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ABSTRACT

LOW PRESSURE CHEMICAL VAPOR DEPOSITION (LPCVD) OF TITANIUM NITRIDE: SYNTHESIS AND CHARACTERIZATION

by
Sameer Dharmadhikari

Titanium tetrachloride and ammonia were used as precursors in a low pressure chemical vapor deposition process to deposit titanium nitride films on silicon wafers. The process was carried out at temperatures from 450 to 850 ºC and the activation energy for the reaction was determined. The order of the reaction, with respect to the partial pressures of the reactant gases, was determined by carrying out the reaction at varying partial pressures of the reactant gases. The following rate equation was established for the reaction:

$$rate = 4.35*10^{-5}\exp(-5150/T)*(P_{NH3})^{1.37}(P_{TiCl4})^{-0.42}$$

The titanium nitride thin films deposited were characterized for properties like resistivity, stress, hardness, and density. The effects of varying the process parameters (temperature, flow ratio, etc.) on these film properties were studied.

LOW PRESSURE CHEMICAL VAPOR DEPOSITION (LPCVD) OF TITANIUM NITRIDE: SYNTHESIS AND CHARACTERIZATION

by
Sameer Narsinha Dharmadhikari

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APPROVAL PAGE

LOW PRESSURE CHEMICAL VAPOR DEPOSITION (LPCVD) OF TITANIUM NITRIDE: SYNTHESIS AND CHARACTERIZATION

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This thesis is dedicated to my

beloved parents and my loving sister.

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CHAPTER 1

INTRODUCTION

1.1 Titanium Nitride Thin Films

Titanium Nitride (TiN) is a widely used material because of its special properties. Apart from its main use as a diffusion barrier adhesion promoter in the microelectronics industry, it has also been used as a wear-resistant coating on tools and as a gold substitute for decorative coatings [1]. Currently, it is being investigated for other applications such as solar energy absorber and transparent heat mirror [1].

TiN has been deposited using various film deposition techniques [1]. Such techniques are discussed in the next section. The principal physical properties of bulk TiN are given in Table 1.1 [2].

Table 1.1 Physical properties of titanium nitride.

Melting Point	3200 °C
Thermal Expansion	8×10^{-6} °C^{-1}
Thermal Conductivity	24 W/m-K
Hardness	1770 kg/mm^2
Resistivity	30×10^{-6} Ω-cm
Density	5.4 g/cm^3
Young's Modulus	36 Msi

1.2 Thin Film Deposition Methods

Thin film deposition has traditionally been used in the microelectronics industry for microchip coating, wear and corrosion resistance, and thermal protection. Deposition methods can be classified under two groups: Physical Vapor Deposition (PVD) and Chemical Vapor Deposition (CVD).

1.2.1 Physical Vapor Deposition

Physical vapor deposition (PVD) is categorized as evaporation and sputtering. The objective of both deposition techniques is to control the transfer of atoms from a source to a substrate where film formation and growth proceed atomistically, independent of a chemical reaction; hence the term *physical* vapor deposition.

In evaporation, atoms are removed from the source by thermal means, whereas in sputtering the atoms are dislodged from a solid target by the impact of gaseous ions. Advances in vacuum-pumping equipment and Joule heating sources spurred the emergence of PVD as a suitable industrial film deposition process. In general, the properties of the film obtained by PVD are governed by evaporation rate of the atoms, vapor pressure of the target materials, deposition geometry, temperature, pressure, and the thermal history of the substrate.

Traditionally, evaporation was the preferred PVD technique over sputtering. Higher deposition rates, better vacuum (resulting in cleaner environments for film formation and growth), and versatility in using all classes of materials, were some of the reasons for the dominance of evaporation.

The microelectronics revolution required the use of alloys, with strict stoichiometric limits, which had to conformally cover and adhere to substrate surfaces. This prompted the need for the sputtering technique and so, as developments were made in the use of radio frequency, bias, and magnetron variants, so were advances made in sputtering. These variants extended the capabilities of sputtering, as did the availability of high purity targets and working gases. The decision to use either technique depends solely on the desired application and has even spurred the development of hybrid techniques.

