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ABSTRACT

Low Temperature Synthesis and Characterization of Silicon Dioxide Films by LPCVD Using Diethylsilane

by
Chakravarthy S. Gorthy

Diethylsilane (DES) has been used as a precursor to produce silicon dioxide films by low pressure chemical vapor deposition. These films were synthesized in the temperature range of 350 to 475^{o}C thus allowing the use of the material as an intermetal dielectric or as a top layer passivation coating in microelectronic devices. In that process, the growth rate was observed to follow an Arrhenius behavior yielding an activation energy of 10 kcal/mol. The growth rate was also observed to increase with higher pressure and to vary as a function of the square root of the DES flow rate and O_2/DES ratio. In both the pressure and the O_2/DES ratio studies, there were points of abrupt cessation in deposition. The density of the films was measured to be close to 2.2 g/cm^3 regardless of deposition conditions. RBS measurements revealed the absence of incorporated carbon and a near stochiometric composition of $SiO_{2.2}$. The dielectric breakdown strength of an SiO_2 film deposited at 400 ^{o}C was found to be 2 MV/cm. Infrared spectra of the films showed the usual Si-O bond stretching and bond bending absorption bands centered at 1060, 810, and 440 cm^{-1}. Si-H bending band at 880 cm^{-1} was also observed in SiO_2 films prepared under certain processing conditions. The refractive index of the films was found to be at 1.46 independent of deposition temperature.

LOW TEMPERATURE SYNTHESIS AND CHARACTERIZATION OF LPCVD SILICON DIOXIDE FILMS USING DIETHYLSILANE

by

Chakravarthy S. Gorthy

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This thesis is dedicated to my parents, brothers and advisors,
for reasons which increase everyday....

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

Table Page

1. INTRODUCTION

1.1 Introduction to Microelectronics

Microelectronics is the life blood of modern technology. It is at the heart of such electronic devices like calculators, television, computers, manufacturing plants, etc. Within the last twenty years the microelectronics industry has been one of the fastest growing industries. This has been possible by the better cost-effectiveness produced from the fabrication of larger number of devices on a single wafer, thus increasing the packing density and the performance of the device. This enhancement in performance (1-4), the higher speed and the lower power consumption, can be achieved by the miniaturization of the devices. This miniaturization of devices in turn has required the use of thin film techniques to isolate or connect specific areas on a device. With this reduction in size reaching the sub micron level, the search for new techniques, as well as new materials which can withstand the stringent requirements of microelectronics, has been intensified.

As the microelectronics technology becomes more and more complex, devices consisting of several different thin film layers deposited on a single substrate are being fabricated. Novel thin film deposition techniques are being used to deposit these layers. A wide variety of materials such as conductors, semiconductors, dielectrics etc. can be conveniently deposited using these thin film deposition techniques. This study focuses on the deposition and characterization of SiO_2 dielectric thin films by using a new liquid precursor 'diethylsilane' by Chemical Vapor Deposition (CVD).

1.2 Dielectric Materials

Dielectric films play an important role in the fabrication of integrated circuits. Dielectric layers are usually used to provide protection to semiconductor surfaces, to serve as implantation or diffusion masks, or to serve as interlayer dielectrics between two levels of metallization and for many other applications. The most commonly used dielectrics are silicon dioxide (SiO_2) and silicon nitride (Si_3N_4) and their modifications like SiO_2 films doped with phosphorus (PSG) or boron and phosphorous (BPSG), or oxynitride films (5-7).

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_2 films on silicon. Extensive research is directed to the growth of SiO_2 films as the properties of these films are compared with those of thermally grown oxide which is taken as a standard.

1.2.1. Requirements of dielectric materials.

The chief requirements of dielectric films for multilevel metallization and passivation layers are given below.

Intermetal dielectric

1) Should have low dielectric constant in order to keep the capacitance between metal lines minimum.

2) Should have high dielectric break down field strengths.

3) Should have no moisture absorption.

4) Posses low compressive stress, as dielectric films tend to crack if they are tensile.

5) Must have good adhesion to aluminium.

6) Should be easily dry or wet etched.

7) Should be permeable to hydrogen to remove interface sites.

8) Have good conformal step coverage.

Passivation Layers

1) Should provide scratch protection to circuit below

2) Have no permeability to moisture.

3) Have low compressive stress.

4) Should have good conformal step coverage.

5) Should be easily patterned.

6) Have good adhesion to conductors and interlayer dielectrics.

1.3 Chemical vapor deposition (CVD)

1.3.1 Introduction to CVD

Of the many techniques available for deposition of dielectric films, Chemical Vapor Deposition (CVD) is one of the most promising one. The main reason for growing thin films by chemical vapor deposition lies in its versatility for depositing a very large variety of materials at relatively low temperatures with excellent step coverage. These properties of CVD look promising for the deposition of dielectric films by this technique. The details of CVD are discussed in detail below.

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 atleast 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 on to 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 byproducts,
7. gaseous diffusion of reactant byproducts,
8. bulk transport of the byproducts out of the process chamber.

The rate at which these three steps are carried out controls the chemical vapor deposition.

If the reaction rate is controlled by the surface reaction rate, we can express the growth rate of the film deposited in the surface reaction rate limited regime as

$$G.R. = Ck = Ck_0 \exp(-E_a/RT)$$

where G.R. is the growth rate of the film, and the reaction rate coefficient k is characterized by an apparent activation energy E_a, C is a proportionality constant, R is gas constant, k_0 is a constant and T is the absolute temperature.

If the Reaction is mass transfer controlled, we can express the deposition rate as:

$$D.R. = Sk_D/RT\ (P-P_{eq})$$

This relation is obtained from the expression of the mass transfer coefficient

$$J = k_D/RT\ (P-P_{eq})$$

where D.R. is the deposition rate, J is the mass flux, S is the surface area of the wafer, k_D is the mass transfer coefficient, R is the gas constant T is the temperature, P_{eq} is the partial pressure of the reactant species that will exist under equilibrium at the surface temperature and P is the partial pressure in the CVD system.

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.

There are many types of chemical vapor deposition, of which the most important and widely used CVD processes are, atmospheric pressure chemical vapor deposition (APCVD), low pressure chemical vapor deposition (LPCVD) and plasma enhanced chemical vapor deposition (PECVD). Only low pressure chemical vapor deposition technique is discussed in detail below as this technique was employed in this study.

1.3.2 Low pressure chemical vapor deposition (LPCVD)

1.3.2.1 Introduction to LPCVD

Low pressure chemical vapor deposition (LPCVD) technique was developed to overcome the uniformity, step coverage, and particulate contamination limitations of APCVD systems (8,9,10). It is sometimes possible to deposit films in the reaction rate limited regime, by operating the LPCVD reactors at medium vacuum (0.25-0.5 torr), and moderate temperatures (550-600 ^{O}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 temperature.

Through the modification of the reactor design, depletion along the axis can be overcame allowing the reactor to accommodate large number of wafers. As the reactions are carried out at low pressures gas phase reactions are almost eliminated, thus the films have lower particulate contamination (13).

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:

a) horizontal tube reactors
b) vertical tube reactors.

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

1.3.2.2 Horizontal tube LPCVD reactors (hot wall)

Horizontal tube reactors are the most widely used LPCVD reactors in Very Large Scale Integrated (VLSI) circuit processing (11). They are employed for depositing poly-silicon, silicon nitride, undoped and doped 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 (12).

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.

1.3.2.3 Diffusion model of LPCVD reactors

A review of the diffusion reactor model based on the work of Middlemann and Yeckel (13) 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 be considered.
4) The gas contains that species highly diluted in an inert carrier gas.
5) Only heterogeneous reactions need be considered.
6) there is no gas flow in the interwafer region.

One of the useful results of the work of Middlemann and Yeckel (13) with the pure diffusion analysis is the uniformity of deposition. One way of expressing uniformity is by the radial thickness variation:

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

where d_{max} and d_{min} are maximum and minimum thicknesses respectively.

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:

$$Sh = k_D d/D$$

where k_D is the mass transfer coefficient of the process, d is the relevant length dimension and 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 Review of past work on 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 film are formed are: 1) Low temperature deposition (300-450 ^oC); 2) medium temperature deposition (450-800 ^oC); and 3) high temperature deposition (above 800 ^oC).

1.4.1.1. Low temperature deposition

In the low temperature range SiO_2 films are formed by the reaction of silane and oxygen (7,14,15). The depositions are carried in atmospheric pressure CVD reactors (APCVD), low pressure CVD reactors (LPCVD) or plasma enhanced CVD reactors (PECVD) reactors (11). LPCVD of SiO_2 films is not favorable from the reaction of SiH_4 and O_2, due to depletion effects (11):

$$SiH_4 + O_2 \text{---->} SiO_2 + 2H_2$$

The reaction between silane and oxygen to form SiO_2 film follows a heterogeneous surface reaction. But sometimes SiO_2 particles are generated due to homogeneous gas phase nucleation which may cause particulate contamination in the deposited film. The deposition rate of the SiO_2 film increases with the temperature between 310 and 450 ^oC and the activation energy is about 38.5 kJ/mol indicating an surface adsorption or gas phase diffusion process (14,15). The deposition rate can also be increased by increasing the O_2/ SiH_4 ratio within a certain range and the deposition rate was observed to decrease eventually due to O_2 being adsorbed on the surface inhibiting the SiH_4 decomposition (14,15). SiO_2 films which are deposited at low temperatures have lower densities and refractive indices than thermally grown oxides (6). They also show higher etch rates in buffered Hydrofluoric acid (HF) solution than thermally grown oxide, while heating of such films around 700-1000 ^oC causes densification causing an increase in the density and decrease in the etch rate (6).

SiO_2 films can be deposited by plasma enhanced reaction between SiH_4 and N_2O or O_2 at temperatures between 200-400 ^oC (16):

$$SiH_4 + 2N_2O \text{ ----> } SiO_2 + 2N_2 + 2H_2$$

Nitrogen and hydrogen may become incorporated in the deposited films often. This results in a low ratio of N_2O/ SiH_4 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 (11). PECVD oxides generally contain H_2 in the form of Si-H, Si-O-H, and H-O-H (16). 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 (11).

1.4.1.2 Medium temperature deposition

In the medium temperature range SiO_2 films are deposited in LPCVD reactors using tetraethylortosilicate (TEOS) (17-20), diacetoxyditertiarybutoxysilane (DADBS) (19,20) etc. The deposition rate of the SiO_2 film shows an exponential increase as the temperature increases from 650-800 ^oC with an apparent activation energy of 183 kJ/mol (11) 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 (11). The films deposited using TEOS have excellent uniformity and conformal step coverage (19,20).

1.4.1.3 High temperature deposition

In the high temperature range SiO_2 films are deposited using LPCVD reactors by the reaction of dichlorosilane and nitrous oxide (21,22). K. Watanabe et al used the following reaction to produce SiO_2 films:

$$SiH_2Cl_2 + 2N_2O \text{ -----> } SiO_2 + 2N_2 + 2HCl$$

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

1.4.2 Properties of SiO_2 films deposited by various CVD techniques

In this section SiO_2 films deposited by various CVD techniques are discussed with relation to their properties such as conformality, water absorption, and stress.

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_2 films deposited from silane, have less thickness on the side walls and bottom corners of the trenches (23). Step coverage gets worse with increasing aspect ratio (height /width) which can lead to the formation of the voids (23).

The step coverage can be improved by flowing the dielectrics at temperatures higher than 900 ^{o}C. SiO_2 has a flow temperature of about 1200 ^{o}C, while the addition of impurities such as boron and phosphorous allows the flow temperature to be reduced (24).

The addition of dopants such as Phosphorous in SiO_2 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 (23).

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 ^{O}C. In this case the step coverage is determined by the angular distribution of the silane molecules impinging on each point of the surface (11). For LPCVD films, the mean free path of the molecule in the gas phase is large enough that the source of the recent specie can be considered to be hemispherical (23). For APCVD, because of the smaller mean free path, the solid angle of arrival of species is 90^{O} or less on a vertical sidewall (11). 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 diacetoxyditertiarybutoxysilane (DADBS) etc. are such compounds which produce excellent conformal films. The main limitation being the requirement of high deposition temperatures (above 650 ^{O}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 (21), the oxide in these areas has lower density then 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 (23,25), both in bulk and surface of the dielectric, enhances crack formation (if the dielectric is under tensile stress) and increases the effective dielectric constant (23). 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 (23).

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 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 (26). The amount of porosity of an oxide film can be determined from the amount of water it tends to absorb. The water, which is loosely bound as H_2O molecules, is easily removed by baking the films at about 200 ^oC . The remaining water which exists as -OH bond to Si, is evolved at 450 ^oC.

In general the lower the temperature of deposition the more porous the oxide films tend to be (25). This is because of the thermal energy is not sufficient to break the Si-O bonds and to cause compaction of the structure (25). SiO_2 CVD films are densified by going to temperatures of 800 ^oC or higher so that moisture absorption is not a problem for dielectrics used over polysilicon or silicides (25).

The presence of dopants can affect the water absorption and permeability. Phosphorus decreases the diffusion of water through the film, whereas boron increases it (27).

Plasma films are more resistant to moisture then 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 ^{0}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.

Stresses 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 (28,29). 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, where as LPCVD films are compressive (23).

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 (23). 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_2 (25). Above a certain temperature the stress in the oxide films decreases with the temperatures (30). The relaxation of the stress is due to the rearrangement of the bonds in the film (25).

