (TMGa), trimethyl arsenic (TMAs) and the hydrides, phosphine (PH<sub>3</sub>) and arsine (AsH<sub>3</sub>). Another important group of MOCVD materials consists of the II-VI compounds such as zinc sulfide (ZnS), zinc selenide (ZnSe), cadmium sulfide (CdS) and cadmium selenide (CdSe). Commonly used precursors are dimethyl cadmium (DMCd), diethyl telluride (DETe), diethyl zinc (DEZn) and hydrogen selenide (H<sub>2</sub>Se). Most MOCVD reactions occur in the temperature range of 600-1000°C and at pressure varying from 1 torr to atmospheric. Because of the highly critical requirements of most semiconductor applications, it is necessary to use the most precise equipment and extremely high purity gases. Electronic mass flow controllers, ultrafast bellows-sealed gas-switching valves, accurate venting control and elimination of dead space allow extremely rapid switching of gases [11]. As a result, extremely thin deposits can be produced (< 100 Å) with abrupt interfaces (< 10 Å). MOCVD is presently used very extensively in microwave and opto-electronics applications, in advanced laser designs such as double heterostructure, quantum well and large optical cavity lasers as well as bipolar, field-effect transistors, infra-red detectors and solar cells [12]. The equipment and chemicals used in MOCVD are expensive and production cost is high. For that reason, MOCVD is considered most often where very high quality is required. It has recently

been investigated for other applications in the area of very high temperature oxidation protection up to 2200°C.

### **1.3 Low Pressure CVD (LPCVD)**

#### **1.3.1 Introduction of LPCVD**

Low pressure CVD technique was developed to overcome the uniformity, step coverage, and particulate contamination limitations of APCVD systems [13][14][15]. In the mid-1970's, it was realized that low pressure CVD processing could have significant advantages over APCVD systems. By reducing the pressure, it was found that the diffusion coefficient was sufficiently enhanced that deposition became surface controlled. In this case, wafers could be stacked closely and placed in a diffusion furnace to be processed (hot-wall system). Since the temperature could be maintained very uniformly, deposition uniformity was excellent. Of equal importance, the large number of wafers that could be processed in each batch made the economics very favorable. The major design problem with such a reactor involves finding conditions for which the deposition is not only uniform on each wafer, but is uniform from wafer to wafer. Of course, the deposition rate has to remain high to retain the throughput advantage. It is sometimes possible to deposit films in the reaction rate limited regime, by operating LPCVD reactors at medium vacuum (0.25-0.5 torr), and moderate temperatures (550-600°C). At reduced pressure the mean free path of the reactant molecules is increased and also diffusion of the reactant gas molecules is sufficiently increased so that mass-transfer to the substrate do not limit the growth rate. The growth rate is limited by the surface reaction and depends on initial partial pressure of the reactants and the temperatures. Though the modification of the

the reactant gas molecules is sufficiently increased so that mass-transfer to the substrate do not limit the growth rate. The growth rate is limited by the surface reaction and depends on initial partial pressure of the reactants and the temperatures. Though the modification of the reactor design, depletion along the axis can be overcome allowing the reactor to accommodate large numbers of wafers. As the reactions are carried out at low pressure, gas phase reactions are almost eliminated, thus the films have lower particulate contamination [16]. The drawbacks of LPCVD are the relatively low deposition rates, and moderate operating temperatures. If we attempt to increase deposition rates by increasing the reactant partial pressures, that in turn can initiate gas phase nucleation. Operating the reactions at lower temperatures mostly results in no deposition at all. LPCVD reactors are designed mostly in two configurations:

- 1) horizontal tube reactors;
- 2) vertical tube reactors.

The horizontal tube reactor configuration which is predominantly used is described below.

### **1.3.2 Horizontal Tube LPCVD Reactors (hot wall)**

Horizontal tube reactors are the most widely used LPCVD reactors in Very Large Scale Integrated (VLSI) circuit processing [3]. They are employed for depositing poly-silicon, silicon nitride, undoped and doped  $\text{SiO}_2$  films etc. Usually these reactors are designed to have good uniformity in temperature obtained by large heating zone. They find broad applications because of their economy, throughput, uniformity of the deposited thin films, and ability to accommodate large diameter wafers. However a major disadvantage is very

low deposition rate and yield [17]. In this type of LPCVD reactors, the wafers are radially heated by resistive heating coils surrounding the chamber. Reactant gases are metered into one end of the horizontal quartz tube using gas flow panel including mass flow controllers, and reaction byproducts are pumped out of the other end. Vacuum pumps are used to attain the required low chamber pressures. An oil-sealed rotary mechanical pump is generally used along with a roots blower to attain low pressures.

### 1.3.3 Diffusion Model of LPCVD Reactors

A review of the diffusion reactor model based on the work of Middlemann and Yeckel [16] is discussed in this section. The following assumptions were made by them:

- 1) The wafers are stacked axially within a tubular reactor;
- 2) Symmetry is assumed about the axis of the reactor;
- 3) Only a single chemical species need to be considered;
- 4) The gas contains that species highly diluted in an inert carrier gas;
- 5) Only heterogeneous reactions need to be considered;
- 6) There is no gas flow in the interwafer region:

One of the useful results of the work of Middlemann and Yeckel [16] with the pure diffusion analysis is the uniformity of deposition. One way of expressing uniformity is by the radial thickness variation:

$$\text{variation [+ or -]} = 100 \times (d_{\max} - d_{\min}) / (d_{\max} + d_{\min}) \quad (1.1)$$

If the interwafer spacing and the dimension of the wafer are fixed, the uniformity shows a strong dependence on the Sherwood number,  $Sh$ , defined as:

$$Sh = k_D d / D \quad (1.2)$$

where,

$k_D$  is the mass transfer coefficient of the process;

$d$  is the relevant length dimension;

$D$  is the diffusion coefficient of the reactive compound.

When  $Sh$  is less than unity, the deposition process is surface controlled and when the  $Sh$  number is greater than unity the deposition process becomes diffusion controlled. If the  $Sh$  numbers are below  $10^{-3}$ , which are easily obtained in a LPCVD reactors, a uniform deposition of the film results.

## 1.4 CVD of $SiO_2$ Films

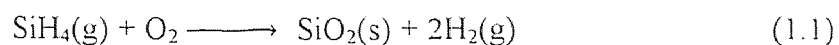
### 1.4.1 Methods of Preparing CVD of $SiO_2$ Films

There are various methods to prepare CVD  $SiO_2$  films. The choice of the reaction depends on the temperature requirements of the system. The deposition variables on which the growth rate of the CVD  $SiO_2$  film depends are: temperature, pressure, flow rate of the reactant gases and their ratios etc. The three temperature ranges in which the CVD  $SiO_2$  films are formed are:

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

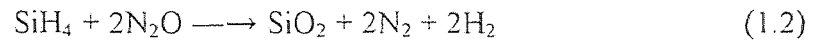
- 2) medium temperature deposition (450-800°C);
- 3) high temperature deposition (above 800°C).

**1.4.1.1 Low Temperature Deposition:** In the low temperature range SiO<sub>2</sub> films are formed by the reaction of silane and oxygen [18][19][20]. The depositions are carried in atmospheric pressure CVD reactors (APCVD), low pressure CVD reactors (LPCVD) or plasma enhanced CVD reactors (PECVD) [3]. LPCVD of SiO<sub>2</sub> films is not favorable from the reaction of SiH<sub>4</sub> and O<sub>2</sub> due to depletion effects [3]:



The reaction between silane and oxygen to form SiO<sub>2</sub> film follows a heterogeneous surface reaction. But sometimes SiO<sub>2</sub> particles are generated due to homogeneous gas phase nucleation which may cause particulate contamination in the deposited film. The deposition rate of the SiO<sub>2</sub> film increases with the temperature between 310 and 450°C and the activation energy is about 38.5 kJ/mol indicating an surface adsorption or gas phase diffusion process [19][20]. The deposition rate can also be increased by increasing the O<sub>2</sub>/ SiH<sub>4</sub> ration within a certain range and the deposition rate was observed to decrease eventually due to O<sub>2</sub> being adsorbed on the surface inhibiting the SiH<sub>4</sub> decomposition [19][20]. SiO<sub>2</sub> films which are deposited at low temperatures have lower densities and refractive indices than thermally grown oxides [21]. They also show higher etch rates in buffered Hydrofluoric acid (HF) solution than thermally grown oxide, while heating of such films around 700-1000 °C causes densification causing an increase in the

density and decrease in the etch rate [21]. SiO<sub>2</sub> films can be deposited by plasma enhanced reaction between SiH<sub>4</sub> and N<sub>2</sub>O or O<sub>2</sub> at temperatures between 200-400 °C [22]:

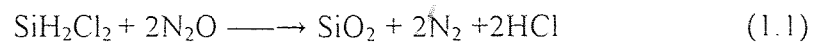


Nitrogen and hydrogen may become incorporated in the deposited films often. This results in a low ratio of N<sub>2</sub>O/ SiH<sub>4</sub> flow causing an increase in the refractive index due to large amount of nitrogen getting incorporated into the films and also in the formation of silicon rich films [3]. PECVD oxides generally contain H<sub>2</sub> in the form of Si-H, Si-O-H, and H-O-H [22]. The hydrogen concentration is a strong function of the deposition variables. Low deposition temperatures, high radio frequency (rf), and high carrier gas flow rates are suggested to prevent gas phase nucleation. The plasma oxide films are usually compressive, the values depending on the deposition temperature and growth rate. Low pinhole count, as well as conformal coating films, were obtained with PECVD oxides and the adhesion was reported to be excellent [3].

**1.4.1.2 Medium Temperature Deposition:** In the medium temperature range SiO<sub>2</sub> films are deposited in LPCVD reactors using tetraethylortosilane (TEOS) [13][23][24], diacetoxyditertiarybutoxysilane (DADBS) [23][24] etc. The deposition rate of the SiO<sub>2</sub> film shows an exponential increase as the temperature increases from 650-800°C with an apparent activation energy of 183 kJ/mol [3] which may cause thickness control problems. The deposition rate also depends on the TEOS partial pressure. The deposition rate was observed to be linearly dependent at low partial pressures and was observed to level off as

adsorbed TEOS saturates the surface [3]. The films deposited using TEOS have excellent uniformity and conformal step coverage [23][24].

**1.4.1.3 High Temperature Deposition:** In the high temperature ranges SiO<sub>2</sub> films are deposited using LPCVD reactors by the reaction of dichlorosilane and nitrous oxide [15][25]. K. Watanabe et used the following reaction to produce SiO<sub>2</sub> films:



The films produced by the above reaction produce excellent uniformity films and properties close to thermally grown oxide.