1.2.2 Chemical Vapor Deposition

Chemical vapor deposition (CVD) is a process in which volatile reactants in vapor phase chemically react near or on the surface of a suitably placed substrate to form a nonvolatile solid product that deposits atomistically on the substrate. A wide variety of thin films utilized in Very Large Scale Integration (VLSI) are prepared by CVD. These materials comprise dielectric, elemental and compound semiconductors, electrical conductors, superconductor and magnetic materials. In addition to its versatility, this materials synthesis and vapor phase growth method can operate efficiently at relatively low temperature, which is an added advantage, especially in those cases where the substrate cannot tolerate higher temperatures.

1.3 Chemical Vapor Deposition (CVD)

1.3.1 Basic Aspects of CVD

The product from a CVD process can be in the form of a thin film, a thick coating, or if allowed to grow, a massive bulk. Deposits can have monocrystalline, polycrystalline, or an amorphous structure. Chemical and physical conditions during the deposition reaction strongly affect the composition and structure of the product. This technology has become one of the principal methods of depositing thin films and coatings in solid state microelectronics where some of the most stringent purity and composition requirements must be met.

The different types of chemical reactions involved in CVD processes include oxidation, reduction, hydrolysis, nitride and carbide formation and synthesis reactions, to name a few. A sequence of several reaction types is usually involved to create a particular end product. The chemical reactions may take place not only on the substrate surface (heterogeneous reaction), but also in the gas phase (homogeneous reaction) [3]. Heterogeneous reactions are much more desirable, as such reactions selectively occur only on the heated surfaces, and are known to produce good quality films. Homogeneous reactions, on the other hand are undesirable, as they form gas phase clusters of the depositing material, which can result in poor adherence, low density or defects in the film. Thus one important characteristic of CVD application is the degree to which heterogeneous reactions are favored over homogeneous reactions [3].

1.3.2 Transport Phenomena in CVD

The sequence of steps in a typical CVD process can be described as follows [3]:

1. Arrival of the reactants
   a. bulk transport of reactants into the chamber,
   b. gaseous diffusion of reactants to the substrate surface,
   c. adsorption of reactants onto the substrate surface.
2. Surface chemistry
   a. surface diffusion of reactants,
   b. surface reaction.
3. Removal of products
   a. desorption of by-products from the substrate surface,
   b. gaseous diffusion of by-products away from the substrate surface,
   c. bulk transport of by-products out of the reaction chamber.

The steps are sequential and the slowest process is the rate-determining step. Depending on the step that is rate-determining, the deposition process can be either in the mass transport limited regime or in the surface reaction limited regime [3].

If the deposition process is limited by mass transfer, the transport process, usually determined by the gas-phase diffusion, is proportional to the diffusivity of the gas and the concentration gradient. This mass transport process that limits the growth rate is only weakly dependent on temperature. In this case, it is very important that the same concentration of reactants be present in the bulk gas regions adjacent to all locations of a wafer, as the arrival rate is directly

proportional to the concentration in the bulk gas. Hence, to ensure films of uniform thickness, reactors that are operated in the mass-transport-limited regime must be designed so that all locations of wafer surfaces and all wafers in a run are supplied with an equal flux of reactant species. The temperature control is this case is not critical [3].

If the deposition process is limited by the surface reaction, the growth rate (r) of the film deposited can be expressed as:

$$r = r_o^* \exp(-E_a/RT)$$

where r_o = frequency factor,

E_a = activation energy (usually 25-100 kcal/mole for surface process),

R = gas constant (1.987cal/mol),

T = absolute temperature (K).

In the operating regime, the deposition rate is a strong function of the temperature and excellent temperature control is required to achieve the film thickness uniformity that is necessary for controllable integrated circuit fabrication. In this case, the rate at which reactant species arrive at the surface is not as important. Thus, it is not as critical that the reactor be designed to supply an equal flux of reactants to all locations of the wafer surface. That is why in horizontal low pressure CVD reactors where high mass transfer rates are prevalent because of the low pressure, wafers can be stacked vertically and at a closely spaced positioning, because such systems operate in a surface reaction rate limited (i.e. kinetic) regime [3].

Figure 1.1 [4] is a typical plot of growth rate as a function of temperature. For lower temperatures, it shows relatively steep temperature dependence and for higher temperatures, it shows a milder dependence, thus indicating that the nature of the rate-controlling step changes with temperature.