Water absorption causes the stress to become more compressive. Thus, the evolution of the water causes an increase in the tensile stresses. From this it can be seen that the stress in deposited films that are porous can change with time at room temperature, under humid conditions.

Dopants can influence the stress in the film. Phosphorus reduces the compressive stresses in PECVD and LPCVD films, and tensile stresses in APCVD films (23). The stresses decrease with increasing Phosphorous content upto a particular concentration (23).

2. ORGANOHYDROSILANES

2.1 Chemical and physical properties of organohydrosilanes.

In this chapter the physical and chemical properties of organohydrosilanes, similarity of dialkylsilanes to silanes and an expectation of their CVD characteristics is discussed. A comparative study between dialkylsilanes and silanes is also presented.

2.1.1 Similarity of Dialkylsilane to silane

Dialkylsilanes are derivatives of silane obtained by the substitution of two alkyl groups in place of hydrogen in silane. These organohydrosilane liquid precursors offer many advantages over silane and other source materials in safety and volatility. The pyrolysis of dialkylsilanes and silanes yields important information.

2.1.1.1 Thermal decomposition of Dialkylsilane and Silane

Many researchers have reported the homogeneous decomposition of silane (SiH_4) and the formation of $:SiH_2$ (sililene) radicals. According to some authors sililene is obtained in the gas phase as a result of partial thermal cracking of silane, after which it is adsorbed and decomposed to silicon and hydrogen (31-34), whereas, some believe that the sililene production is a result of silane interaction with the surface of the deposited film, and not from the bulk reaction (35). The initiation reaction of sililene formation according to Newman et al is believed to be

$$SiH_4 <====> :SiH_2 + H_2$$

The sililene is considered to migrate over the surface to a kink position, where incorporation into the silicon lattice takes place, followed by the subsequent desorption of hydrogen which explains the observed non-linear growth dependency with the input pressure (36).

It has been determined that the primary decomposition pathway for dialkylsilanes involves sililene formation by extrusion of H_2. The pyrolysis of dimethylsilane (DMS) is an example of the formation of sililene radical (37):

$$(CH_3)_2SiH_2 \text{ -----> } :Si(CH_3)_2 + H_2$$

At temperatures below 725 ^{o}C the homolytic cleavage of silicon-carbon bonds are negligible, but can be important above these temperatures.

$$(CH_3)_2SiH_2 \text{ -----> } SiH_2CH_3 + CH_3$$

The temperature of homolytic cleavage of Si-C bonds decreases with the increase in the length of alkyl radical. For example the temperature of homolytic cleavage of Si-C bond in dimethyl silane is greater than that required for diethylsilane.

From the above discussion, it is proposed that a surface diffusion process in which the sililene (R_1R_2Si:) is adsorbed on the surface takes place at low temperatures (39). The related kinetic equations are expected to be similar to that of silane (30,32). But, the details of the reaction mechanism change at high temperatures due to the homolytic cleavage of the Si-C bonds (37).

2.1.1.2 Homogeneous reaction in CVD

Homogeneous decomposition of silane was studied by some authors (38). Van den Brekel et al (33), observed a large cluster of monocrystalline character in the gas stream during the deposition of polycrystalline silicon from silane in a LPCVD reactor equipped with a mass spectrometer and a photomultiplier. They also discussed the gas phase polymerization on the growth rate distribution in an LPCVD system. Since, homogeneous coverage in the CVD processes is possible when the Sherwood number (36) is small enough, the presence of heavy polymers results in inhomogeneous deposition, in contrast to the homogeneous coverage by the monomers at the same temperature, pressure and substrate arrangement. The shape of the radial thickness profile in LPCVD is a result of superposition of all i-mers (polymers) present in the gas phase. The superposition effect was evidenced by the observation of inhomogeneity in layer thickness on those parts of the wafers where they rest in narrow grooves on the boat. They concluded that the masked areas were formed by the silicon from monomers or low i-mers. They also concluded that the radial thickness profile on the wafer in the presence of gas phase polymerization depends on the wafer radius and the distance between the wafers.

Murthy et al (39) investigated the polymerization of silane in an conventional horizontal epitaxial reactor and ascertained that fine crystallines of silicon can be obtained when input silane concentration exceeds a critical value dependent on the temperature.

The mechanism of the dimerization process by the initial reaction of the decomposition of silane, was studied by Newmann et al (34). They proposed a mechanism for the dimerization process:

$$2\,{:}SiH_2 \text{ -------> } Si_2H_2 + H_2$$

Based on this principle, van den Brekel et al (33) suggested further polymerization reactions in which sililene reacts with a j-mer, Si_jH_2, with the elimination of hydrogen:

$$SiH_2 + Si_jH_2 \text{ -----> } Si_{j+1}H_2 + H_2$$

and the combination of two polymers:

$$Si_iH_2 + Si_jH_2 \text{ -----> } Si_{i+j}H_2 + H_2$$

From the work of Yi Tong et al (40), it is evident that dialkylsilanes also undergo polymerization at some conditions (39).

2.1.2 CVD from Organohydrosilanes

As discussed above, the sililenes get adsorbed on the substrate surface and an adsorption mechanism, or a heterogeneous process, has been proposed. In addition, the polymerization processes based on the combination of the sililenes are suggested in order to explain the radial thickness variation and homogeneous reaction effect.

The following data and experimental results support these models described above and help give a general picture of the CVD of organohydrosilanes.

1) The bond of Si-H is the weakest of the bonds Si-H, Si-C, Si-Cl and C-H. The percentage decomposition of the homolytic cleavage of the two Si-H bonds versus temperature profiles for members of the dialkylsilanes and silane are similar, with decomposition beginning at 460-480 ^{o}C and ends at 625-725 ^{o}C.

2) In the depositions from silane and DES, the radial thickness variation occurs; however, the deposition from $SiCl_4$ results in the uniformity of the films, that is, no polymerization occurs (40). These experimental results on the radial thickness variation strongly support the model of polymerization .

A hypothetical general picture of the CVD of organohydrosilanes can be expected:

1) In organohydrosilanes, dialkylsilanes ($R_1R_2SiH_2$) can form sililenes (R_1R_2Si:) in a low temperature range (40,41). The decomposition begins at 460-480 and ends at 625-725 ^{o}C. Above this temperature range, the homolytic cleavage of silicon-carbon bonds cannot be negligible.

2) The formed sililenes are adsorbed on the substrate surface and an heterogeneous process occurs.

3) All the dialkylsilanes are expected to polymerize in a similar pathway, but the effect of polymerization decreases with the increase in the length of the alkyl substituent (40) due to the volume effect described below.

4) In dialkylsialnes, the longer alkyl substituent is expected to result in lower activation energy than shorter alkyl substituents is rate limiting in the reaction mechanism (40). However volume effect in collisions of molecules (or radicals) or adsorption on a substrate surface, resulted from the length of the alkyl, will become

important when the alkyl is long. In kinetics, the effect will result in a lower effective probability factor in a longer alkyl substituent than in a shorter alkyl substituent.

5) Because the temperature of the homolytic cleavage of a silicon-carbon bond decreases with the increase in the length of the alkyl substituent in dialkylsilanes, the kinetic characteristics are expected to become complex when the substituent alkyl length increases.

2.1.3 Diethylsilane as a source for CVD of SiO_2 deposition

As was discussed earlier, with the increase in the length of the alkyl group in organohydrosilanes, the temperature of pyrolysis decreases. Thus, the organosilane with a large alkyl group has lower deposition temperature.

However, the volatility of the organohydrosilane decreases with the increase in the length of the alkyl radical and the delivery system for CVD becomes very complex. Diethylsilane (DES) has a vapor pressure of 200 torr at 21 ^{O}C, which makes it suitable for delivery by commercially available mass flow controllers without the use of heated lines. The boiling point of some organohydrosilanes is shown in the table 1 and the physical properties of diethylsilane in table 2. The vapor pressure of diethylsilane (DES), tetramethylcyclotetrasiloxane (TMCTS) and tetraethoxysilane as a function of temperature is shown in fig 2.1 (42).

Table 1. Volatility of some organohydrosilanes

Compounds	Name	Boiling point °C
H_3SiCH_3	Methylsilane	-57
$H_3SiC_2H_5$	Ethylsilane	-14
$H_3SiC_4H_9$	Butylsilane	56
$H_3SiC_6H_{13}$	Hexylsilane	114-115
$H_2Si(CH_3)_2$	Dimethylsilane	-20
$H_2Si(C_2H_5)_2$	Diethylsilane	56

Table 2 Physical properties of diethylsilane

Chemical name	Diethylsilane
Formula	$C_4H_{12}Si$
Molecular weight	88.2
Normal boiling point	56 °C
Density	0.6843 g/cm^3 @ 20 °C
Vapor density (air = 1)	>1
Appearance	colorless liquid
Freezing point	<-76 °C
Solubility in water	Insoluble
Flash point	-20 °C (closed cup)
Autoignition temperature	218 °C

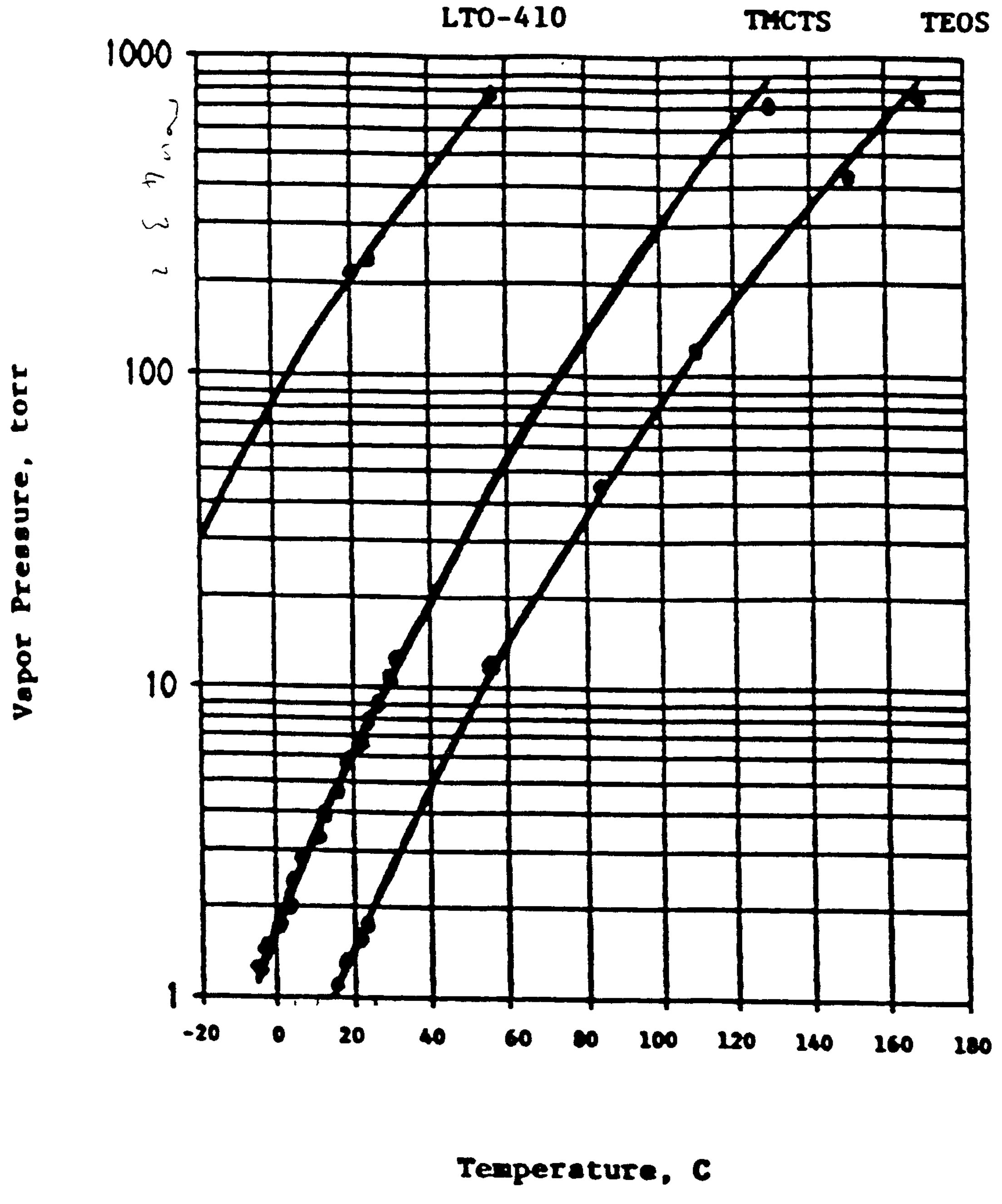

Figure 2.1 Vapor pressure as a function of temperature of diethylsilane (LTO-410), tetemethylcyclotetrasiloxane (TMCTS) and tetraethoxysilane (TEOS).

In this study the suitability of diethylsilane as a source for low temperature deposition of SiO_2 films by LPCVD is demonstrated. The kinetic study yielded many interesting results.