## 1.4.2 Properties of SiO<sub>2</sub> Films Deposited by Various CVD Techniques

**1.4.2.1 Conformal Coverage:** 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 the subsequent film depositions and patterning of conductors can become easier. For example, CVD SiO<sub>2</sub> films deposited from silane, have less thickness on the side walls and bottom corners of the trenches [26]. Step coverage gets worse with increasing aspect ratio (height/width) which can lead to the formation of the voids [26]. The step coverage can be improved by flowing the dielectrics at temperatures higher than 900 °C. SiO<sub>2</sub> 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 [27]. The addition of dopants such as phosphorous in SiO<sub>2</sub> films can degrade step coverage, but dopants such as boron facilitate the improvement of step coverage. Borosilicate glasses have excellent step coverage and can convert reentrant angles to



positive angles and can fill narrow spaces between metal lines without voids [26]. For CVD films the step coverage is related to the mobility of the recent species on the surface prior to the reaction to form the dielectric. For reactions involving silane the mobility of the absorbed precursor species is low for temperatures below 450 °C. In this case the step coverage is determined by the angular distribution of the silane molecules impinging on each point of the surface [3]. For LPCVD films, the mean free path of the molecule in the gas phase is large enough that the source of the recent species can be considered to be hemispherical [26]. For APCVD, because of the smaller mean free path, the solid angle of arrival of species is 90° or less on a vertical side wall [3]. This accounts for the good step coverage of LPCVD films. PECVD films have step coverage similar to LPCVD films. A different approach lies in improving the step coverage by the use of a silicon source precursor which has a higher surface mobility than silane. Tetraethoxysilane (TEOS) and diacetyditertiarybutoxysilane (DADBS) etc. are such compounds which produce excellent conformal films. The main limitation being the requirement of high deposition temperatures (above 650 °C). One of the most important problem related to step coverage is the quality of the oxide on the side walls and corners. Because of shadowing effects, which are also responsible for poor step coverage [28], the oxide in these areas has lower density than the oxide over the flat areas, which can be observed after an HF etch. Even electrical properties like dielectric breakdown will also be inferior. Films that have conformal coverage do not have these problems because the high surface mobility also helps to keep the density of the film constant over topography. Thus borosilicate films show uniform etch rates.

**1.4.2.2 Water Absorption:** Water is the most common impurity in low temperature deposited oxide and exists as absorbed water or in the form of silanol groups (SiOH) in the film. It is undesirable because it decreases the resistivity [26][29], both in bulk and surface of the dielectric, enhances crack formation (if the dielectric is under tensile stress) and increases the effective dielectric constant[26]. This water can be evolved by the heating of the dielectric film. The release of -OH group with temperature can lead to degradation of short channel silicon devices, causing a problem for reliability of VLSI circuits [26]. Moisture diffuses through the micropores of the porous oxide films and then travels as a function of time. Thus high density (nearing that of thermal oxide  $2.2 \text{ g/cm}^3$ ) are desired to minimize the water absorption. The absorption of water has a close relation to the density of the oxides. As the porosity of the oxides increases the water absorption capacity of the oxides increases [30]. The amount of porosity of an oxide film can be determined from the amount of water it tends to absorb. The wafer, which is loosely bound as  $\text{H}_2\text{O}$  molecules, is easily removed by baking the films at about  $200 \text{ }^\circ\text{C}$ . The remaining water which exists as -OH bound to Si, is evolved at  $450 \text{ }^\circ\text{C}$ . In general the lower the temperature of deposition the more porous the oxide films tend to be [29]. This is because of the thermal energy is not sufficient to break the Si-O bonds and to cause compaction of the structure [29].  $\text{SiO}_2$  CVD films are densified by going to temperatures of  $800 \text{ }^\circ\text{C}$  or higher so that moisture absorption is not a problem for dielectrics used over polysilicon or silicides [29]. The presence of dopants can affect the water absorption and permeability. Phosphorus decreases the diffusion of water through the film, whereas boron increases it [31]. Plasma films are more resistant to moisture than CVD films

dielectrics used over polysilicon or silicides [29]. The presence of dopants can affect the water absorption and permeability. Phosphorus decreases the diffusion of water through the film, whereas boron increases it [31]. Plasma films are more resistant to moisture than CVD films deposited at the same temperature, because of ion bombardment from the plasma. However, even plasma films require deposition temperatures greater than the 300 °C to form moisture resistant films.

**1.4.2.3 Stress:** 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 generated in the films below the dielectric film can cause many problems. 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 [32][33]. The intrinsic stress depends on the deposition techniques and the process parameters. The stresses discussed below are of the films deposited on silicon and are the total stresses. APCVD oxide films tend to have tensile stresses, whereas LPCVD films are compressive [26]. PECVD oxides have compressive stresses, and the stress is a function of applied radio frequency (rf), pressure etc. The stress becomes more compressive as the pressure is reduced [26]. Low temperature oxide films tend to become more tensile with increasing temperatures then would be expected from the thermal expansion coefficients of Si and SiO<sub>2</sub> [29]. Above a certain temperature the stress in the oxide films decreases with the temperatures [34]. The relaxation of the stress is due to the rearrangement of the bonds in the film [29]. Water absorption causes the stress to become more compressive.

Phosphorus reduces in APCVD films [26]. The stresses decrease with increasing phosphorous content up to a particular concentration [26].

### 1.5 Objectives of this Thesis

In this study, ditertiarybutylsilane (DTBS) has 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 550 to 850°C at a constant pressure of 0.2 torr, a DTBS flow rate of 10 sccm, and varied an O<sub>2</sub> flow rate to get desired flow rate of DTBS/O<sub>2</sub> ratio. The effects of deposition parameters on the growth rate and physical properties of the LPCVD SiO<sub>2</sub> films were investigated. Some properties of ditertiarybutylsilane (DTBS) are listed in Table 1.2.

**Table 1.2.** Properties of ditertiarybutylsilane (DTBS)

formula	SiH <sub>2</sub> (C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>
molecular weight	144 g/mol
vapor pressure	20.5 torr at 20°C
boiling point	120°C at 760 torr

## CHAPTER 2

### EXPERIMENTAL

#### 2.1 Set-up of LPCVD Reactor

The schematic for hot wall low pressure chemical vapor deposition reactor is shown in the Fig 2.1. The reactor consists of fused quartz tube of 5 inch<sup>φ</sup> in diameter and about 50 inch in length. The tube is kept inside a *Lindberg* 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 provided inside the quartz tube. Heating is provided by Lindbar silicon carbon heating elements. It is equipped with Platinel II thermocouples which senses the temperature of the zone and the voltage developed by it is used for automatic control. The tube and the coils are covered with ceramic enclosure. The tube is sealed on both ends by end caps and metallic lids. During heating process, thermal expansion of 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 done by fans when the temperature of the furnace is increased more than 400°C. A MKS Baratron gauge with a range of 10 torr is used to monitor the pressure at the input end. The monitored pressure is displayed by MKS display unit. The input seal consists of three provisions for gas inlet, so that, if more than one precursor are used, they will mix together and diffuse inside. The system will be kept at low pressure by vacuum pumps. This system uses a booster pump and a mechanical backing pump. Booster pump is used to enhance the flow of gases and thereby pumping speed.

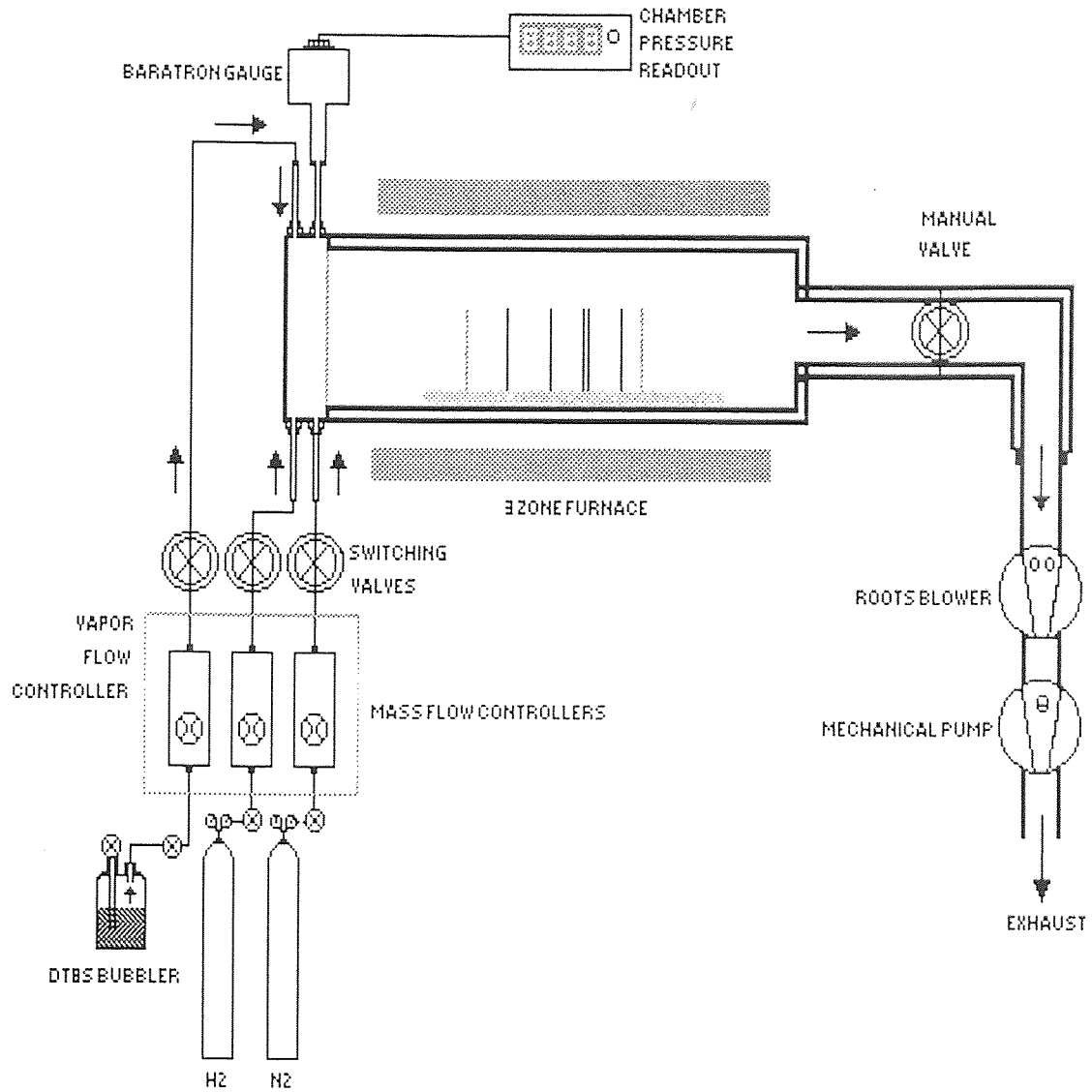


Figure 2.1 A schematic for LPCVD reactor

Mechanical backing pump does the real pumping and this combination provides a vacuum as low as a milli torr. Booster pump is a *Ruvac* single stage roots pump operated at 220 V supply and that 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 pumping process.