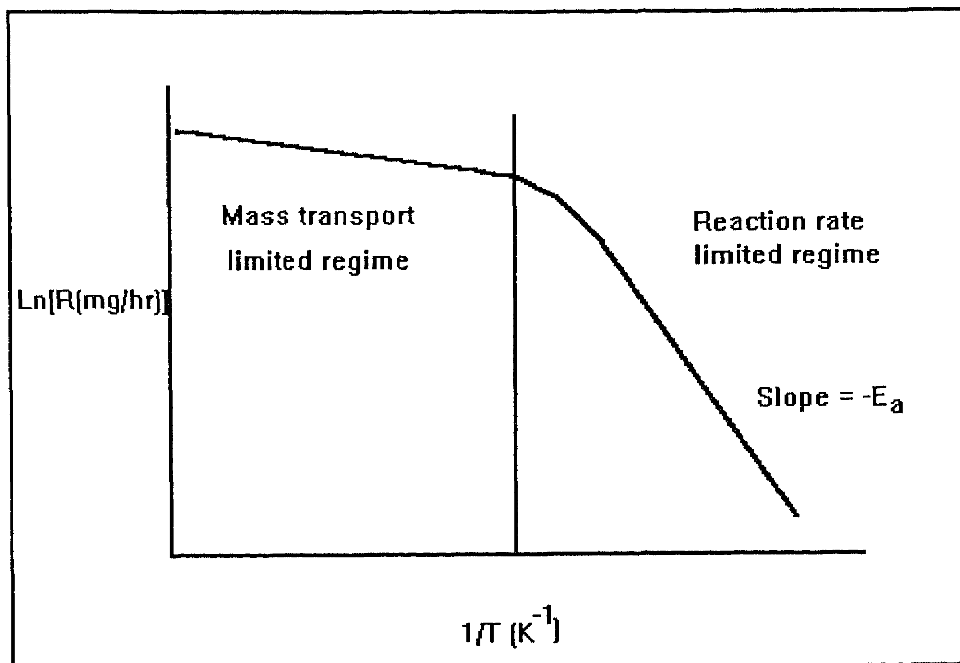


Figure 1.1 Deposition rate as a function of substrate temperature.

1.3.3 Film Growth Aspects of CVD

In general, lower temperature and higher gas phase concentration favor formation of polycrystalline deposits. Under these conditions, the arrival rate at the surface is high, but the surface mobility of adsorbed atoms is low. Many nuclei of different orientation are formed, which upon coalescence result in a film consisting of many differently oriented grains. Further decrease in temperature and increase in supersaturating result in even more nuclei, and consequently in

finer-grained films, eventually leading to the formation of amorphous films when crystallization is completely prevented. Amorphous films, which include oxides, nitrides, and carbides, are of great importance for microelectronics applications.

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

1.3.4 Reaction Mechanism in CVD

As mentioned in the previous sections, adsorption, surface reaction and desorption are the important steps in the CVD process, which need to be understood properly in order to be able to explain the reaction mechanism.

- ***Adsorption and Desorption:*** CVD reactions being surface catalyzed, reactants adsorb on the surface. The simplest expression for the amount of a gas adsorbed on a surface, is given by the Langmuir Adsorption Isotherm [5] as:

$$\theta = KP/(1+KP)$$

where θ = fraction of the total sites adsorbed by the gas,

P = pressure of the gas,

K = equilibrium adsorption constant for the gas.

In CVD reactions, many times, both the reacting species adsorb onto the surface, thereby resulting in what is known as competitive adsorption. The adsorption isotherm in this case is given by:

$$\theta_A = K_A P_A \,/\, (1 + K_A P_A + K_B P_B) \qquad (1.1)$$

$$\theta_B = K_B P_B \,/\, (1 + K_A P_A + K_B P_B) \qquad (1.2)$$

where θ_A, θ_B = fraction of total sites covered by species A and B,

K_A, K_B = equilibrium adsorption constant for species A and B,

P_A, P_B = partial pressure of species A and B.