3. EXPERIMENTAL PROCEDURES

3.1 LPCVD apparatus and the calibration of the automatic mass flow controllers.

The experiments were carried out in a LPCVD reactor, consisting of a fused insert quartz reactor tube, 13.5 cm in diameter and a length of 150 cm, which was enclosed in a feed tube 19.3 cm in diameter and a length of 155 cm mounted within a five zone Lindbderg furnace. Both ends of the silica tube were sealed by O-rings in stainless steel flanges. The insert tube was modified by adding a aluminium baffle to cover the flanged opening, preventing the back flow of the reactants. The deposition equipment is shown schematically in fig 3.1. The apparatus was equipped with a Edwards high vacuum pump model E2M 80, backed by a Edwards mechanical booster pump model EH 500. The reactor pressure is controlled by an automatic control valve. The reactor temperature was measured by a Omega type K thermocouple. Gas flows were regulated by Applied Materials model AFC 550 automatic N_2 mass flow controllers which were corrected for DES and O_2 flows, the procedure for which is described below. The pressure in the reactor was measured with a baratron gauge from MKS.

Boron doped monocrystalline silicon wafers from Silicon Sence Inc., oriented in <100> direction and 100 mm in diameter, were placed vertically in the silica boat with a 9.0 mm spacing between them. In all the deposition experiments only six wafers were loaded in the boat, out of which two dummies were positioned in the front and one dummy was positioned at the back. Between these dummies three test wafers were placed. The boat was placed at the center of the reaction chamber.

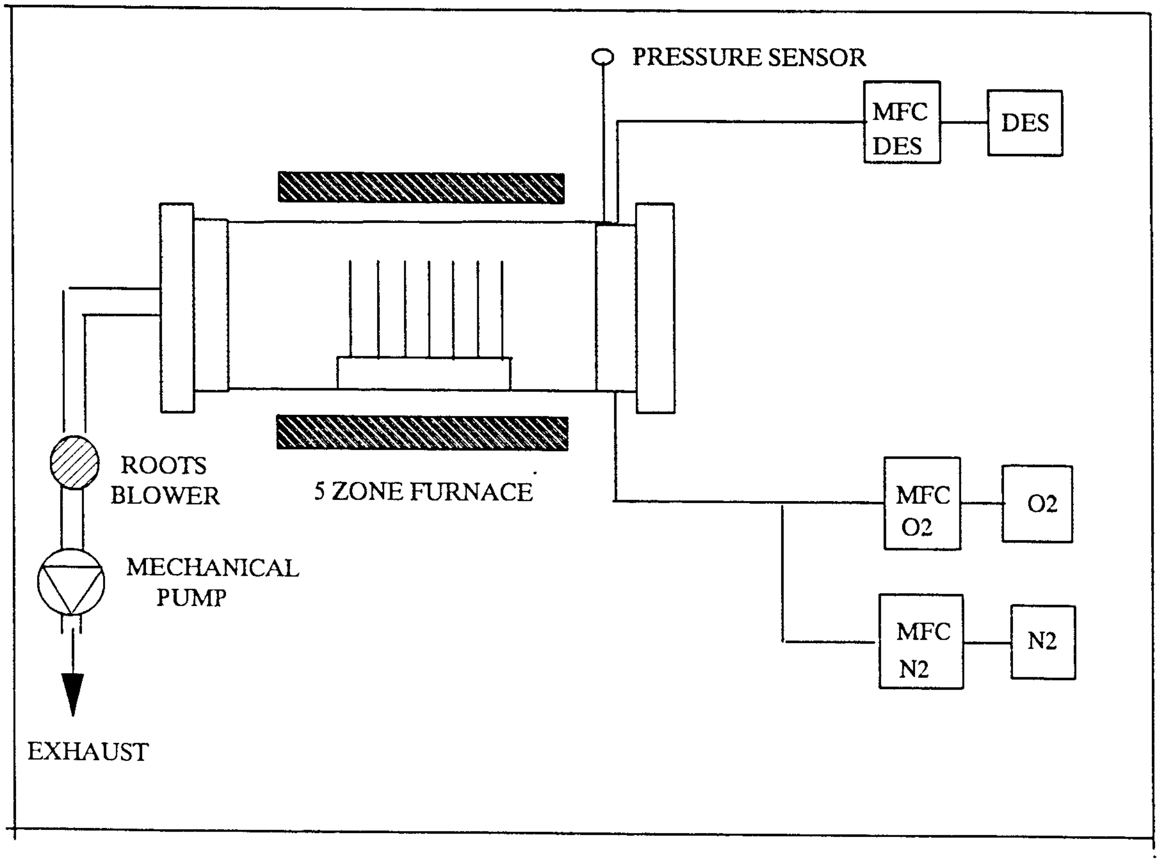

Figure 3.1 A schematic diagram of the LPCVD reactor

The volume of the CVD chamber was determined by flowing a known amount of N_2 into the CVD chamber at a known initial pressure and room temperature, and keeping the booster valve closed for a known amount of time. The difference in pressures for the known time interval and the gas flow rate was measured, and the ideal gas law, PV = nRT was used to calculate the volume of the reactor.

Assuming the N_2 in the reaction chamber to be an ideal gas the volume of the chamber can be found approximately by

$$V = \frac{760 * FR * t * T}{273\,(P_{fN} - P_{iN})} * 10^{-3}$$

Where flow rate of N_2 is in sccm; t is the time in min; T is the temperature inside the chamber in K; P_{iN} and P_{fN} are the pressures of the nitrogen in torr initially and finally, respectively; FR is the flow rate and V is the volume of the reaction chamber.

Using the equation above the volume of the chamber was found to be 57.4 liters.

The same type of automatic mass flow controller was used to determine the flow rate of the DES vapor because there was no special DES mass flow controller commercially available. A correction of the N_2 mass flow controller which was used for DES vapor flow, was necessary. The correction factor for DES flow can be obtained by calculating the ratio of the real flow rate of the DES to the N_2 flow rate in the mass flow controller.

DES vapor flow into the chamber was metered through a N_2 mass flow controller. The initial and final chamber pressure at room temperature for a known time interval of the vapor flow was measured using a pressure gauge.

Assuming the DES vapor to be an ideal gas, The actual flow rate of the DES vapor, and the factor for DES can be obtained approximately by:

$$FR\ (a) = \frac{57.4 * (P_{fc} - P_{ic})}{760 * t} \frac{273}{T} * 10^{3}$$

$$Factor = \frac{FR\ (a)}{FR}$$

Where FR (a) and FR are the real flow rate of DES and N_2 in sccm respectively; P_{ic} and P_{fc} are the pressures of DES in the CVD chamber initially and finally; t is the time in min and T is the temperature of the chamber and 57.4 liters is the volume of the chamber.

A plot of the flow of DES in sccm (standard cubic centimeters per minute) and the corresponding digital meter readout is shown in the fig 3.2.

3.2 Experimental procedure of the SiO_2 film deposition

Experiments at various DES flow rates, O_2/DES ratio's, chamber pressures and temperatures were performed. In the temperature dependence study, the deposition of the SiO_2 films was carried out between 350 and 475 ^{o}C at a constant pressure of 0.5 torr, and a DES flow rate of 50 sccm; Pressure dependence study was carried out between 0.2 and 0.75 torr with a constant temperature of 400 ^{o}C and DES flow rate of 50 sccm; Flow rate study was carried out with DES flow rates between 12 sccm and 150 sccm at 450 ^{o}C temperature and 0.5 torr pressure; and ratio study was carried out with O_2/DES ratio's between 0.5 and 3 at a constant pressure of 0.5 torr, 450 ^{o}C temperature and a constant DES flow rate of 50 sccm.

The deposition rate values were obtained by the difference in initial mass before deposition and final mass after deposition for a known time interval, in units of mg/hr.

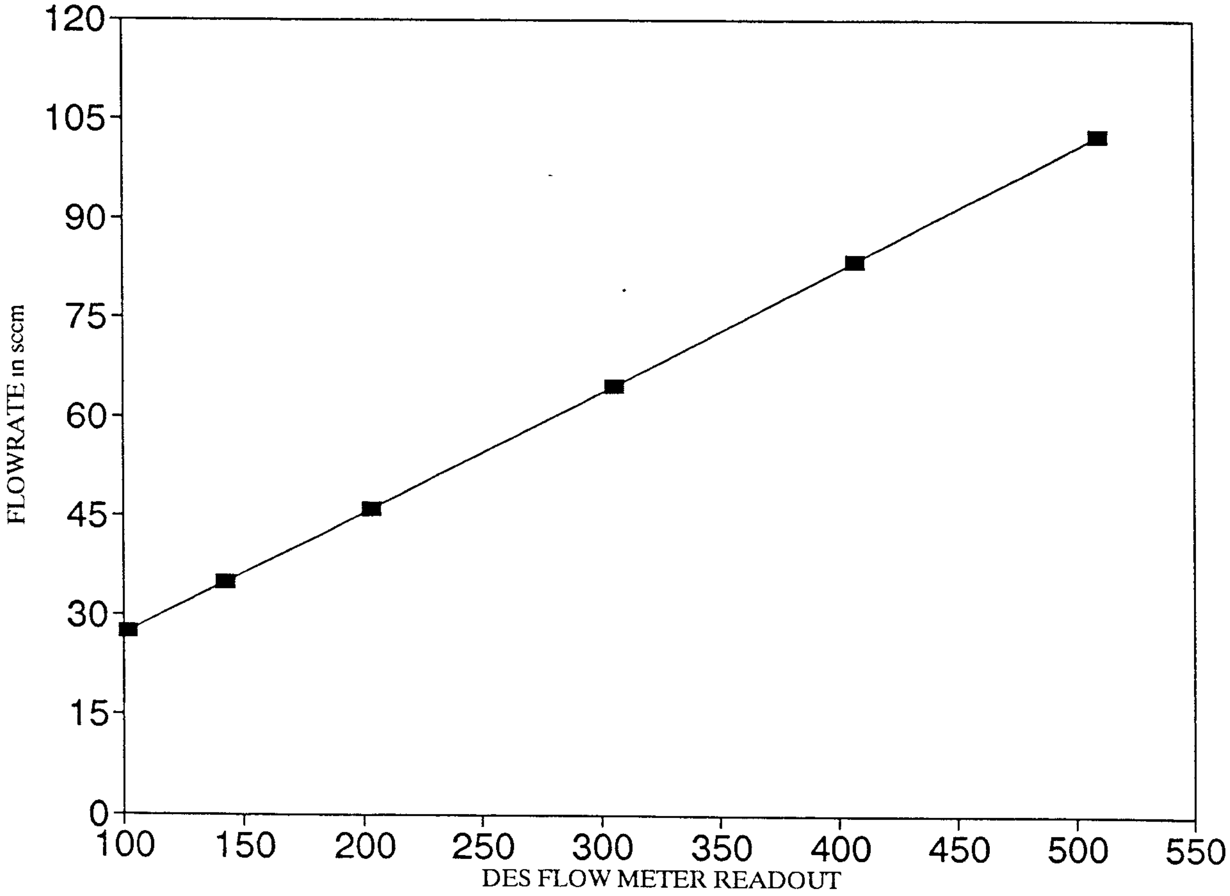

Figure 3.2 The relationship between DES flowrate in sccm and the meter readout.

3.3 Characterization of the deposited SiO_2 films.

The thickness of the SiO_2 films deposited on the silicon substrates was measured by a Nanospec interferometer. The index of refraction was obtained by an Rudolph Research automatic ellipsometer. An ellipsometer employs an monochromatic, plane polarized light with its plane of polarization at 45^o to the plane of incidence. The plane polarized light passes through a compensator and becomes elliptically polarized, which then is reflected by the absorbing surface. The polarizer and the analyzer are rotated by the operator till the smallest intensity of the reflected light is obtained. The values of delta and psi obtained from the polarizer and the analyzer angles were fed to a computer coupled to the ellipsometer, which solves the equations numerically and gives the refractive index and thickness of the film. Five points on the deposited film were taken in this study for the measurement of both thickness and refractive index and the mean of these values were determined.

The chemical composition of the deposited SiO_2 thin films were determined by an Rutherford Back Scattering (RBS) analysis. Rutherford backscattering is a surface analysis technique that can give quantitative information on elemental composition and depth profiling without the use of standards. High energy ions are allowed to collide with atoms and the energy of the recoiled ions are measured. If the collision is perfectly elastic, the energy of the backscattered ion depends upon the energy of the atom with which it collides. Usually doubly ionized helium ions accelerated to 2 MeV are used for this purpose. This procedure is sensitive to detect only heavier atoms and cannot be used for hydrogen.