## 2.2 Pre-experiments

### 2.2.1 Flow Rate Calibration

Gas flows were regulated by Applied Materials model AFC 550 automatic N<sub>2</sub> mass flow controllers which were corrected for DTBS and O<sub>2</sub> flows. The pressure in the reactor was measured with a baratron gauge from MKS. The N<sub>2</sub> calibration of the AFC was checked by delivering a fix volume of gas (product of the metered flow rate and the 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:

$$\text{F.R.} = 60(\Delta P/\Delta t)(T_0 V/P_0 T) \quad (2.1)$$

Where  $\Delta P$  = pressure increase, Torr

$$T_0 = 273 \text{ K}$$

$$P_0 = 760 \text{ Torr}$$

$$V = \text{volume of the chamber; cm}^3$$

$$\Delta t = \text{time of delivering gas, sec.}$$

Routine flow rate calibrations were conducted once a week for 2:1 O<sub>2</sub>/DTBS ratio, each experiments for 5:1 and 10:1 O<sub>2</sub>/DTBS ratio.

### 2.2.2 Leakage Check

Routine leakage checks were conducted everyday. After evacuating the chamber with valves and flow controller fully open, close the valves and check the leakage.

## 2.3 Experimental Procedures

### 2.3.1 Wafer Loading

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 wafers 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 sided polished wafers are 10 cm in diameter, 525 μm in thickness, labeled and weighed by electronic weighing balance. In most of deposition experiments



three wafers were loaded in the boat with three dummies were positioned at the back of each wafers. The boat was placed at the center of the reactor, 64 cm from the chamber.

### **2.3.2 Setting Deposition Conditions**

After loading, the furnace was brought to low pressure by pumping down the chamber for about an hour. Then temperature was raised to desired level in steps of 250°C. Once the temperature readings for each of three zones was reached at 250°C, then the temperature was raised with the similar way until it was reached at desired temperature.

### **2.3.3 Film Deposition**

Once the desired temperature was reached, waited about 20 to 30 min for annealing, then started depositions by flowing DTBS and oxygen into the reactor. Then started closing the valve until the readings were reached at 0.2 torr. From this moment, recorded the starting time and kept depositing until a desired deposition hour was reached.

## **2.4 Characterization of SiO<sub>2</sub> Thin Films**

### **2.4.1 Thickness**

Film thickness was measured by Nanospec Interferometer which bases its estimation on the monochromatic light interface fringes formed within a zone limited by the 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 thin film. 1.46 is the typical

value, then used the real value measured by the ellipsometer. The average value was taken as the film thickness. Deposition rate was determined as the film thickness over the deposition time,  $D.R. = \Delta T/\Delta t$ , and averaged over the three wafers in each run.

#### 2.4.2 Film Density

Film density was estimated from the mass-volume relationship. Since the wafer area is known to be  $78.5 \text{ cm}^2$  and deposition occurred only on one side, the density can be calculated from the mass increase of the wafer due to film formation and the average thickness of film.

$$\rho = \Delta \text{ mass} / (\pi r^2 \times \text{thickness}) \quad (2.2)$$

where,

$\rho$  is density;

$\Delta$  mass is the mass difference, before and after deposition;

$\pi$  is constant, equals to 3.14;

$r$  is radius of wafer, equal to 5 cm;

$\pi r^2$  is area of wafer,  $78.54 \text{ cm}^2$ .

#### 2.4.3 Refractive Index

The refractive index of the deposits was determined by a Rudolph Research AutoEL ellipsometer, which consists of a polarizer and a compensator. Plane ( $45^\circ$ ) polarized light from 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 the 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, then the average value was taken.

#### **2.4.4 Infrared Spectra**

Infrared spectroscopic 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 reflected IR spectrum versus wave number (reciprocal of wavelength) can be used to detect the presence of vibrational mode of a particular molecule. IR spectroscopic analysis were carried out for various samples. The three absorptions at  $1080\text{ cm}^{-1}$ ,  $800\text{ cm}^{-1}$ , and  $460\text{ cm}^{-1}$  characterized  $\text{SiO}_2$  films.

#### **2.4.5 Stress**

The stress of the film was determined by a house-developed device, employing a laser beam equipment which measures change in the 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 thus their separation could be measured more accurately. The change in the separation of these two points was then fed into Stony's Equation [7] to obtain actual stress value. The calculation formula is:

$$\delta = 12.3D/T \quad (2.3)$$

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

T = thickness of the films ( $\mu\text{m}$ );

$\delta$  = stress of the film (MPa), negative value indicates compressive stress.

## CHAPTER 3

### RESULTS AND DISCUSSIONS

#### 3.1 Temperature Effects

##### 3.1.1 Film Growth Rate Analysis

One of the most important aspects of the film is the rate of film growth, with respect to deposition temperature. Since a chemical reaction is involved in the formation of the film, the rate of 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 SiO<sub>2</sub> dielectric films deposited using ditertiarybutylsilane precursor. In this study, the average deposition rate of the three wafers has been used for the investigation of growth rate and characterizations of the film properties. SiO<sub>2</sub> films were deposited at different temperatures, from 550-850 °C. Other parameters like pressure, flow rate, deposition time and wafer spacing were kept constant. For the other study, producing crack-free thick oxide films, pressure and wafer spacing were kept constant, whereas flow rate and deposition time were varied. For every experiments the growth rate, that is, thickness deposited per hour is calculated for each wafer and average was taken. Generally, the rate of most reactions increases as the temperature is increased. But the temperature dependence of the rate has been found to fit the expression proposed by an Arrhenius curve:

$$\text{Growth Rate}(G.R) = A \exp(-E_a/RT) \quad (3.1)$$

where,

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

$E_a$  is the apparent activation energy of the chemical reaction;

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

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 negative slope. This type of curve is called an *Arrhenius plot*. The negative slope of the curve gives the ratio between 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 the Ln of growth rate (in Å per minute) plotted against reciprocal of deposition temperature in Kelvin scale. The experiments were carried out between temperatures of 550 and 850 °C; DTBS and O<sub>2</sub> flow rate of 10 sccm and 20 sccm; pressure of 0.2 torr. Figure 3.2 shows the activation energy and from the graph, the growth rate follows Arrhenius behavior between 550 and 750 °C. After 750 °C, the growth rate was slightly decreased as the temperature was increased. There was no or little deposition below 550 °C. The slope of the curve was found to be -6.3172 giving an activation energy of about 12.6 K cal/mol.