- ***Reaction:*** The surface catalyzed reaction in a CVD process is usually a bimolecular reaction between the two adsorbed species. In that case, the rate of the reaction is dependent on the concentration or the fraction of the sites occupied by each of the species. If this reaction is the rate determining step, which it usually is, the rate of film deposition can be given as:

$$\text{rate} = k\theta_A\theta_B$$

$$\therefore \text{rate} = kK_AK_BP_AP_B/(1+K_AP_A+K_BP_B)^2 \qquad (1.3)$$

This method of treating a surface catalyzed reaction is known as the Langmuir-Hinshelwood kinetics [5]. If one of the pressures is maintained constant and the other is varied, the rate first increases, passes through a maximum and then decreases. The falling off of the rate at high pressures can be explained to be due to the fact that one reactant displaces the other reactant, as its pressure is increased. Two special cases of equation 1.3 are [5]:

1) Sparsely covered surfaces, where both P_A and P_B are sufficiently low (due to dilution or very high vacuum), for the pressure terms in the denominator to be neglected, so that the rate equation (1.3) becomes,

$$\text{rate} = kK_AK_BP_AP_B \qquad (1.4)$$

2) When reactant A is weakly adsorbed (i.e. $K_A << 1$), the term K_AP_A in the denominator in equation 1.3 might be neglected to give,

$$\text{rate} = kK_AK_BP_AP_B/(1+K_BP_B)^2 \qquad (1.5)$$

Further if the reactant B is very strongly adsorbed so that $K_Bp_B >> 1$, we have,

$$rate = kK_AP_A/K_BP_B \quad (1.6)$$

1.4 Types of CVD Process

As mentioned in the previous section, chemical reactions are very intrinsic to any CVD process and hence energy in some form or the other must be provided for the desired chemical reaction to take place. This energy could be supplied by heat (thermal), by an electric glow discharge (plasma) or by some kind of electromagnetic radiation (e.g. laser). Depending on the type of energy supplied to initiate and sustain the reaction, CVD processes have been classified as [6]:
(i) Plasma enhanced CVD, (ii) Photo induced CVD, or (iii) Thermally activated CVD.

1.4.1 Plasma Enhanced CVD (PECVD)

In this method, gaseous reactants are introduced in a region of glow discharge (plasma) created by applying an electric field, using A/C, D/C or microwave sources, between two electrodes. This results in the formation of highly reactive species, which react and form a solid thin film product on the substrate and electrode surfaces. The molecules can be near to the ambient temperature but the breakdown electrons will be at higher temperatures, causing the reaction. Thus this method can be employed at relatively low temperature and is useful for temperature sensitive materials. Film deposition rates are substantially higher in this method than in thermally activated CVD. Also, conformal step coverage can

be achieved. However, the disadvantage of this method is the complex process that occurs in the plasma state making the synthesis of stoichiometric films difficult.

1.4.2 Photo Induced CVD

Short wavelength UV radiation is used to activate the reactants in the gaseous phase forming the product material. A selective absorption of photon energy by the reactant molecules or atoms initiates the process. The advantage of this method is low deposition temperature (needed for films like SiO_2) and absence of radiation damage. The limitation of this method is unavailability of effective production equipment. In another type, laser beams are used for activating the reactants. In yet another type, the reactant atoms or molecules absorb a specific wavelength of the laser energy applied resulting in chemical gas phase reaction that are very specific, leading to highly pure film deposits. But, these methods are still in developing stages [6].

1.4.3 Thermally Activated CVD

This process uses direct thermal energy for the chemical reaction. The simplest type of this CVD is the conventional atmospheric pressure CVD (APCVD) where the reactant gases are allowed into the chamber at normal atmospheric pressure. Energy is supplied by heating the substrate directly. The temperature and the reactant flow rates determine the film growth rate. The advantage of the APCVD is its simplicity in that no vacuum pumps are needed. The disadvantage

is the tendency for homogeneous gas phase nucleation, which leads to particle contamination, unless special optimized gas injection techniques are used. The deposition rate and uniformity of the films deposited using CVD process can be determined by the rate of mass transfer of reactant gases to the substrate, or the rate of surface reaction of the reactant gases. In atmospheric pressure CVD, these two rates are of the same magnitude.

Lowering the gas pressure by about 3-4 orders of magnitude enhances the mass transfer rate relative to the surface reaction rate. This makes it possible to deposit films uniformly with a highly economical close spaced positioning of the substrate wafers kept vertically inside the chamber. Thus low pressure CVD (LPCVD) is a widely used method in cost competitive semiconductor industry. Another advantage of this method is that the gas phase nucleation is reduced.

Depending on the method of supply of thermal energy, CVD reactors can be classified as either hot wall or cold wall reactors. In a hot wall reactor system, the reactor is heated to a high temperature and the gas molecules hitting the wall receive the thermal energy. Here, the substrate is indirectly heated. The advantage of this system is a temperature gradient that can be provided to the chamber, which results in uniform thickness. In the cold wall system, the substrate is heated to high temperature directly. The reactants that are adsorbed on the surface undergo chemical change due to the temperature of the substrate. But in this case, controlling the wafer's temperature is difficult and hence uniform deposition is difficult to achieve.