The bonding and the presence of hydrogen in the deposited films was obtained by IR spectoscopy. This technique is based on the principle that some materials absorb certain frequencies in the infrared region due to the excitations resulting from various transitions in molecular species. Similar to the electronic transitions in the atoms when exposed to certain frequencies, vibrating molecules (stretching, bending

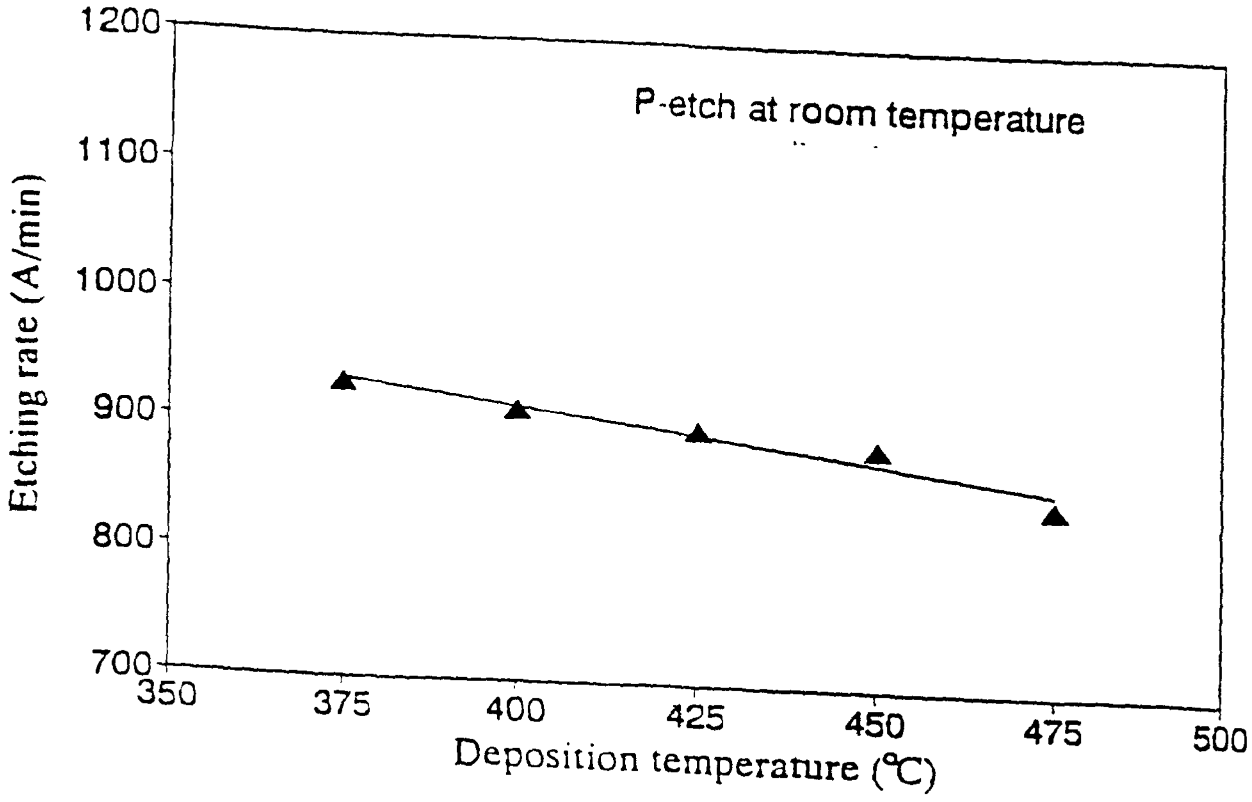

Figure 3.3 Relationship between etch rate and deposition temperature

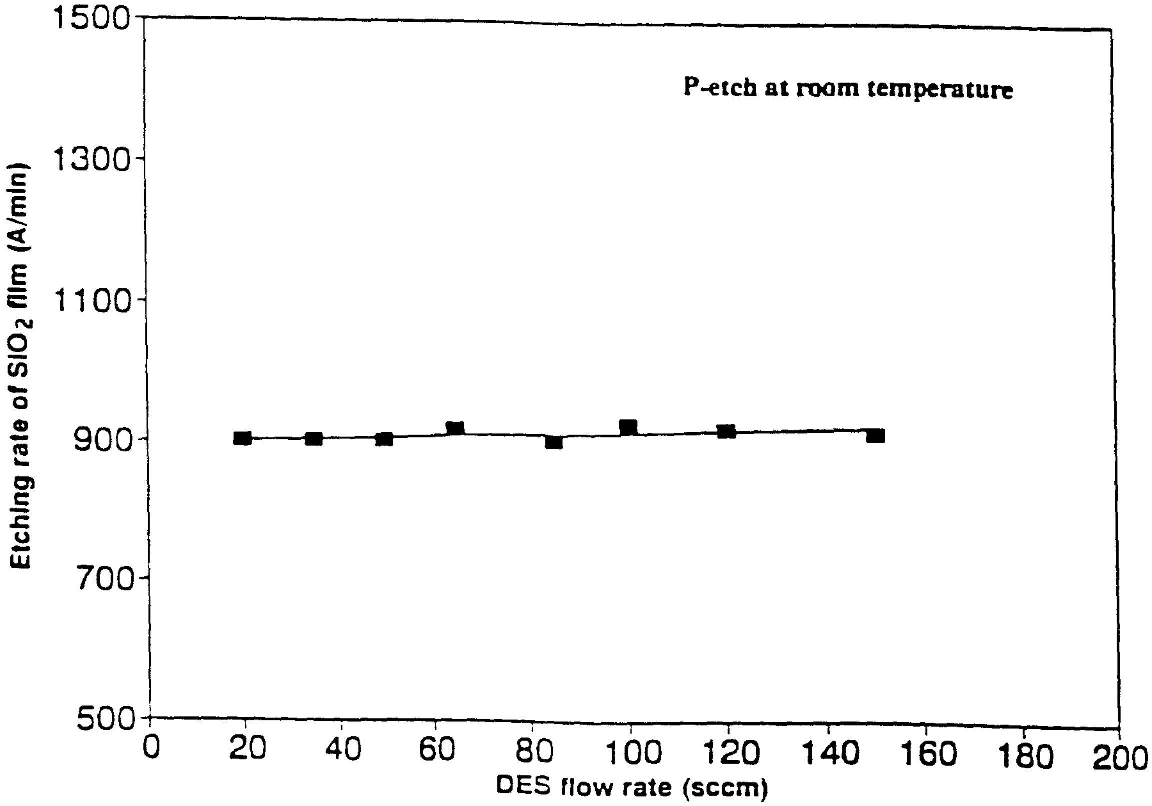

Figure 3.4 Relationship between etch rate and DES flowrate

or rocking) are also excited when frequencies of the exposed radiation and the resonant frequencies of the vibrating molecules are identical.

If IR radiation of a particular frequency impinges on a sample containing an molecular species, it may or may not be absorbed. If a wide range of IR frequencies are passed through, some will be absorbed to varying degrees depending on the molecular specie involved. The intensity of the reflected radiation depends on the vibrational mode of the molecules and the molecular vibrational mode can be detected by an absorption peak in the spectrum.

The dielectric breakdown strength was found by an Keithley-236 source measurement unit coupled to a computer. Model 251 software was used to plot the I-V characteristics from which the dielectric breakdown strength was calculated.

The wet etch rates of the films in P-HF solution (15 parts Hydrofluoric acid (49%), 10 parts nitric acid (70%), and 300 parts of water) were determined by measuring the wafer's mass before and after the etching (43). The etch rate was found to be independent of the DES flowrate but was found to decrease with the increase in the temperature (43). Fig 3.3 and Fig 3.4 illustrate the variation of etch rate as a function of DES flow rate and deposition temperature.

4. RESULTS AND DISCUSSION

4.1 Kinetics of film growth

The purpose of this study is to evaluate the growth kinetics and characterize SiO_2 dielectric films deposited using diethylsilane precursor.

In this study, the average deposition rate of the three test wafers has been used for the investigation of growth kinetics and characterization of the film properties, in order to account for the depletion effects. G(i)(i=1,...6) is defined as the deposition rate of the i-th wafer. A plot of G(i)/G(0) versus the wafer position on the boat shows the depletion effects. The lower the value of G(i)/G(o), the stronger is the depletion along the axis of the reactor tube.

The degree of relative deposition rate along the length direction G (i)/G (0), at different temperatures is shown in fig 4.1. It can be seen that the axial growth rate along the test wafers, almost remains constant, independent of deposition temperature. It was also found that the depletion effects were very small, irrespective of the variation in deposition conditions.

4.1.1 Temperature dependence and Activation energy.

The temperature dependence of the growth rate with natural logarithm of deposition rate on Y-axis and 1000/Temperature in K^{-1} on X-axis is shown in fig 4.2. The surface reaction on the substrate can be modelled by a thermally activated phenomenon which proceeds at a rate

$$G.R = R_0 \, e^{[-Ea/RT]}$$

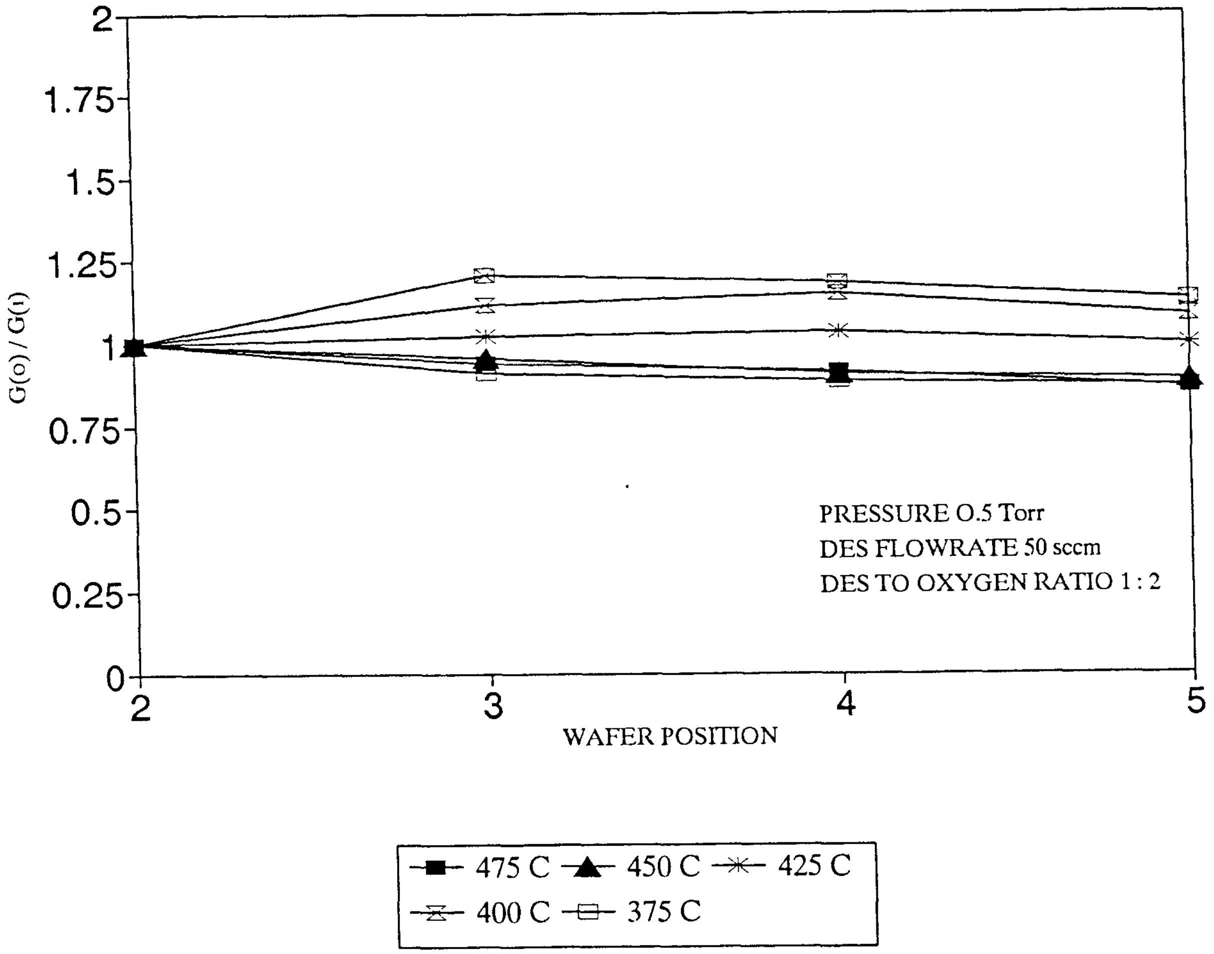

Figure 4.1 Normalized deposition rate versus wafer position in the reactor at different temperatures.

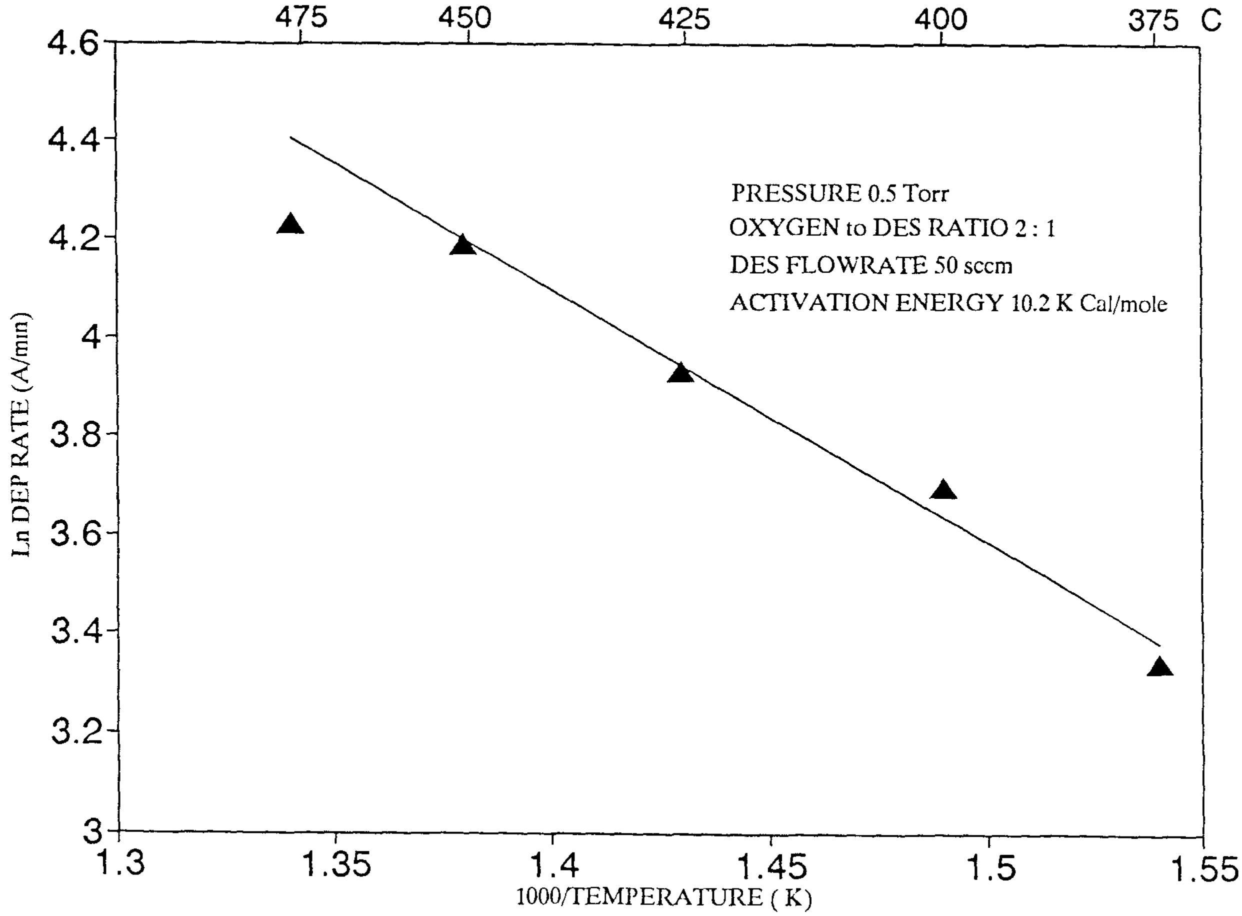

Figure 4.2 Effect of temperature on the deposition rate, showing the Arrhenius behaviour between 375 and 475 ^{o}C.