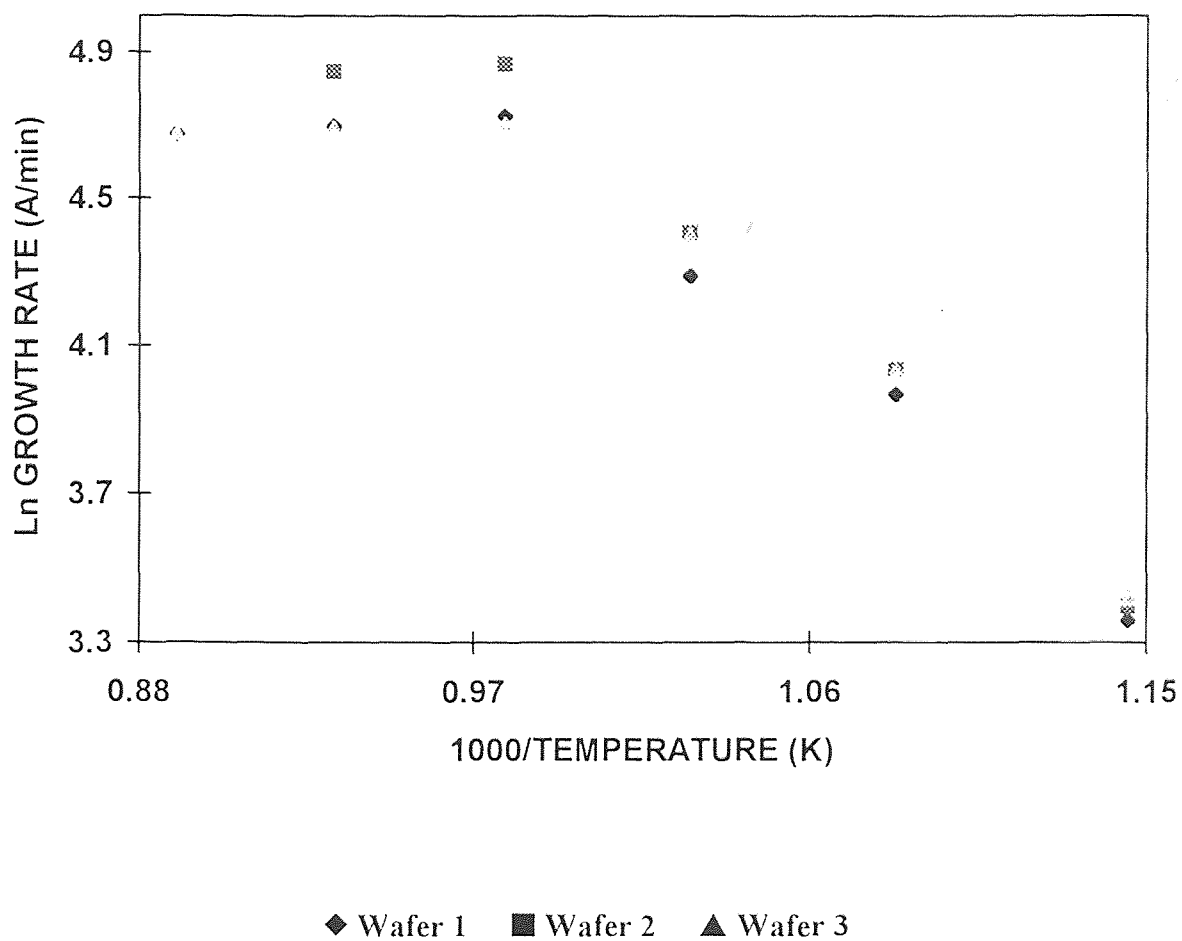
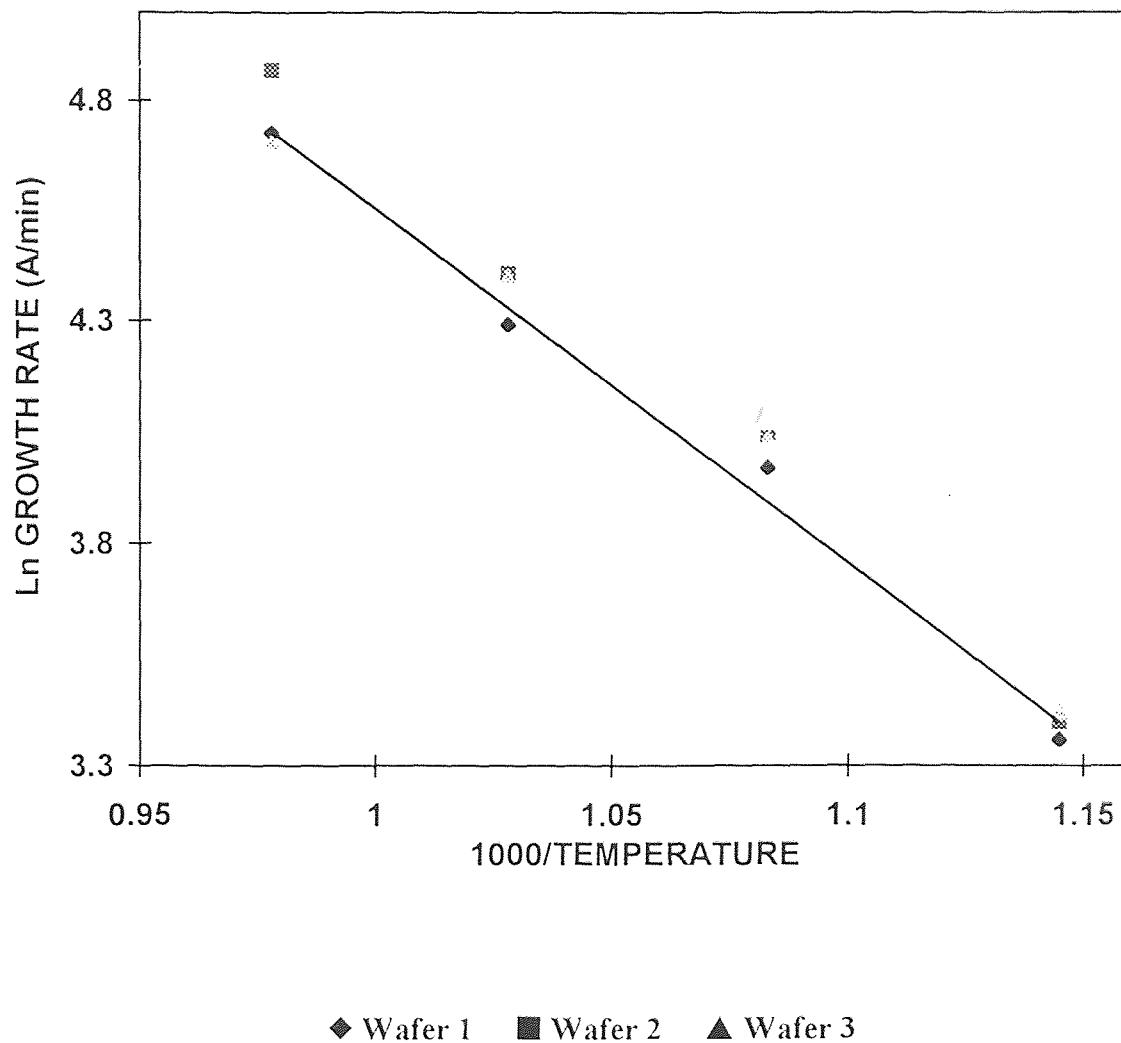


Figure 3.1 Variation of Growth Rate as a Function of Temperature at Fixed Flow Rate  
Ratio  $O_2/DTBS = 2/1$ , Pressure = 200 mTorr



**Figure 3.2** Activation Energy, Effect of Temperature on the Growth Rate, Showing Arrhenius Behavior between 600 and 750 °C, Slope = -6.3172, Flow Rate Ratio  $O_2/DTBS = 2/1$ , Pressure = 200 mTorr



### 3.1.2 Density Analysis

The density of the deposited film was found to be independent of deposition temperatures. A graph plotted by taking thickness of the films deposited at various temperatures and for various length of time, against the mass deposited on the same wafer, is shown in Figure 3.3. The thickness of the film deposited on each side is measured using Nanospec at five different points. The average thickness for each wafers was added together and was taken for plotting the graph. The mass deposited on the film<sup>f</sup> was measured using electronic weighing balance before and after each depositions. The graph shows the mass of the film deposited for a various deposition temperatures in the x-axis. The y-axis shows the corresponding thickness deposited on each wafers. The linearity of the curve indicates that the density is independent of temperature. Density was calculated from the fundamental mass-volume relation:

$$\rho = \Delta mass / (\pi^2 \times thickness)$$

where,

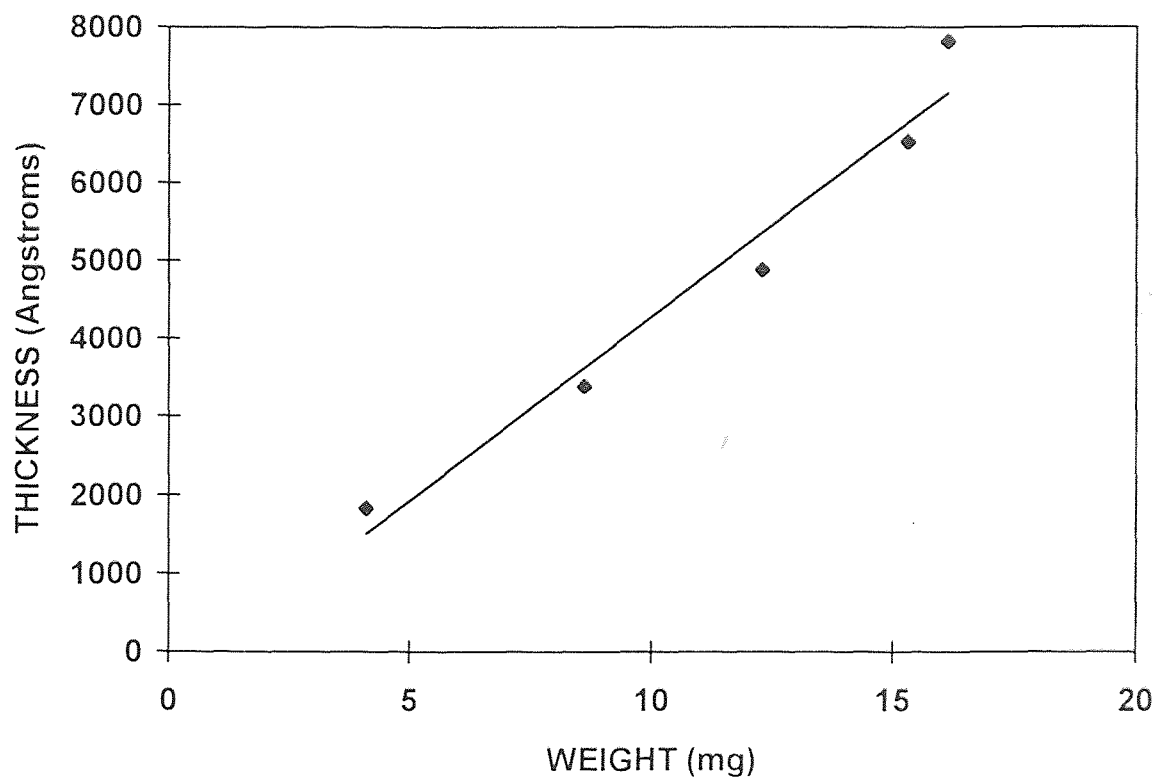
$\rho$  is density;

$\Delta mass$  is the mass difference, before and after deposition;

$\pi$  is constant, equals to 3.14;

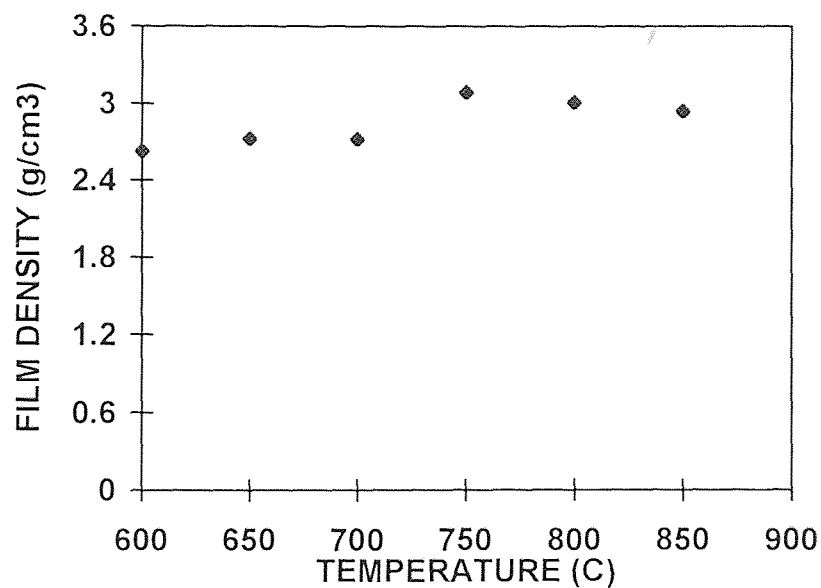
$r$  is radius of wafer, equals to 5 cm;

$\pi^2$  is the area of wafers, 78.54 cm<sup>2</sup>



**Figure 3.3** A plot of Thickness of the Film versus Mass Deposited on the Wafers at Various Temperatures, from 550 to 850 °C, slope = 470.68, Flow Rate Ratio  $O_2/DTBS = 2/1$ , Pressure = 200 mTorr