1.5 Low Pressure Chemical Vapor Deposition (LPCVD) Process

Most LPCVD processes use resistance heating to attain isothermal conditions so that the substrate and the reactor walls are of similar temperature. However, infrared radiation heating techniques are also sometimes used.

The mass transfer of the gases involves their diffusion across a slowly moving boundary layer adjacent to the substrate surface. The thinner this boundary layer and the higher the gas diffusion rate, the greater is the mass transport that results. Surface reaction rates, on the other hand, depend mainly upon reactant concentration and deposition temperature. In LPCVD, the rate of mass transfer is enhanced with respect to the heterogeneous surface reaction rate by lowering the gas pressure. This improved rate of mass transfer makes it possible to deposit films uniformly even on closely placed wafers. Moreover, high deposition rates are attainable with LPCVD because of the large mole fraction of reactive gases in the reactor, since no or little diluent gas is required [3].

Some of the main factors affecting the film thickness and uniformity in LPCVD are the temperature profile in the reactor, the pressure level of the reactor and the reactant gas flow rates. To obtain a uniform thickness profile across each substrate wafer throughout the reactor, a judicious adjustment of these parameters is required [7]. In general, the uniformity of thickness and step coverage of the films obtained by LPCVD is very good. These films have fewer defects, such as particulate contaminants and pinholes, due to their inherently cleaner hot wall operations and the vertical wafer positioning that minimize the formation and codeposition of gas phase particulate [7].

1.6 Advantages of CVD

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

CVD processes are often selected over competitive deposition techniques because they offer the following advantages [7]:

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

1.7 Limitations of CVD

CVD process is basically limited by the feasibility of the chemical reaction involved therein. Furthermore, the kinetics of that reaction governs the process

as a whole. Technological limitations of CVD include the unwanted and possibly deleterious by-products of the reaction that must be eliminated, and the ever present particle generation induced by homogeneous gas phase nucleation that must be minimized.

1.8 Objectives of this Study

In this study, titanium tetrachloride ($TiCl_4$) and ammonia (NH_3) are used as precursors to deposit a titanium nitride film on silicon substrates by low pressure chemical vapor deposition (LPCVD). The deposition was carried out at pressures of the order of 0.01 to 0.1 torr. Some properties of $TiCl_4$ used for the study are listed below in Table 1.2.

Table 1.2 Properties of titanium tetrachloride.

Formula	$TiCl_4$
Molecular Weight	189.7 g/mol
Vapor Pressure	10 mm Hg at 20 °C
Boiling Point	136.4 °C at 1 atm.

This thesis seeks to: (a) study and determine the kinetics of the reaction and establish a rate equation, (b) characterize the deposited films for their properties, and (c) study the effect of variation in the process parameters on these film properties.

In the next chapter, a literature survey of the work done on TiN deposition by different researchers is presented. In chapter 3, the experimental setup and the procedures for the deposition process are described, followed by the different characterization methods used for determining the film properties. In chapter 4, the results obtained are put forth and the significance of these results discussed.

CHAPTER 2

LITERATURE SURVEY

In this chapter a range of deposition techniques used for titanium nitride have been reviewed. The kinetic study and the characterization of titanium nitride films as carried out by different workers have also been presented.

2.1 Deposition Techniques

Titanium nitride (TiN) thin films have been deposited over the past years using the different techniques mentioned in the previous chapter. And different reactants have been used as the precursors for these depositions.

The choice of the deposition method as well as the precursors is dictated by the temperature requirements and the equipment availability. The properties of the deposited film are dependent to a great extent on the deposition technique (CVD, PVD, etc) as well as on the precursors used.

TiN has been commonly deposited using reactive sputtering or by rapid thermal nitridation of sputter deposited titanium [8]. However the sputter deposited films suffer from a lot of disadvantages like poor conformality, low step coverage, etc. In the recent years, as the aspect ratios of features have increased, CVD methods have been sought as a better alternative for TiN thin film deposition. Many workers have studied the deposition of TiN films by different types of CVD. Table 2.1 shows a summary of the methods and reactants different researchers have used to deposit titanium nitride.