Where R_0 is the frequency factor, E_a is the activation energy, R is the gas constant and T is the temperature in K.

The experiments were carried out between temperatures of 350 and 475 ^{0}C; DES flow rate of 50 sccm; pressure of 0.5 torr. The activation energy calculated from the fig 4.2 is about 10.2 K cal/mol. At higher temperatures (> 450 ^{0}C) the deposition rate is almost independent of the temperature, as the reaction proceeds towards the mass transfer limited regime.

4.1.2 Effect of pressure

The deposition process is extremely surface controlled at relatively low DES input pressures. The growth rate variation with the pressure in fig 4.3. shows the nonlinear behavior. When deposition rate values in A/min are plotted against various chamber pressures at 400 ^{0}C, and at a DES flow rate of 50 sccm, it is found that the deposition rate increases drastically from 0.35 torr to 0.5 torr and then a saturation is observed. No deposition was observed below a chamber pressure 0.35 torr.

4.1.3 Effect of DES flowrate

A plot of deposition rate against DES flowrate in the range of 12 to 150 sccm, at a temperature of 450 ^{0}C; pressure of 0.5 torr is shown in the fig 4.4., which shows that the deposition rate increases with increase in the DES vapor flow rate. In fig 4.5 the deposition rate is plotted against the square root of flow rate. A linear variation of the deposition rate with the square root of flow rate is observed showing that the deposition rate varies quadratically with the flow rate of DES.

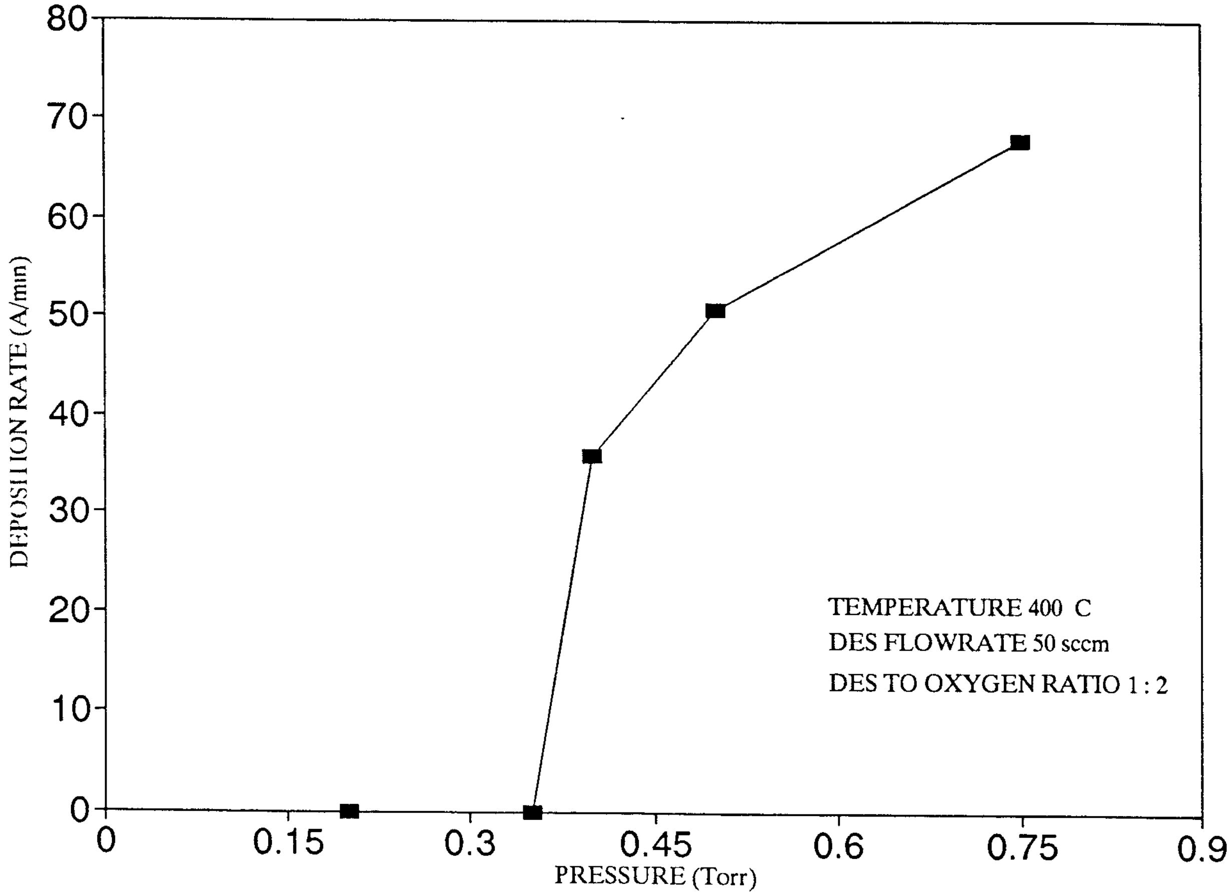

Figure 4.3 Relationship between pressure and the deposition rate

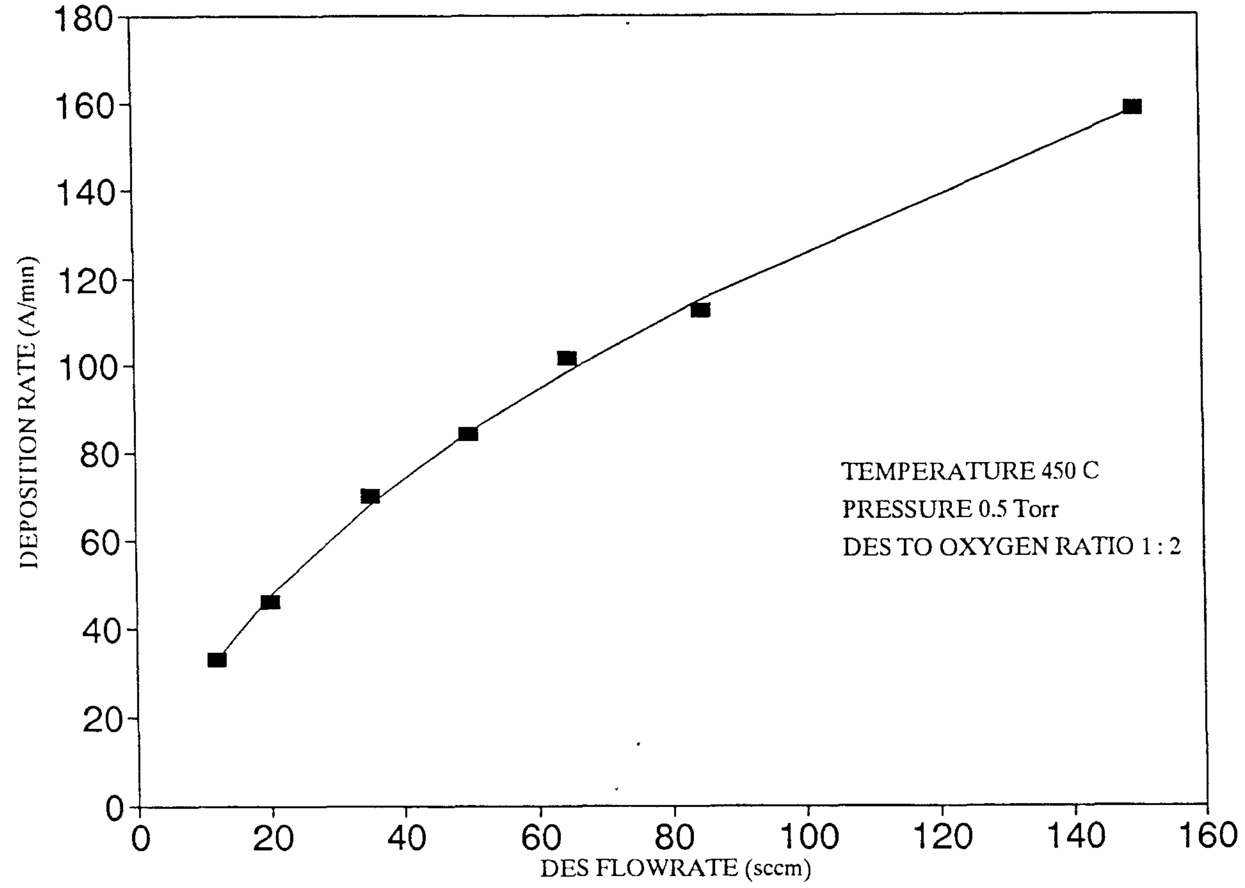

Figure 4.4 Relationship between DES flowrate and the deposition rate.

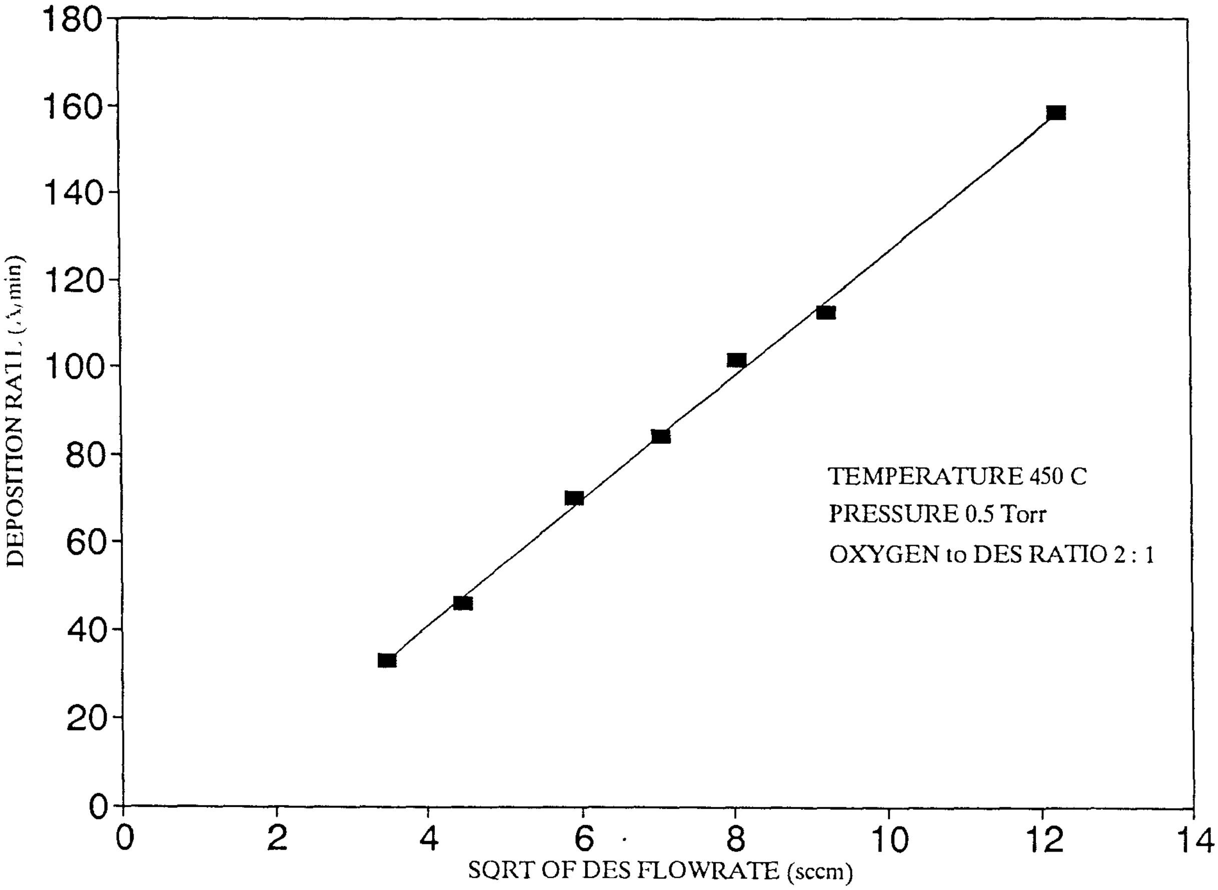

Figure 4.5 Relationship between square root of DES flowrate and the deposition rate.