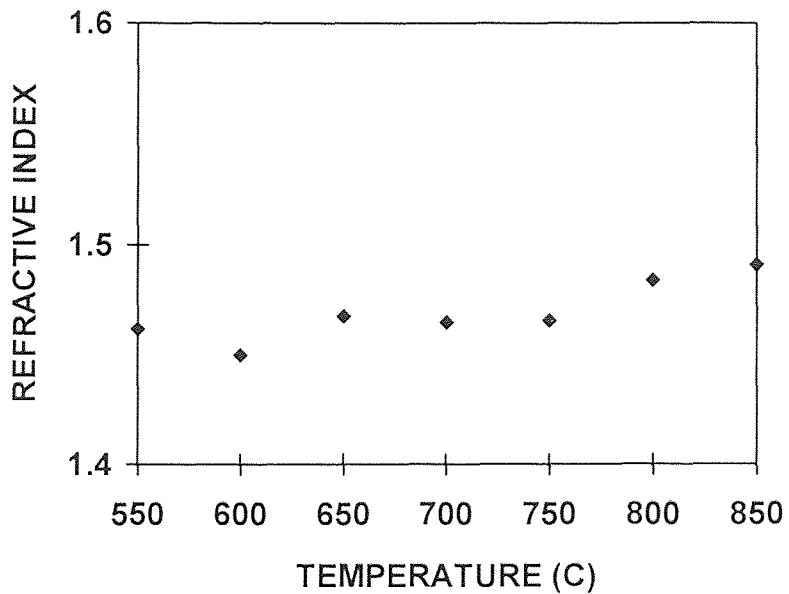
From Figure 3.3, as the area of the wafer is constant, density can be calculated from the slope of the curve. The slope of the curve was about  $470.68 \text{ \AA/gm}$ , and the density thus estimated was around  $2.71 \text{ gm/cm}^3$ . Figure 3.4 shows variation of film density as a function of various temperatures. The slope slightly increases as temperature is increased.



**Figure 3.4** Variation of Film Density as a Function of Various Temperature, Flow Rate Ratio  $O_2/DTBS = 2/1$ , Pressure = 200 mTorr

### 3.1.3 Refractive Index

Figure 3.5 shows the variation of refractive index as a function of various temperatures at fixed flow rate ratio and pressure. The refractive index of the deposits was determined by using a Rudolph Research AutoEL Ellipsometer at five different points. The average was then taken for plotting.



**Figure 3.5** Variation of Refractive Index as a Function of Various Temperatures, from 550 to 850 °C, Flow Rate Ratio O<sub>2</sub>/DTBS = 2/1, Pressure = 200 mTorr

### 3.2 Film Characterizations at Various Flow Rate Ratio

#### 3.2.1 Densities at Various Flow Rate Ratio

Film characterizations were also performed at various flow rate ratio,  $O_2:DTBS = 2:1, 5:1$  and  $10:1$  at  $750\text{ }^\circ\text{C}$  and  $850\text{ }^\circ\text{C}$ . Figure 3.6 and 3.7 show the plotting of density, respectively at  $750\text{ }^\circ\text{C}$  and  $850\text{ }^\circ\text{C}$ .

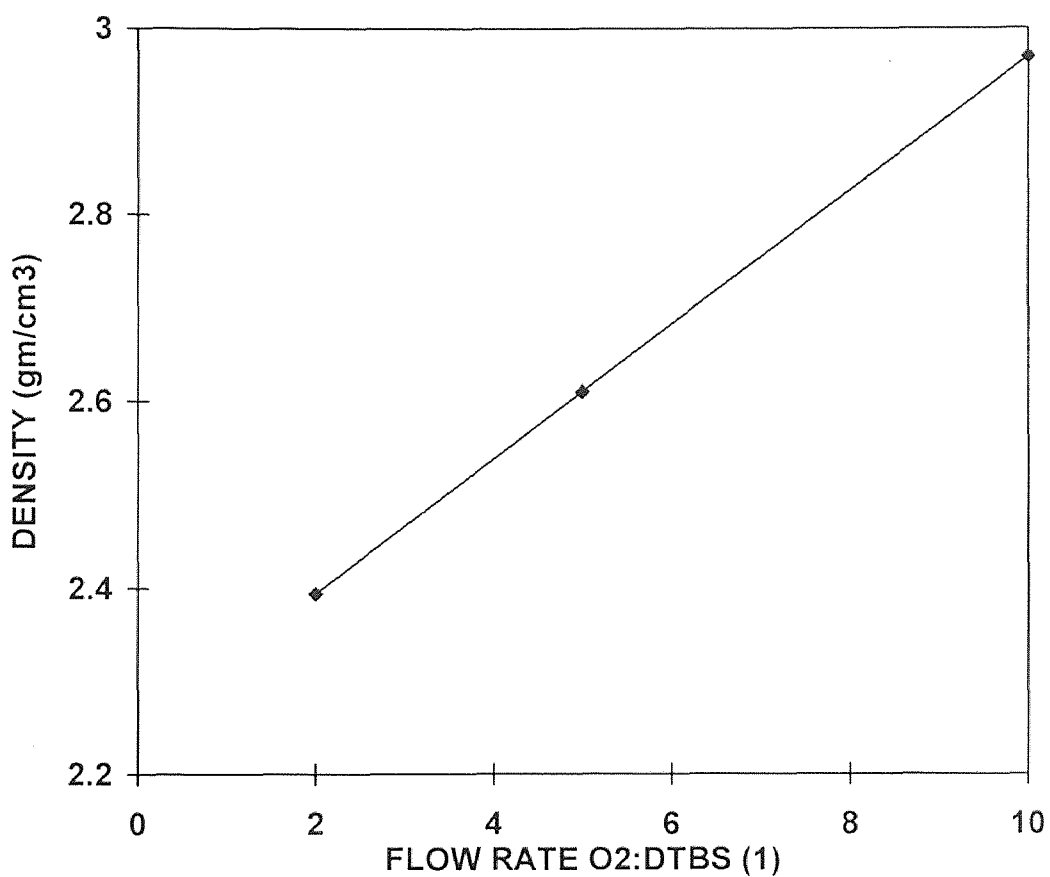


Figure 3.6 Densities at Various Flow Rate Ratio  $O_2/DTBS = 2/1, 5/1,$  and  $10/1,$   
Pressure = 200 mTorr, Temperature =  $750\text{ }^\circ\text{C}$

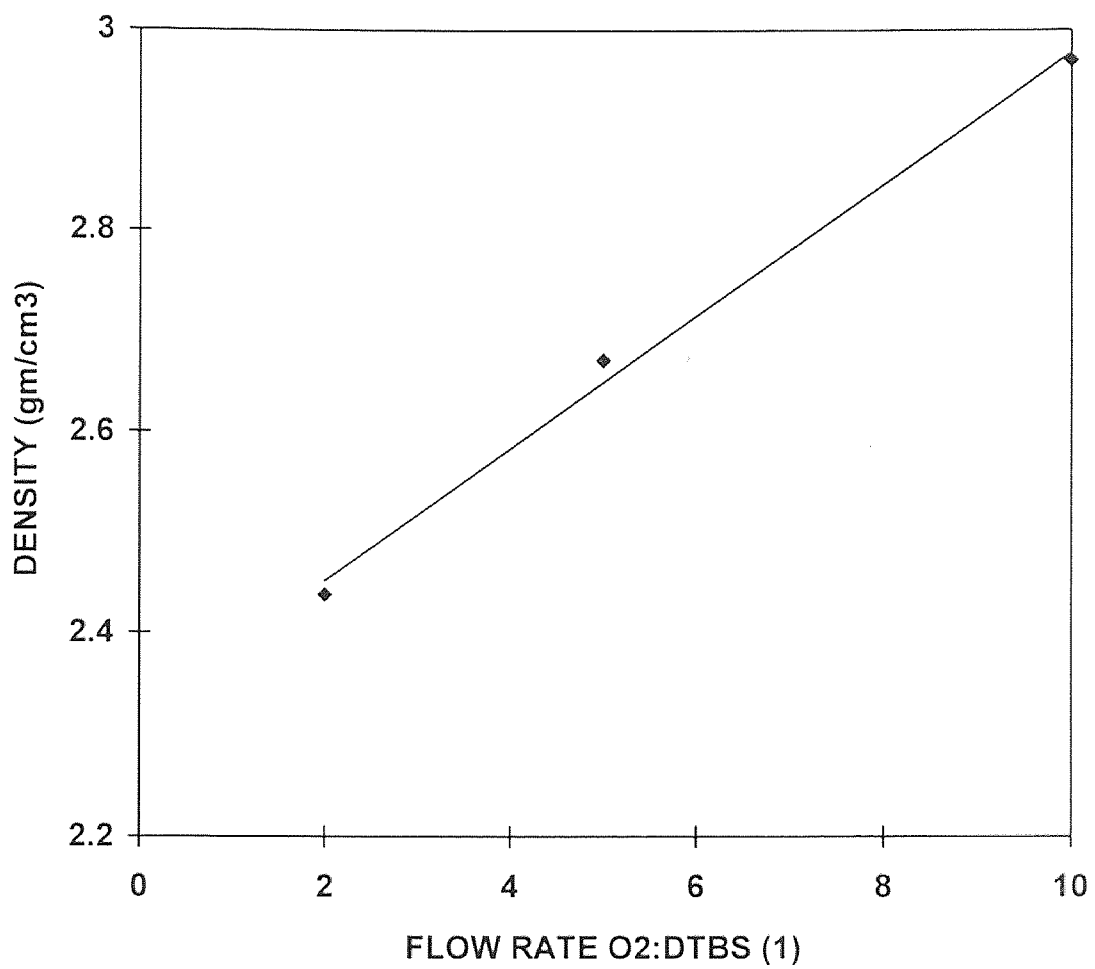
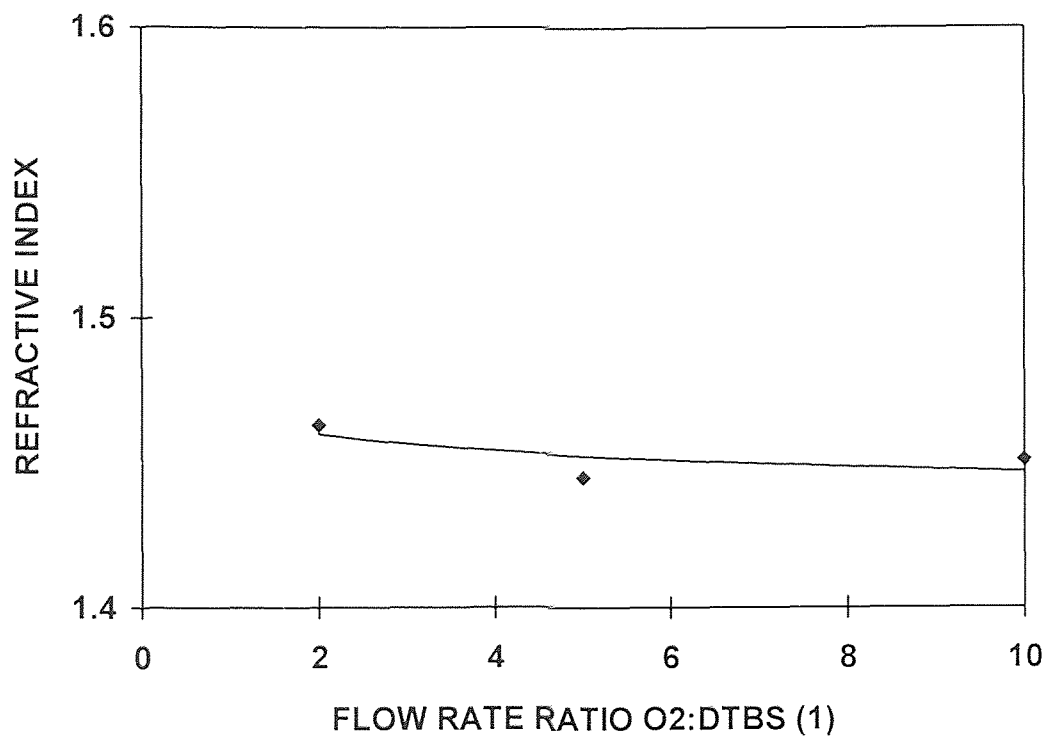