Table 2.1 Summary of different deposition techniques and reactants used for TiN thin film deposition.

Technique	Reactants	T (°C)	P(torr)	Remarks	Ref.
LPCVD (cold wall)	TDMAT, NH_3	327	0.1	Single wafer reactor, argon used as a diluent, steam injected into the reactor.	8
LPCVD (cold wall)	$TiCl_4$, NH_3	650		Single wafer reactor, nitrogen used as a diluent.	9
LPCVD	$TiCl_4$, NH_3	480	20	Single wafer rotating disk reactor, nitrogen used as a diluent.	10
LPCVD (cold wall)	TDEAT, NH_3	250-450	10-500	Single wafer MOCVD reactor.	11
LPCVD (hot wall)	$TiCl_4$, NH_3	450-750		Single wafer load-locked reaction chamber	12
LPCVD (cold wall)	$TiCl_4$, NH_3, H_2	550-750	0.15	Argon used as a diluent	13
APCVD	$TiCl_4$, NH_3	400-700	760		1
APCVD (hot wall)	$TiCl_4$, N_2, H_2	800-900	760	Deposition of film on molybdenum substrates.	14
PVD (sputtering)	Ti cathode, N_2	300		Bias at a power of 250 W was used.	15
PVD (cathodic arc deposition)	Ti cathode, N_2	280, 460		Bias of 350-600 V	16

2.2 Properties and Applications

In the last few years there has been a great interest in the study of the physical properties of titanium nitride thin films. This is due to the variety of applications found for this material in several areas. It is widely used as a wear resistant coating on tools, as a gold substitute for decorative coatings and for thin film resistors [1]. Recently it has been investigated as a diffusion barrier in various

semiconductor metallization schemes (as a diffusion barrier), a contact layer for silicon, a gate electrode in metal/oxide/semiconductor integrated circuits and even as a solar energy absorber and transparent heat mirror because of its optical properties in the visible and IR regions. These different applications of TiN are a result of its properties, which depend on the composition (N:Ti ratio), impurity (O_2,Cl,etc.) content and the structure, which in turn depend on the growth technique used and the deposition parameters employed. Table 2.2 gives a brief summary of the different properties of TiN film and the process by which these films were deposited.

Table 2.2 Summary of properties of TiN films deposited by different processes.

Deposition Technique	Density (g/cc)	Resistivity (μΩ-cm)	Chlorine cont. (%)	Hardness (Mohs)	Step coverage	Ref.
LPCVD (450-750 °C)	4.2-4.9	200-650	2-6	-	-	12
APCVD (400-700 °C)	-	200-6000	0.5-50	8.5	-	1
PECVD	3.7	550-4500	NA	-	30-90% for an aspect ratio of 1:1.	17
LPCVD (550-750 °C)	-	100-1100	0.5-10	-	100% for an aspect ratio of 1.9.	13
LPCVD (rotating disk reactor)	-	80-1000	1-14	-	100% for aspect ratios > 2.	18

2.3 Kinetic Studies on TiN CVD

As can be seen from Table 2.1, TiN CVD has been done using different combinations of reactants. Commonly NH_3 and N_2 have been used as sources of N while titanium halides (more commonly $TiCl_4$), titanium dialkylamides, tetrakisdimethyl (or ethyl) amino titanium (TDMAT/TDEAT) have been the common sources for Ti. But whatever the reactants, the reaction rate is always important since it ultimately determines the film growth rate. This study of the reaction rate and mechanism, better known as the kinetic study, has been carried out by several researchers, for different reactant combinations and reactor geometries.

Buiting et. al. [13] deposited TiN films from $TiCl_4$, NH_3, H_2 and Ar gas mixtures, in a small cold wall LPCVD system. They found out that the reaction rate and hence the deposition rate to be proportional to the 1.3 power of the partial pressure of NH_3 and inversely proportional to 0.5 power of the partial pressure of $TiCl_4$. They proposed the following rate equation:

$$\text{rate} = 1.3*10^{-5} \exp(-7500/T)\ (P_{H2})^{0}(P_{NH3})^{1.3}(P_{TiCl4})^{-0.5}$$

The activation energy of their process was 61 kJ/mol.