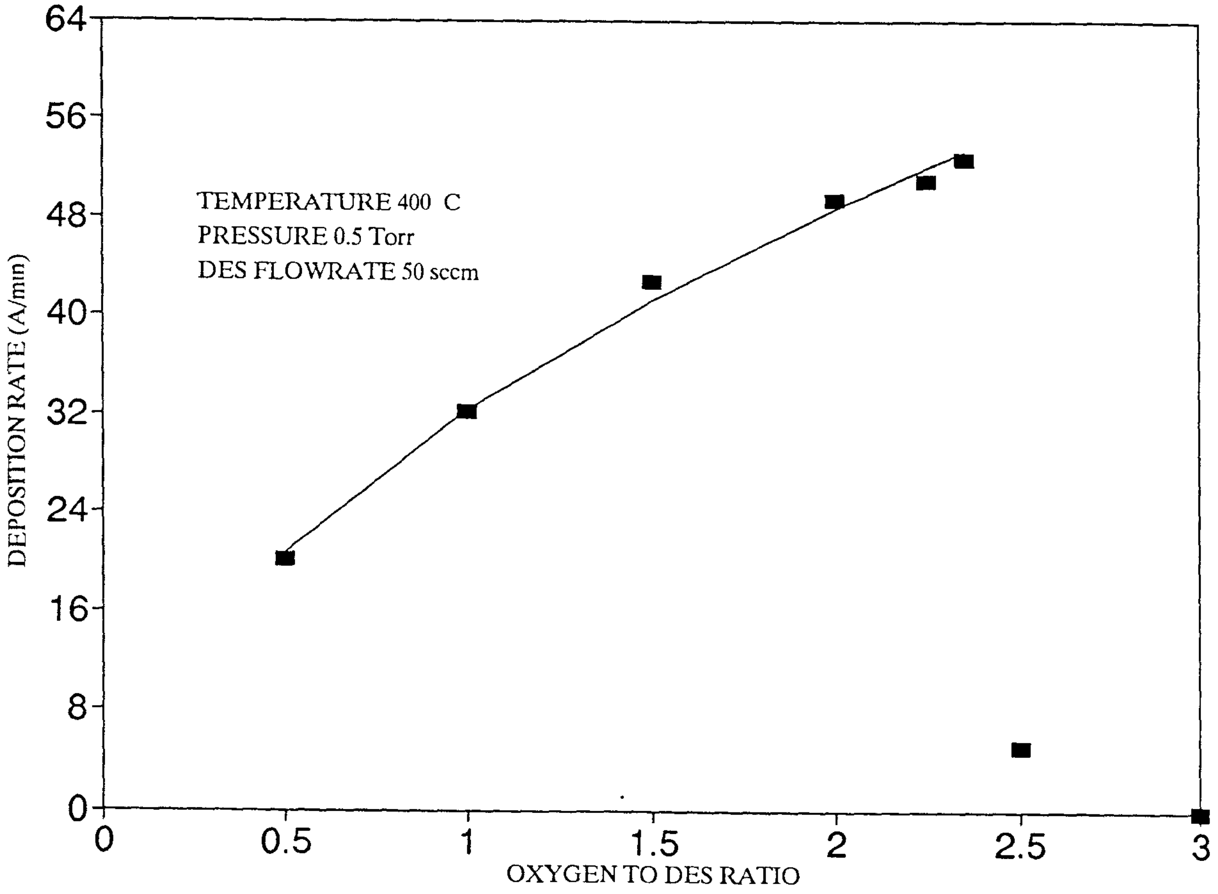

Figure 4.6 Relationship between O_2/DES ratio and the deposition rate.

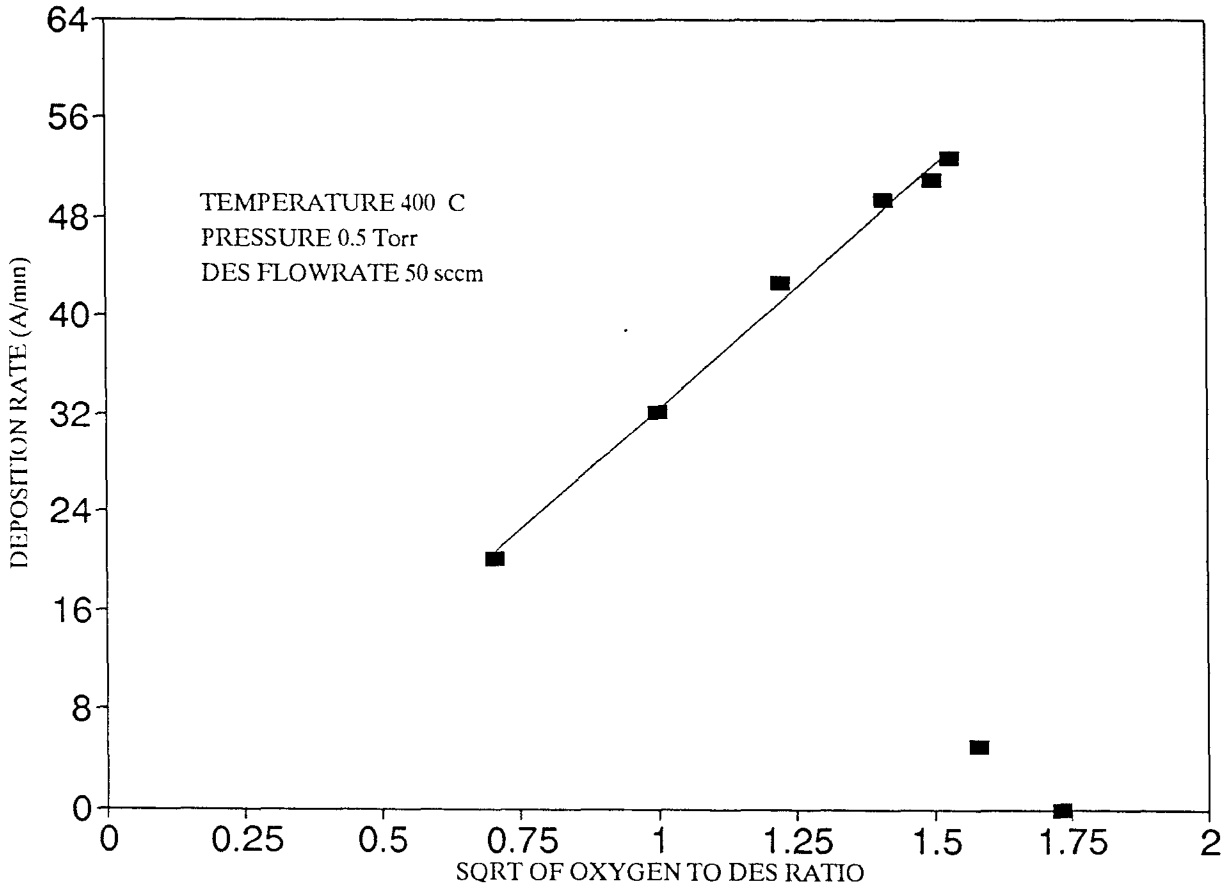

Figure 4.7 Relationship between square root of O_2/DES ratio and the deposition rate.

4.1.4 Effect of O_2/DES ratio

In fig 4.6 the deposition rate is plotted against the O_2/DES ratio and in fig 4.7 the deposition rate is plotted against square root of O_2/DES ratio both of which show a which a similar behavior observed in the study of DES flowrate variation. Within the range of 0-2.35 the deposition rate of the SiO_2 film varies linearly as function of the square root of O_2/DES ratio. As the O_2/DES ratio increases beyond 2.35 the deposition rate was observed to fall down abruptly to zero. One possible explanation of this behavior is that the oxygen being adsorbed on the substrate surface inhibits the diethylsilane decomposition.

4.2 Reaction mechanism

Bimolecular surface reactions

The reaction between two adsorbed molecules: Surface reaction between two adsorbed substances occurs by the reaction between two molecules that are adsorbed on the neighboring surface sites. This mechanism is referred to as bimolecular reaction mechanism (44) If A and B are two reacting species then the rate of such a reaction is proportional to the probability of A and B getting adsorbed on the neighboring sites. This probability is proportional to the fraction of the surface, Θ and Θ', covered by A and B respectively. These fractions are given by (44),

$$\Theta = \frac{Kp}{1+Kp+K'p'} \tag{1}$$

$$\Theta' = \frac{K'p'}{1+Kp+K'p'} \tag{2}$$

where K and K' are the equilibrium constants of A and B; and p and p' are partial pressures of A and B respectively

From the above relations the rate of reaction is therefore

$$v = k_2\Theta\Theta' \tag{3}$$

$$= \frac{k_2KK'pp'}{(1+Kp+K'p')^2} \tag{4}$$

If the pressure p' is kept constant and p is varied, the rate first increases, passes through a maximum, and then decreases. There is a similar variation with p' if p is held constant. The maximum rate corresponds to the existence of the maximum number of neighboring A-B pairs on the surface.

Two special cases of the equation (4) can be considered.

1. Sparsely Covered Surfaces: If the pressures p and p' are both sufficiently low that Kp and Kp' may be neglected in comparison with unity, the rate equation becomes

$$v = k_2KK'pp' \tag{5}$$

The reaction is therefore second order, being first order in both A and B.

2. One Reactant Very Weakly Adsorbed: If reactant A is very weakly adsorbed, the term Kp in the denominator of Eq. (4) may be neglected, and the rate equation becomes

$$v = \frac{k_2KK'pp'}{(1 + K'p')^2} \tag{6}$$

The rate is now proportional to the pressure of A, but as the pressure of B increases, passes through a maximum, and then decreases.

From the above discussion, the SiO_2 film deposition can be analyzed based on the heterogeneous reaction between oxygen and diethylsilane adsorbed on the surface.

If p_T is the total chamber pressure, the rate of SiO_2 film deposition can be expressed as (45):

$$v_{SiO2} = \frac{K_1p_T^2}{(1 + K_2p_T)^2} \tag{7}$$

where

$$K_1 = \frac{K_1'f_{DES}{\cdot}f_{O2}}{f_{DES} + f_{O2}} \tag{8}$$

$$K_2 = \frac{K_2'f_{DES}}{f_{DES} + f_{O2}} \tag{9}$$

f_{DES} and f_{O2} are flowrates of DES and K_1' and K_2' are temperature dependent constants.

Equation (7) for rate of deposition of SiO_2, at high chamber pressures can be modified as the

$$v_1 = K_1/K_2^2$$

i.e., the deposition rate reaches a saturation value K_1/K_2^2.

(since at high pressures $K_2p_T >> 1$, 1 can be neglected).

One possible explanation of the abrupt fall in growth rate at low pressures can be attributed to the occurence of an auto catalytic type of reaction, which prevents the adsorption of diethylsilane on the substrate surface.

The experimental curve shown in fig 4.3 fits the above theoretical model reasonably well.

4.3 Film Characterization

The deposited films were evaluated by optical, electrical, mechanical and compositional measurements. An RBS analysis on the film revealed the composition to be oxygen rich. The chemical composition of the film was found to be $SiO_{2.2}$ independent of the deposition conditions. Table 4.3 shows the composition of SiO_2 film as a function of various process variables.

The usual Si-O bonds stretching and bending were identified at 1060, 800 and 440 cm^{-1} by IR spectroscopy. Fig 4.14 shows an IR spectrum of an SiO_2 film deposited at 400 ^oC. Besides the standard peaks, a small peak at 880 was also observed which was identified as $HSiO_3$. This peak was found to decrease with the decrease in flow rates and was found to disappear at very low flow rates in agreement with the work of Huo et al (45).

The refractive index data obtained by an ellipsometer with a He-Ne source of wavelength 6328 A^o was found to be 1.46 independent of the deposition temperature as shown in the fig 4.8. The refractive index was also found to be independent of the other process variables such as pressure, DES flow rate and O_2/DES ratio.