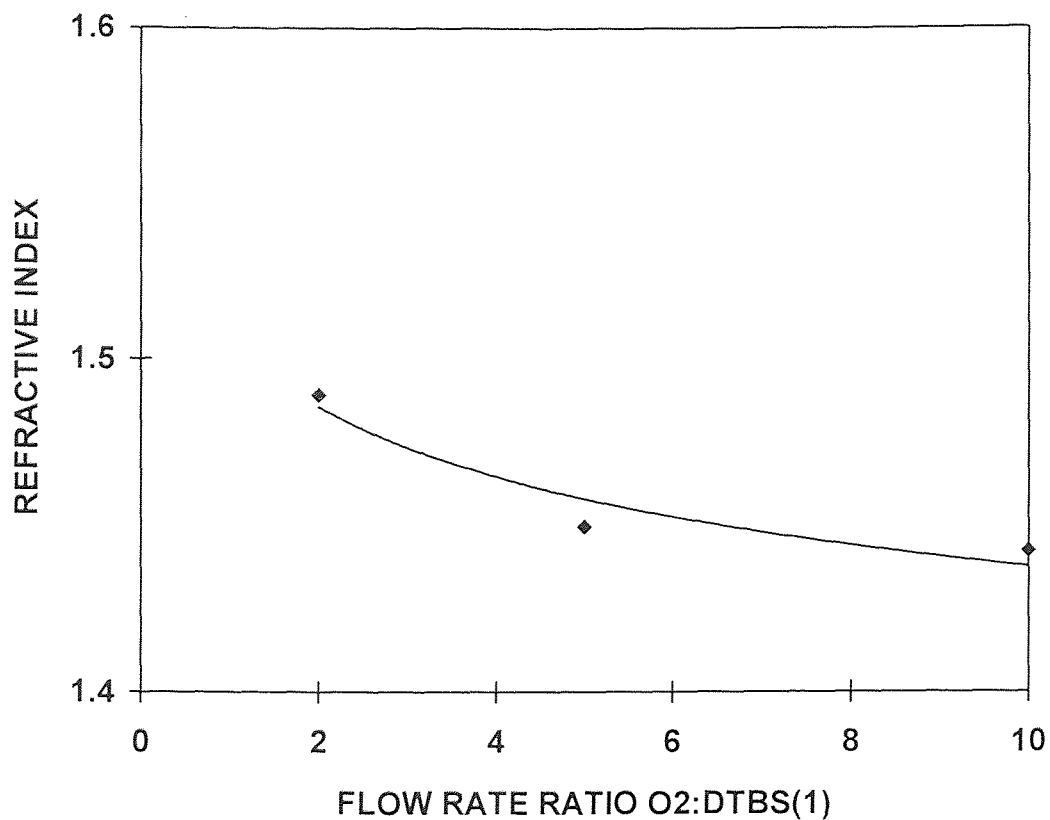
Figure 3.7 Densities at Various Flow Rate Ratio O<sub>2</sub>/DTBS = 2/1, 5/1, and 10/1  
Pressure = 200 mTorr, Temperature = 850 °C

### 3.2.2 Refractive Index at Various Flow Rate Ratio

Figure 3.8 and 3.9 show the plotting of refractive index at various flow rate ratio  $O_2/DTBS = 2/1, 5/1, \text{ and } 10/1$  at  $750\text{ }^\circ\text{C}$  and  $850\text{ }^\circ\text{C}$ . From each graphs, refractive index was consistent regardless of flow rate ratio.



**Figure 3.8** Refractive Index at Various Flow Rate Ratio  $O_2/DTBS = 2/1, 5/1, \text{ and } 10/1$   
Pressure = 200 mTorr, Temperature =  $750\text{ }^\circ\text{C}$

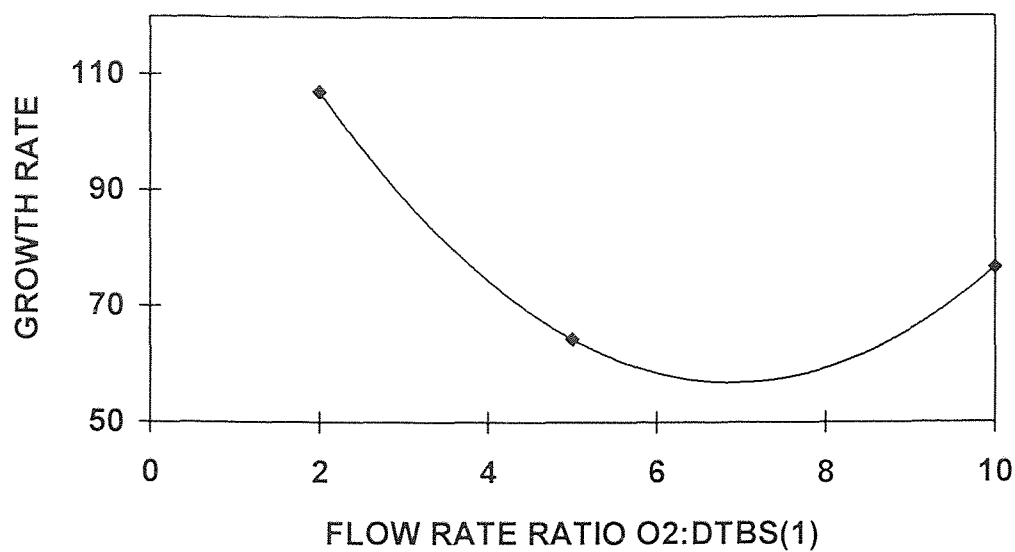


**Figure 3.9** Refractive Index at Various Flow Rate Ratio O<sub>2</sub>/DTBS = 2/1, 5/1, and 10/1  
Pressure = 200 mTorr, Temperature = 850 °C

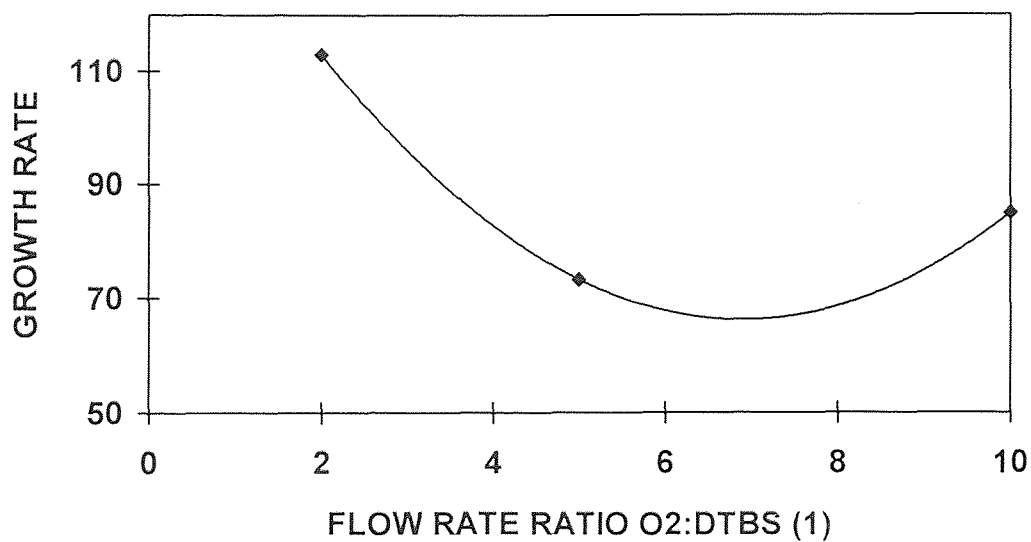
### 3.2.3 Thickness

Figure 3.10 and 3.11 show the plotting of thickness at various flow rate ratio O<sub>2</sub>/DTBS = 2/1, 5/1, and 10/1 at 750 °C and 850 °C. In both graphs, when the flow rate ratio O<sub>2</sub>/DTBS was 2/1, they have the highest thickness.





**Figure 3.10** Growth Rate at Various Flow Rate Ratio O<sub>2</sub>/DTBS = 2/1, 5/1, and 10/1  
Pressure = 200 mTorr, Temperature = 750 °C



**Figure 3.11** Growth Rate at Various Flow Rate Ratio O<sub>2</sub>/DTBS = 2/1, 5/1, and 10/1  
Pressure = 200 mTorr, Temperature = 850 °C

### 3.3 Deposition of Crack-free Thick Oxide Films

#### 3.3.1 Flow Rate Ratio $O_2/DTBS = 5/1$ at $850\text{ }^\circ\text{C}$

Another purpose of my study was to produce crack-free thick oxide films. Parameters like flow rate ratio and deposition temperatures were varied each experiments until crack-free film was produced. In order to have crack-free films, the stress must be compressive. A piece of quartz was put into reactor chambers along with other wafers to see transparency after each depositions. Refractive index could not be measured since the films were too thick to be measured. Therefore, refractive index was assumed to be 1.45 through out experiments. The best conditions for producing crack-free thick oxide films was found out to be flow rate ratio  $O_2/DTBS = 5/1$ , temperature =  $850\text{ }^\circ\text{C}$ , pressure = 200 mTorr. The average of compressive stress was found to be 26.4 Mpa. Figure 3.12 shows the plotting of thickness as a function of deposition time. Figure 3.13 shows the plotting of stress as a function of deposition time. Films were deposited for exactly 5 hours, then continuously deposited for 5 hours again using the same wafers until about  $10\lambda\text{m}$  oxide films were produced with no sign of cracks on them. From figure 3.12, it indicates that thickness linearly increases as deposition time is increased. From figure 3.13, it shows the stress was fairly consistent through out experiments.