A similar study was carried out by Imhoff et. al. [19] using the same reactants and a similar reactor system, with the only difference being that in this case, instead of $TiCl_4$, NH_3 was introduced closer to the substrate. In this case, the deposition rate was obtained to be:

$$\text{rate} = 2.7*10^{-5} \exp(-9600/T)\ (P_{H2})^{0}(P_{NH3})^{-0.63}(P_{TiCl4})^{1.27}$$

Imhoff et. al. proposed that these contradictory rate orders were a result of a difference in the gas injection configuration in the two reactor systems. The gas (say A), which was injected closer to the substrate, poisoned the sites for adsorption by the other gas (say B). As a result, increasing the partial pressure of A, gave lesser sites for adsorption of B, thereby leading to a decrease in the deposition rate, hence the negative power. The apparent activation energy was determined to be 79 kJ/mol.

Dekker et. al. [14] carried out TiN deposition in a hot wall CVD reactors at temperatures higher than 800°C, using $TiCl_4$, N_2 and H_2 as the reactants. They found the growth rate dependence on $TiCl_4$ concentration to change from a positive order to a negative order with increasing $TiCl_4$. The rate order was 0.5 with respect to N_2 concentration and changed from 1 to 1.5 for H_2 concentration. The apparent activation energy was around 100 kJ/mol.

Jiang et. al. [20] used a cold wall CVD to deposit TiN on graphite substrates using $TiCl_4$, NH_3 and H_2 at temperatures from 1100-1600 °C and for different NH_3:$TiCl_4$ flow ratios. For low flow ratios, they found the deposition rate to increase with increasing flow ratio and deposition temperature. For higher flow ratios, the deposition rate decreased with increasing flow ratio and was almost constant with increasing deposition temperature.

Bouteville et. al. [21] have carried out a thermodynamic study of titanium nitride formation on a patterned silicon substrate, using $TiCl_4$, NH_3 and H_2. They performed calculations in the temperature range of 700-1300 K and in the pressure range 27-133 Pa so as to determine the yield.

2.4 Characterization Studies on TiN

TiN is widely used in a variety of applications due to its different properties. Many researchers have studied the properties of thin film and coatings of TiN by a variety of methods.

Wu et. al. [23] demonstrated the capabilities, advantages and limitations of different techniques, namely scanning electron microscopy (SEM), transmission electron microscopy (TEM), thin film X-ray diffraction (XRD), secondary ion mass spectroscopy (SIMS), X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectroscopy (RBS), to obtain valuable information primarily about the morphology of TiN thin films.

Several researchers [8,9,17,23] studied conformality and step coverage of TiN films deposited by different methods. Almost all of them found TiN films to be nearly 100% conformal for aspect ratios as high as 1.7. For higher aspect ratios, conformality was found to be pretty good.

Many researchers [1,13,23] have studied the variation of film resistivity. They found that the Cl content was responsible for high resistivity and that Cl content decreased with increasing temperature. Thus, high deposition temperature led to the formation of films with low resistivities of around 100 μ ohm-cm. Presence of oxygen in the film was also found to cause an increase in the film resistivity [15]. Roman et. al. [16] found out that presence of oxygen during deposition even resulted in weaker adhesion of the film because of the TiO_2 formed. Arena et. al. [18] used XPS and Auger electron spectroscopy (AES)

to obtain qualitative information about Cl in TiN films and even studied its effect on the corrosion and step coverage of the films.

Oh et. al. [22] have studied the preferred orientation of TiN thin films using XRD technique. They observed that as the thickness of the TiN deposited increased, the preferred orientation changed from (200) to (110) to finally (111). They concluded it to be a combined effect of strain energy and surface energy of the film. Yokoyama et. al. [24] also found the preferential orientation to be (200) by carrying out XRD of TiN films deposited by cold wall LPCVD.

Kurtz and Gordon [1] tested hardness of TiN film 3 µm thickness grown on stainless steel substrate and found it to be 8.5 on Moh's hardness scale, on which diamond is 10. Roman et. al. [16] used Vicker's method to determine hardness of sputter deposited TiN on high-speed steel, to be around 2000 kg/mm^2.