The dielectric breakdown strength of an SiO_2 film of thickness 4500 A^o was found to be 2 MV/cm. This value is low compared to the dielectric breakdown

Table 4.1 Compositional Analysis by RBS

I.D.	Temp	Pressure	O_2/DES Ratio	Flowrate(sccm)		composition	
	°C	Torr		DES	O_2	Si	O_2
J102	475	0.5	2 : 1	50	100	1.0	2.2
J99	425	0.5	2 : 1	50	100		
J96	375	0.5	2 : 1	50	100	1.0	2.5
J132	400	0.5	2.35:1	50	117.5	1.0	2.2
J123	400	0.5	2 : 1	50	100		
J135	400	0.5	0.5:1	50	50	1.0	2.2
J144	400	0.4	2 : 1	50	100	1.0	2.1
J138	400	0.5	2 : 1	50	100	1.0	2.2
J141	400	0.75	2 : 1	50	100	1.0	2.3
J72	450	0.5	2 : 1	150	300	1.0	2.2
J50	450	0.5	2 : 1	50	100	1.0	2.3
J62	450	0.5	2 : 1	12	24	1.0	2.2

A table showing the composition of the SiO_2 film deposited by using diethylsilane as a function of various process parameters

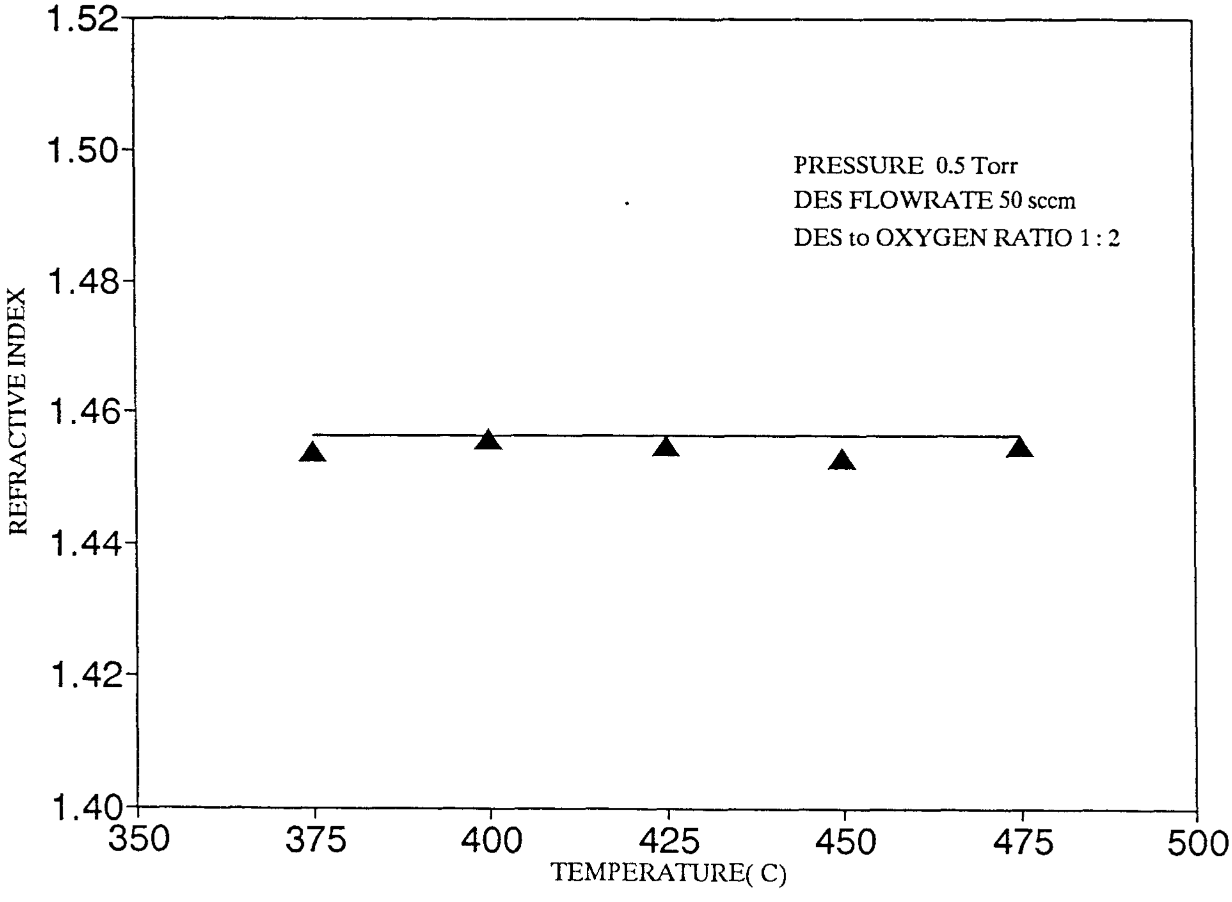

Figure 4.8 Relationship between refractive index and temperature.

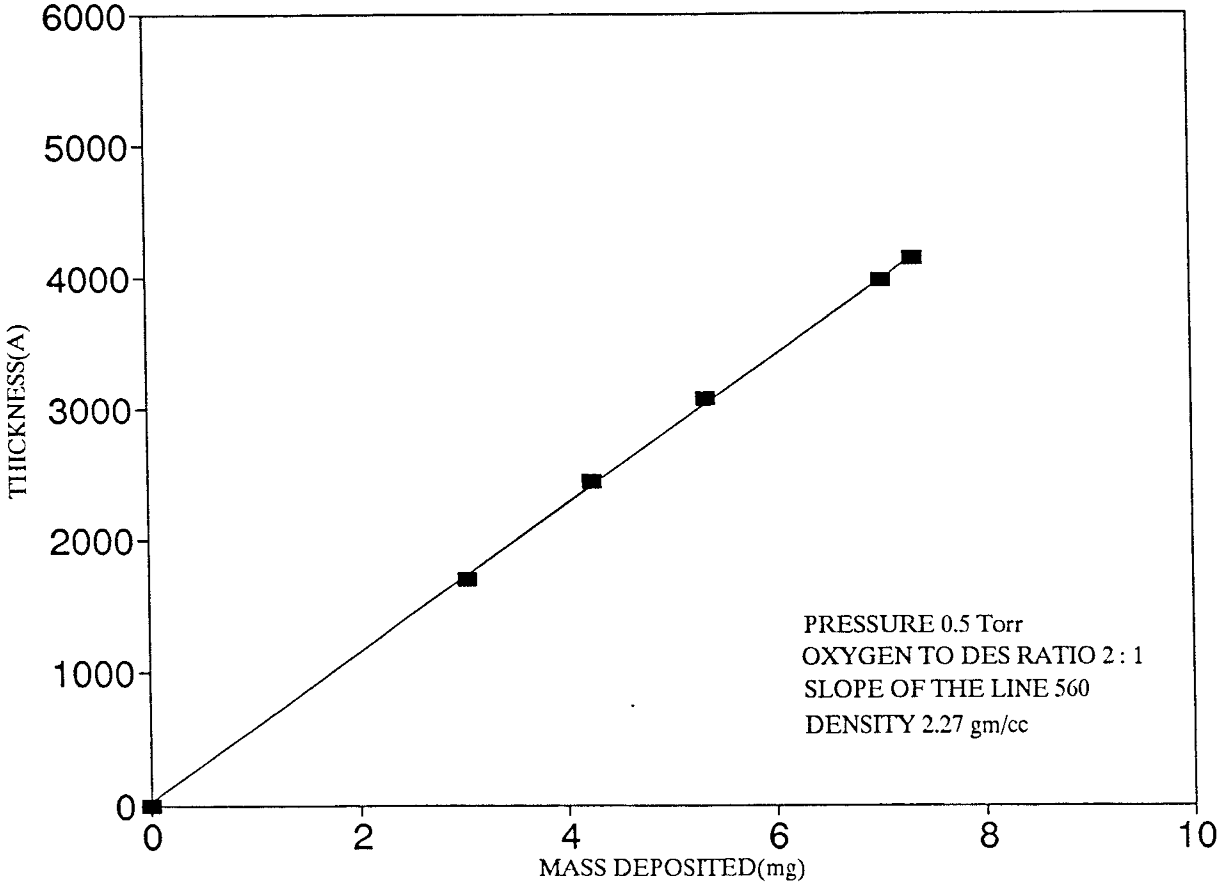

Figure 4.9 A plot of thickness of the film versus mass deposited on the wafer, showing that the density of the film is independent of the temperature.

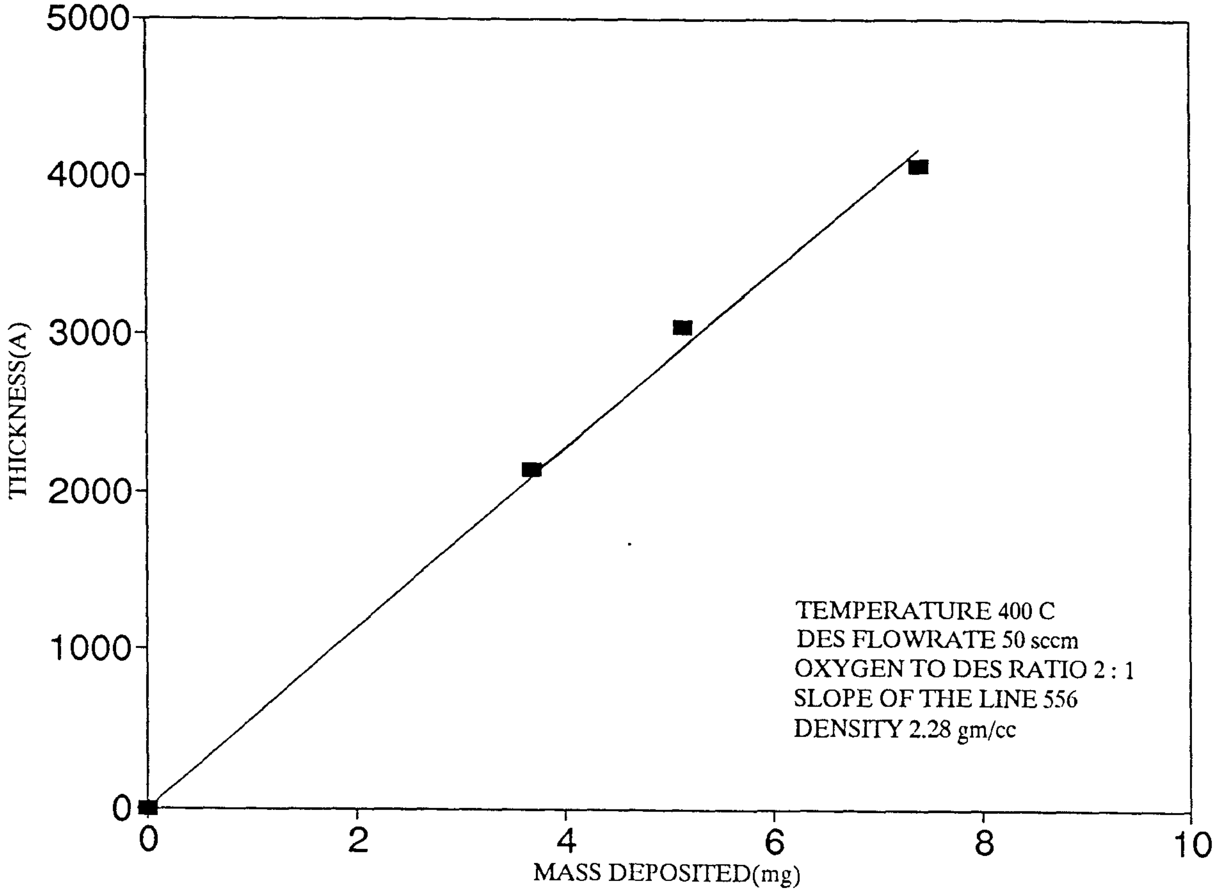

Figure 4.10 A plot of thickness of the film versus mass deposited on the wafer, showing that the density of the film is independent of the pressure.

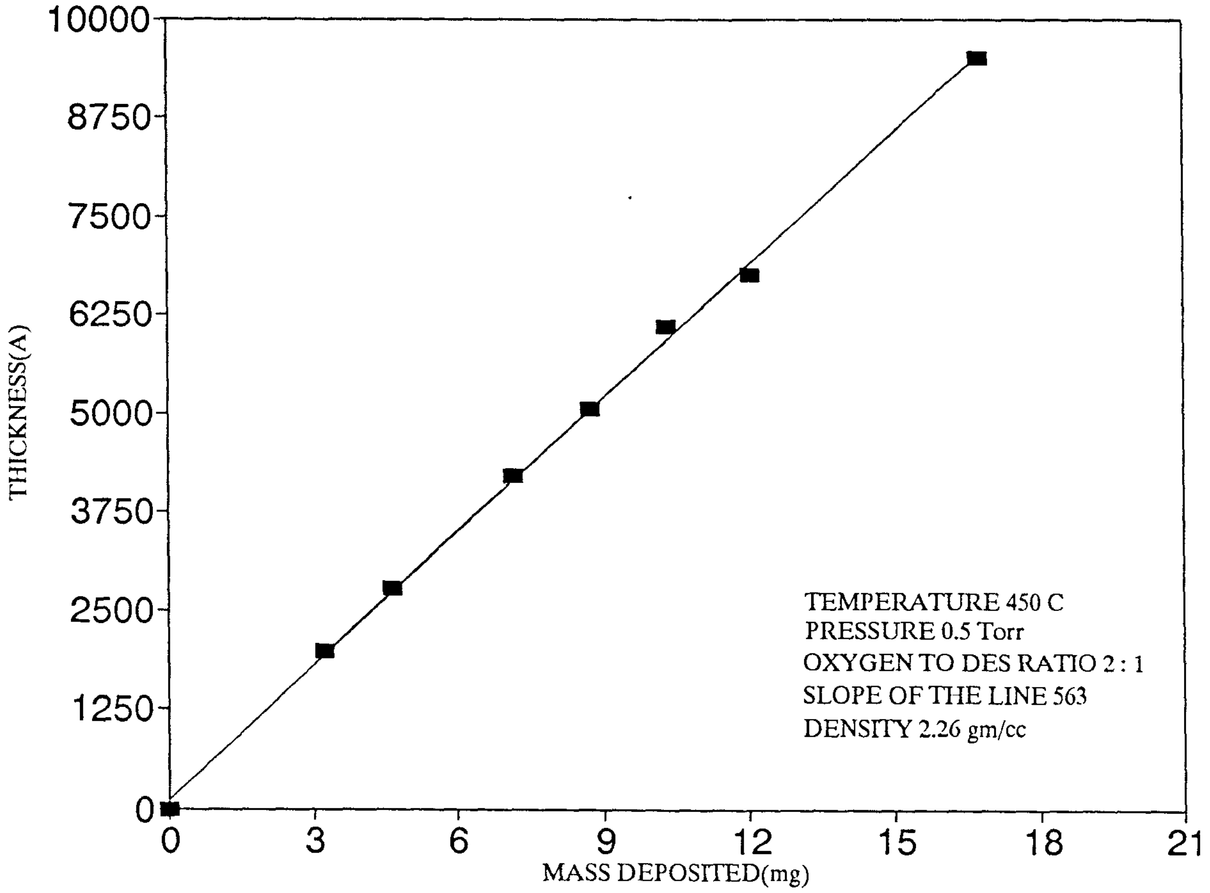

Figure 4.11 A plot of thickness of the film versus mass deposited on the wafer, showing that the density of the film is independent of the flowrate.