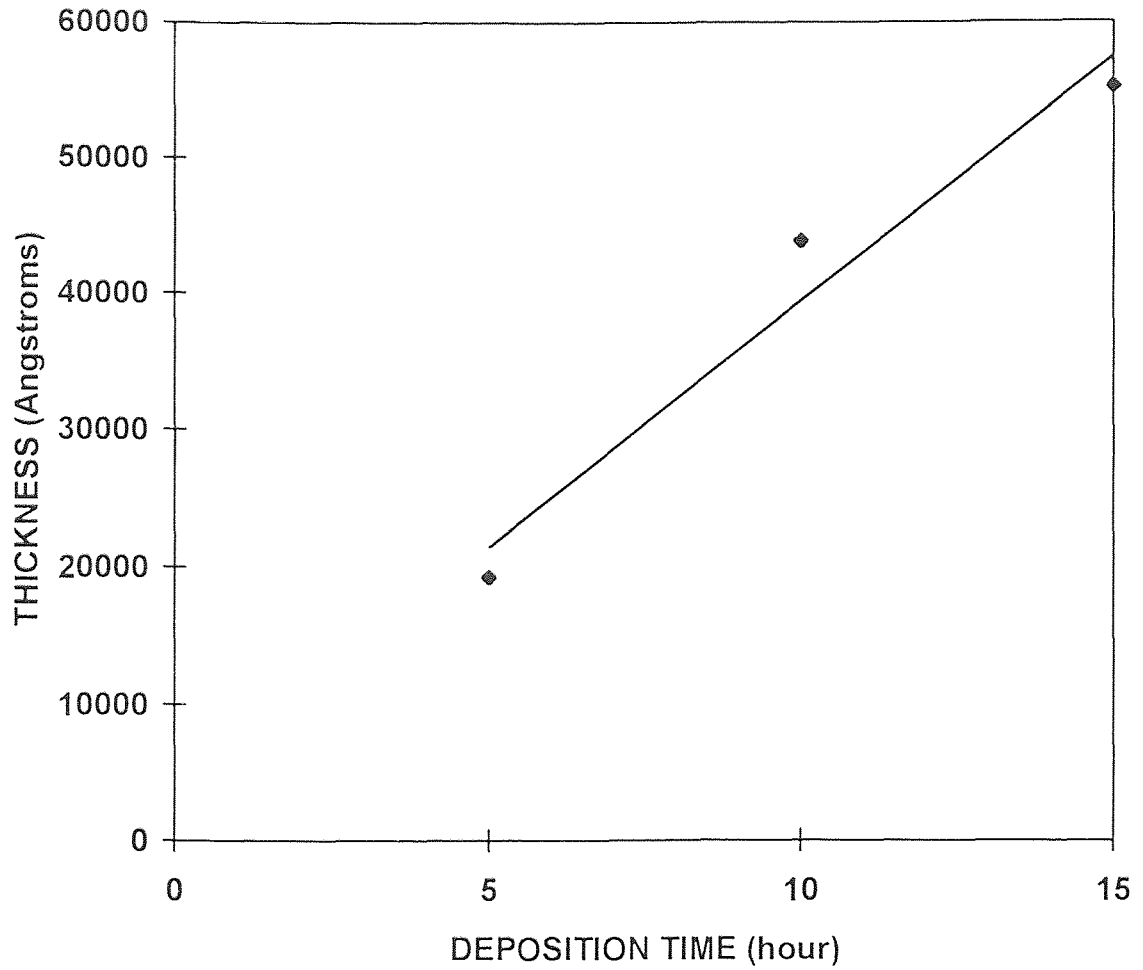
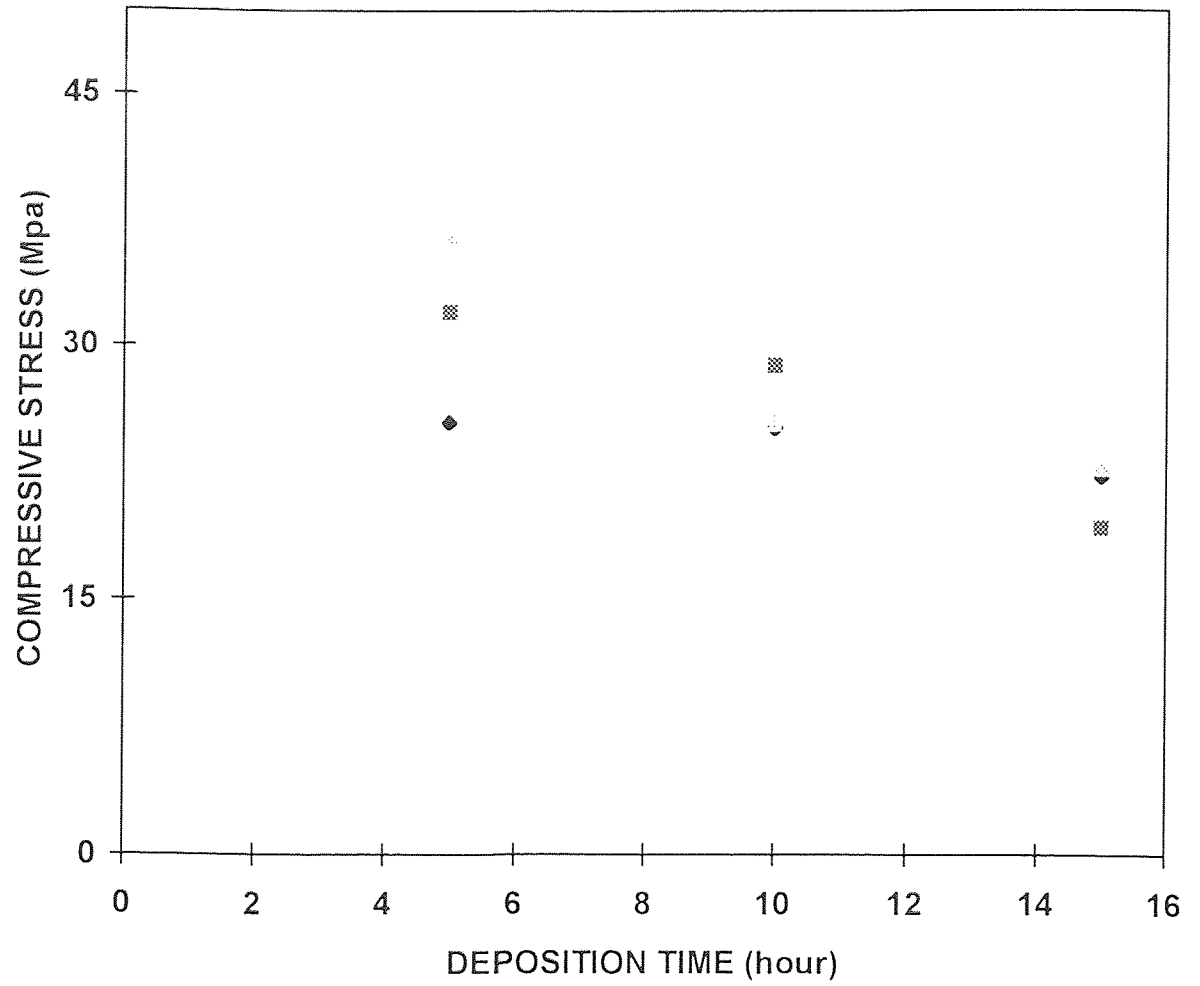


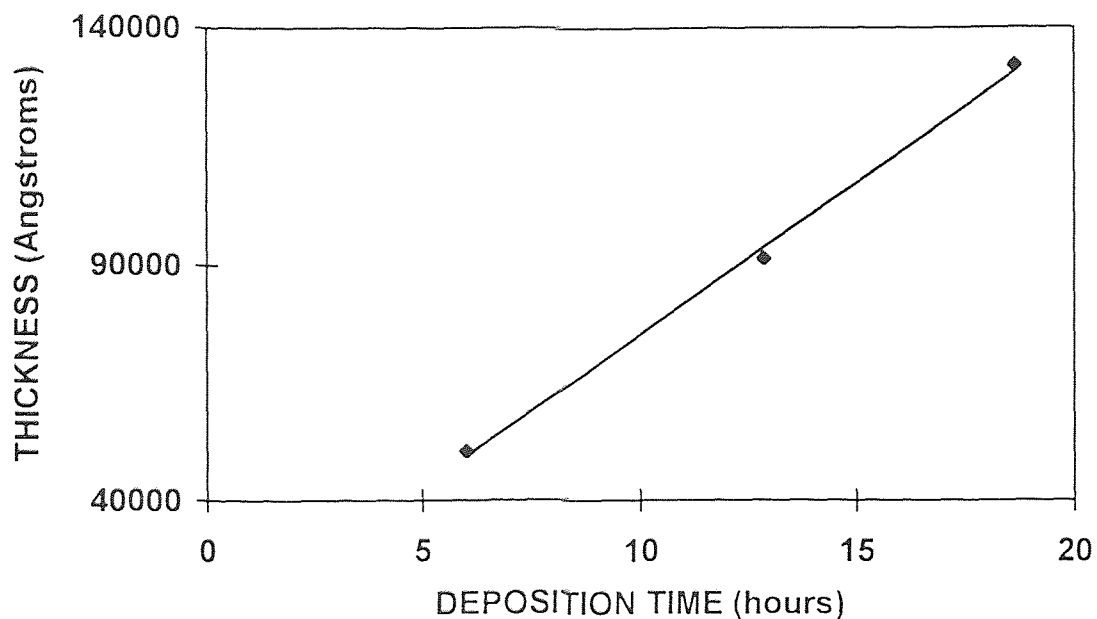
Figure 3.12 Thickness as a Function of Deposition Time, Temperature = 850 °C  
Pressure = 200 mTorr, Flow Rate Ratio O<sub>2</sub>/DTBS = 5/1



**Figure 3.13** Compressive Stress as a function of Deposition Time, Pressure = 200 mTorr  
Temperature = 850 °C, Flow Rate Ratio O<sub>2</sub>/DTBS = 5/1

### 3.3.2 Flow Rate Ratio $O_2/DTBS = 10/1$ at $700\text{ }^\circ\text{C}$

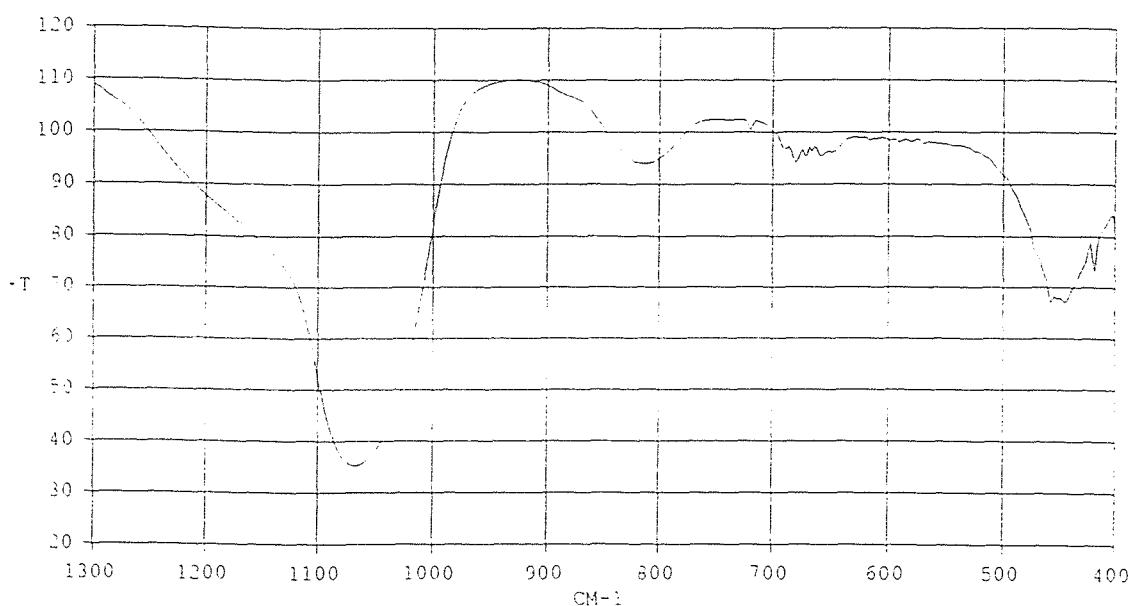
Another experiments were performed to produce crack-free thick oxide films with flow rate ratio  $O_2/DTBS = 10/1$ , temperature =  $700\text{ }^\circ\text{C}$ . Although this conditions did produce thick oxide crack-free films after 13 hours, stress was tensile and the piece of quartz started blackening. Figure 3.14 shows the plotting of thickness as a function of deposition time at  $700\text{ }^\circ\text{C}$ .



**Figure 3.14** Thickness as a Function of Deposition Time, Temperature =  $700\text{ }^\circ\text{C}$ , Pressure = 200 mTorr, Flow Rate Ratio  $O_2/DTBS = 10/1$

### 3.4 IR Spectroscopic Analysis

A plot of energy level of the reflected IR spectrum versus wave number (reciprocal of wavelength) can be used to detect the presence of vibrational mode of a particular molecule. IR spectroscopic analysis were carried out for various samples. The three absorptions at  $1080\text{ cm}^{-1}$ ,  $800\text{ cm}^{-1}$ , and  $460\text{ cm}^{-1}$  characterized  $\text{SiO}_2$  films. Very little shift of each peaks was observed with changing temperatures. Figure 3.15 shows infrared spectrum of  $\text{SiO}_2$  at  $700\text{ }^\circ\text{C}$ .



**Figure 3.15** FTIR Spectrum of LPCVD  $\text{SiO}_2$  film, Flow Rate Ratio  $\text{O}_2/\text{DTBS} = 2/1$   
Pressure = 200 mTorr, Temperature =  $700\text{ }^\circ\text{C}$

## CHAPTER 4

### CONCLUSIONS

Silicon dioxide thin films were deposited on silicon wafers 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 films were characterized by measuring growth rate, density, refractive index, stress and infrared spectra. The growth rate was found to follow an Arrhenius with the variation in the temperature with an activation energy of 12.6 kcal/mol. The growth rate was found to be inversely proportional to the temperature in the range 550-750 °C. The refractive index and density were observed to be close to 1.47 and 2.71 g/cm<sup>3</sup> respectively, comparable with the values of that of a thermally produced oxide. IR spectroscopic analysis were carried out, the three maxima absorptions at 1080 cm<sup>-1</sup>, 800 cm<sup>-1</sup>, and 460 cm<sup>-1</sup> characterized the SiO<sub>2</sub> films. Very little shift of each peaks was observed with temperature change. Producing crack-free thick oxide films were performed at two different conditions. One was at 850 °C with flow rate ratio O<sub>2</sub>/DTBS = 5/1 and the other was at 700 °C with flow rate ratio O<sub>2</sub>/DTBS = 10/1. The former condition produced compressive stress with lower growth rate, and the latter condition produced tensile stress with higher growth rate. A flow rate ratio O<sub>2</sub>/DTBS = 5/1 at 850 °C was found to be a better condition to produce crack-free thick oxide films.

## REFERENCES

1. Pierson, O.Hugh, *Handbook of Chemical Vapor Deposition (CVD)*, Noyes Publications: New Jersey, 1992
2. Sherman, Arthur, *Chemical Vapor Deposition for Microelectronics*, Noyes Publications: New Jersey, 1987
3. Coulson, A.R and Tauber, R.N., *In Silicon Processing for the VLSI ERA* ;Wolf, R. Tauber, R.N.,Eds; Lattice Press: California, 1987
4. Riedling, K., *Ellipsometry for Industrial Applications*, Springer-Verlag/Wien: New York, 1988
5. Kern, W., V.S. Ban, *Chemical Vapor Deposition of Inorganic Thin Films*, Thin Film Processes, edited by J.L. Vossen and W. Kern Eds.; Academic Press, New York, 1978
6. Van den Brekel, C.H.J., *Chemical Vapor Deposition*, Blocher, J.M.; Vuilland, G.E.and Wahl, G. Eds., The Electrochemical Society: Pennington, New Jersey, 1981
7. O'Mara, W.C. and Herring, R.B. and Hunt, L.P., *Handbook of Semiconductor Silicon Technology*, Noyes Publications: New Jersey, 1990
8. Kern W., *In Microelectronic Material and Processes*, R.A. Levy Eds., Kluwer Academic: New Jersey, 1986
9. R.A. Levy, *Microelectronic Material Processes*, Kluwer Academic, New Jersey, 1989
10. Ghandhi, S.K., Bhat, I.B., *Organometallic Vapor Phase Epitaxy*, MRS Bullentin, Nov. 1988
11. Emanuel, M., *Metalorganic Chemical Vapor Deposition for the Heterostructure Hot Electron Diode*, Noyes Publications: New Jersey, 1989
12. "Infrared Detectors and Solar Cells," *Proc. 3d Int. Conf. on Metallo-organic Vapor Phase Epitaxy*, American Association of Crystal Growth: Universal City, California, 1986



13. Singer, P., "Introduction of Low Pressure Chemical Vapor Deposition," *Semiconductor Intl.*, May, 1984: pp.72
14. Kern, W., G.C. Schneble. "Low Pressure CVD Techniques," *RCA review*, 43, 1982: pp.423
15. Rosler, R.S., " Step Coverage of Low Pressure CVD," *Solid State Technol.*, 20 (4), April, 1977: 63
16. Middlemann, S., A. Yeckel, " Reactions of Low Pressure CVD," *J.Electrochem. Soc.*, 133, 1986: 1951
17. Weiss, A., PECVDS: "Silicon Nitride and Beyond," *Semiconductor Intl.*, 6(7), July, 1983: 88
18. Goldsmith, N., and W. Kern. "Role of Oxygen and Silane in SiO<sub>2</sub> Films," *RCA rev.*, 28, 1967: 153
19. Cobianu., and C. Pavelescu. "Gas Phase Diffusion Process," *Journal of Electrochemistry Soc.*, 130, 1983: 1988
20. Cobianu., and C. Pavelescu., *Thin Solid Films*, 117, 1984: 211
21. Kern, W. "Low Temperature SiO<sub>2</sub> Film," *Semiconductor Intl.*, 3(3), 1982: 89
22. Adams, A.C. and F.B. Alexander and C.D. Capio and T.E. Smith. "Plasma Enhanced Reactions," *Journal of Electrochemistry Soc.*, 128, 1981: 1545
23. Adams, A.C., and C.D. Capio., "Medium Temperature Deposition in LPCVD Reactors," *Journal of Electrochemistry Soc.*, 126, 1979: 1042
24. Huppertz, H., and W.L. Engl., "Methods of Preparing LPCVD Films," *IEEE Trans. Electron Devices*, Ed-26, 1979: 658
25. Watanabe, K., T. Tanigaki, and S. Wakayama, "High Temperature Deposition," *Journal of Electrochemistry Soc.* 128, 1981: 2630
26. Pramanik, D. "Formation of Voids," *Semiconductor Intl.*, June, 1988: pp 94
27. Kern, W., and G.L. Shenable. "Important Aspect of Flow Temperature in SiO<sub>2</sub>," *IEEE Trans. Electronic Devices*, Ed-26, 1979: 647
28. Rosler, R.S. "Effects of Shadowing in Conformal Coverage," *Solid State Technology*, 20 (4), April, 1977: 63

29. Pliskin, W.A. "Common Impurities in Low Temperature Deposited Oxide," *Journal of Vac. Sci. Technology.*, 14, 1977: 1064
30. Pliskin, W.A., and H.S. Lehman., "Water Absorption in Oxide Films," *Journal of Electrochemistry Soc.*, 112, 1965: 1013
31. Yashimura, M., H. Matsuharu, T. Ajioka and H. Matsui, "Effect of Dopants in Water Absorption and Permeability," *Proc. of IRPS*, 1987: p22
32. Pliskin, W.A., D.R. Kerr, and J.A. Perri, *Physics of Thin Films*, Vol. 4, edited by G. Hass and R.E. Thun, Academic Press, New York, 1967: pp 257-324
33. Perri, J.A., and J. Reisman, "Thermal Coefficients of the Film and Substrate," *Electronics*, October 3, 1966: pp 108
34. Shimbo M., and T. Matsuo, "The Stress in Oxide Films," *Journal of Electrochemistry Soc.*, 130, 1983: pp 135