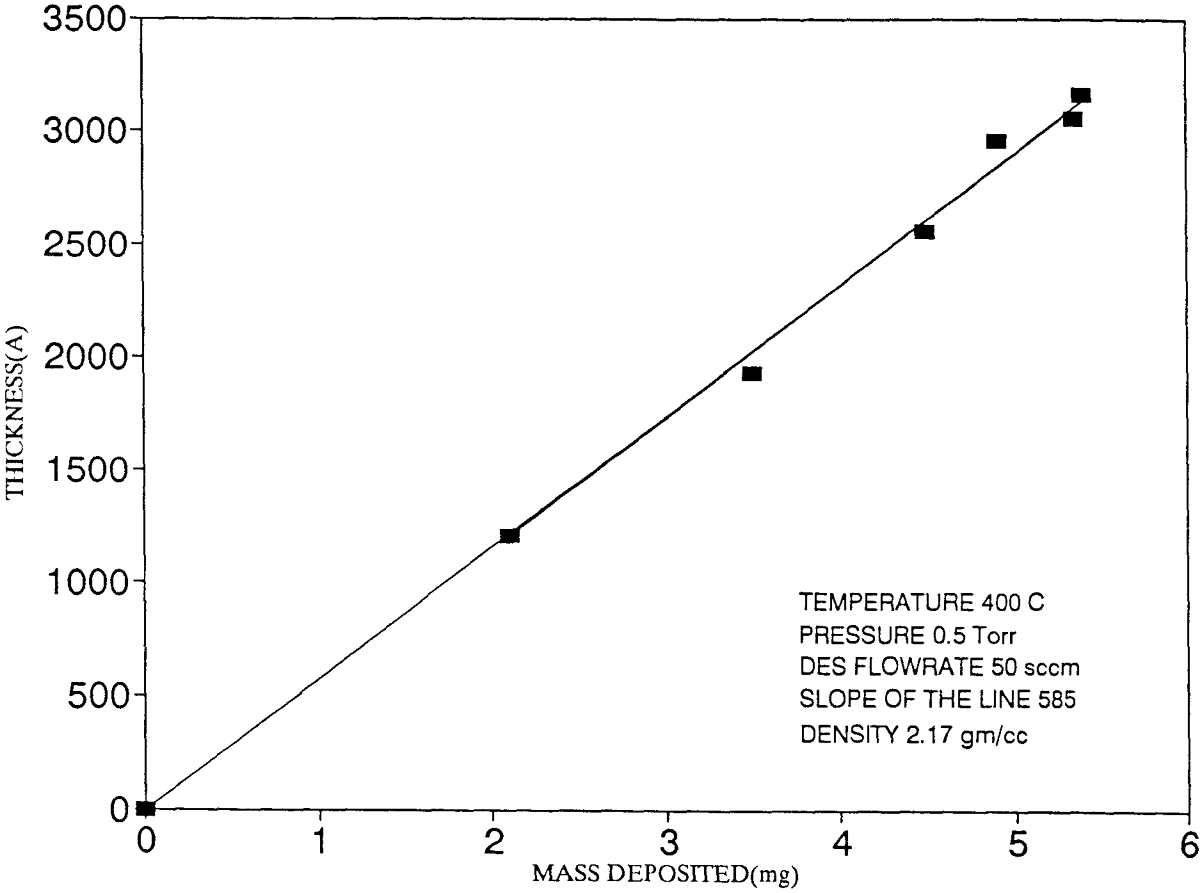

Figure 4.12 A plot of thickness of the film versus mass deposited on the wafer, showing that the density of the film is independent of the O_2/DES ratio.

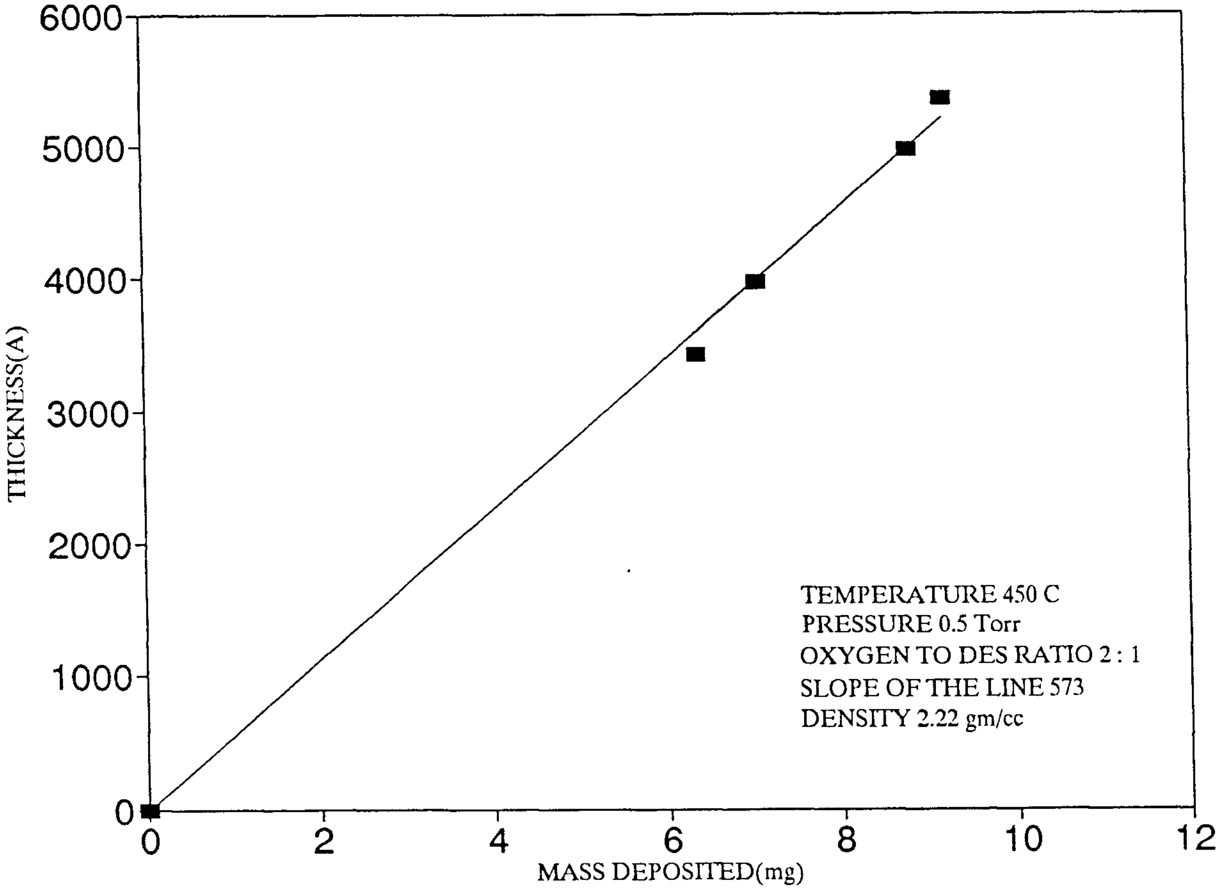

Figure 4.13 A plot of thickness of the film versus mass deposited on the wafer, showing that the density of the film is independent of the wafer spacing.

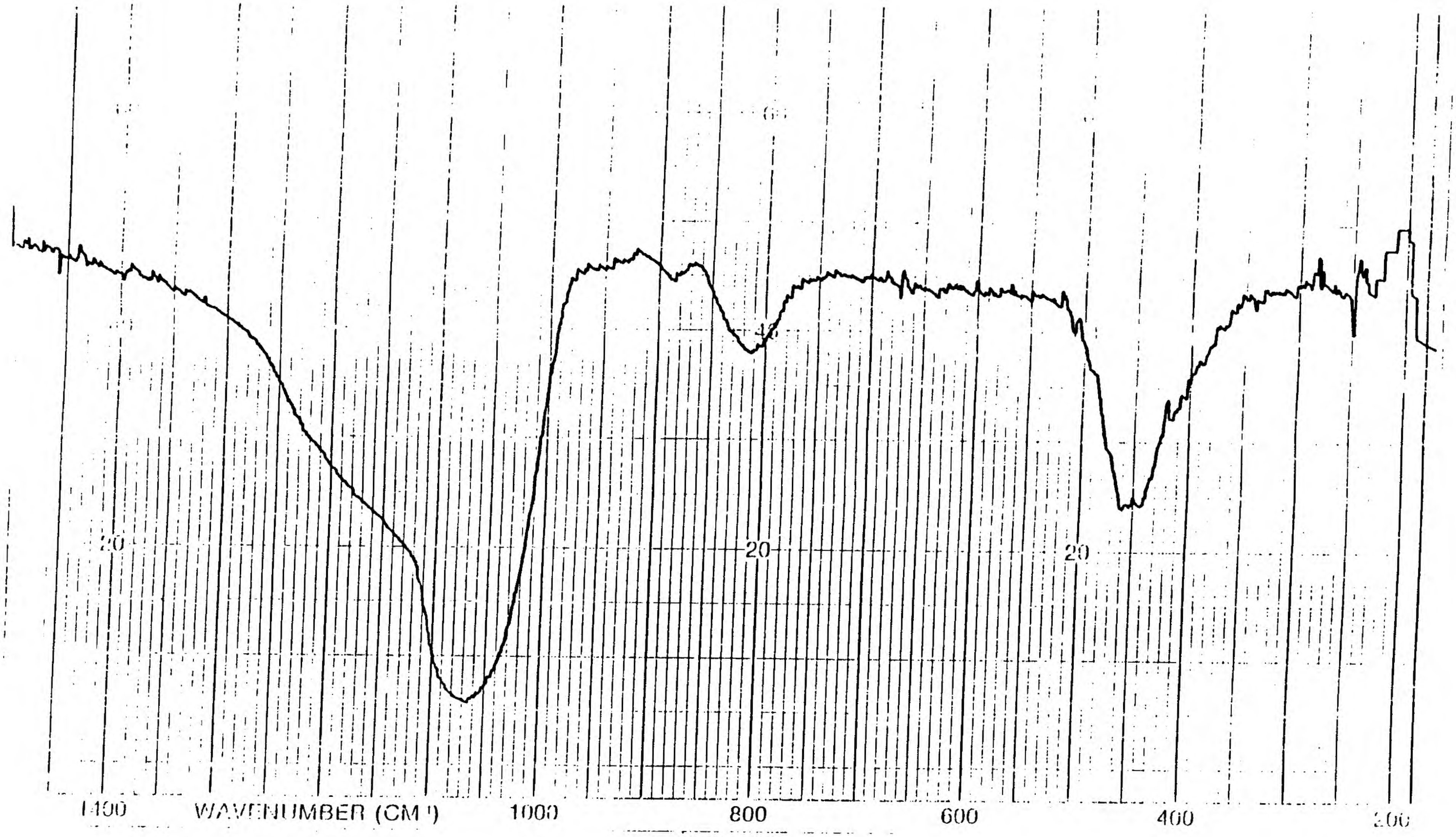

Figure 4.14 IR spectrum of a sample deposited at 400 ^{O}C showing the Si-O streching, bending and rocking vibrations.

strength of thermal oxide which is around 10 MV/cm for an oxide thickness of 1000 A^o.

Density of the deposited SiO_2 films was studied as a function of the various deposition variables viz., temperature, pressure, DES flow rate and O_2/DES ratio. A graph plotted by taking the thickness of the deposited film in angstroms against the half of total mass deposited on both sides of the wafer in milligrams for different temperatures is shown in the fig 4.9. The straight line observed in the graph indicates that the density of the film is independent of the temperature. The variation of density as a function of other process variables is also shown in the fig 10-13. The density can be calculated from the fundamental mass volume relation and as the area of the wafer is constant, the density of the film can be obtained from the slope of the graph. The density thus estimated was found to be 2.2 g/cm^3 independent of the deposition temperatures, close to that of thermal oxide 2.2 g/cm^3. The density was also found to be independent of the other deposition conditions.

5. CONCLUSIONS

Diethylsilane was used to prepare amorphous SiO_2 glass films on Si <100> wafers by low pressure chemical vapor deposition technique. The composition of the film was $SiO_{2.2}$ and the carbon content was below the detection limit. The dependence of film growth rate on various process parameters were studied. The growth rate was found to follow an Arrhenius behavior with the variation in the temperature with an activation energy of 10 kcal/mole. IR spectra were used to detect hydrogen bonded silanol group, Si-OH at 880 cm^{-1}. The refractive index and the density were observed to be close to 1.46 and 2.2 g/cm^3 respectively, comparable with the values of that of a thermally produced oxide. The dielectric breakdown values were found to be 2 MV/cm, which is low compared to that of the thermal oxide.

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