CHAPTER 3

EXPERIMENTATION

3.1 Experimental Setup

The schematic diagram of the LPCVD reactor is shown in Figure 3.1. This reactor was manufactured by Advanced Semiconductor Materials (ASM) America Inc. as a polysilicon micro-pressure CVD system. The horizontal reaction chamber consists of a 13.5 cm diameter and 135 cm long fused quartz tube encapsulated within a 10 kW, Thermco MB-80 heating furnace. The reactor door is constructed of 300 series stainless steel, with a side hinge and sealed with an O-ring. The vapors of the precursor coming from the $TiCl_4$ bubbler were passed to the reactor through a MKS vapor source mass flow controller. UNIT mass flow controllers (UFC-1100) control the flow of ammonia and argon into the reaction chamber. A simple manual valve was used to control the flow of nitrogen into the reactor during the operation of devacuuming the reactor.

The other end of the reaction chamber is connected to a vacuum station comprised of a Leybold-Heraeus TRIVAC dual stage rotary vane pump backed by a Leybold-Heraeus RUVAC roots blower. The rotary pump helps maintain the necessary vacuum, while the blower increases the exhaust flow rate out of the reactor. A wire mesh at the blower inlet was used to prevent solid particulate material, from entering the blower and the pump. A ceramic tube was setup between the chamber and the heater to enhance the radiation heat transfer thus reducing the temperature deviation through the reaction tube. The temperature

was maintained constant across all zones and confirmed using a calibrated K type thermocouple. Mass flow controller set points were programmed with a MICON 3 microprocessing controller which produces the set point voltage and automatically monitors the flow vs. the programmed flow limits. The pressure in the reactor was monitored with an automatic exhaust valve and measured at the reactor inlet using a capacitance manometer (13 torr MKS baratron pressure gauge).

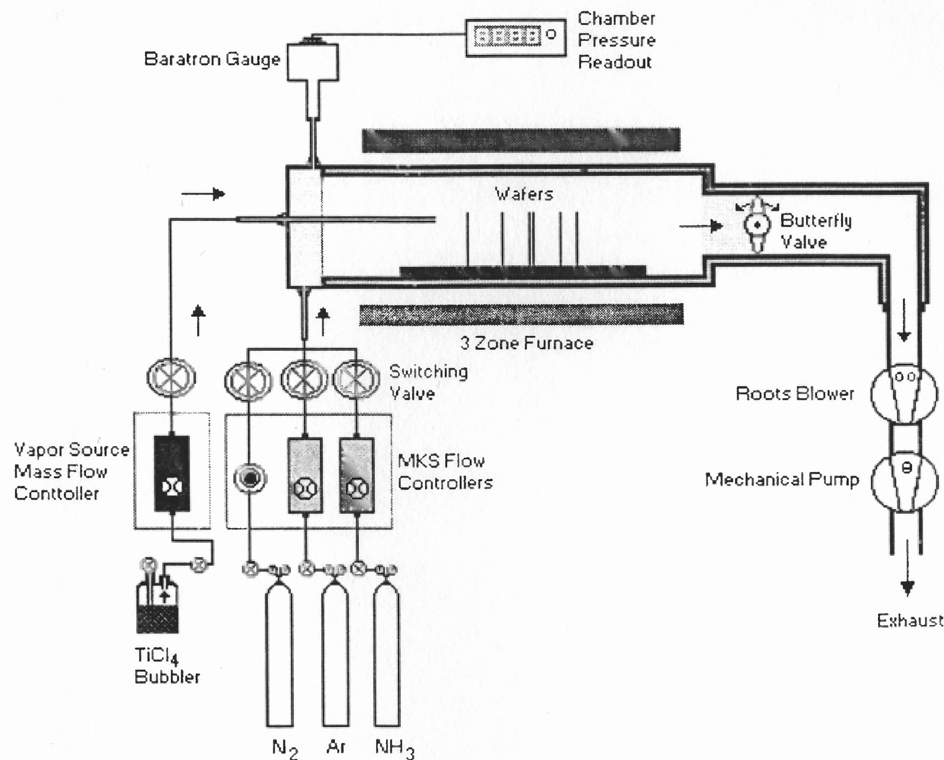


Figure 3.1 Schematic diagram of the experimental setup.

3.2 Pre-experiments

3.2.1 Flow Meter Calibration

Since the flow ratio as well as the actual flow rates of the reactant gases were important parameters, the flow meters for the reactant gases were calibrated first, before starting with the main experiments. The flow rate of ammonia and argon, obtained from respective cylinders, was measured and controlled using UNIT mass flow controllers. Flow rate of gaseous $TiCl_4$, coming from a bubbler containing pressurized liquid $TiCl_4$, was measured and controlled using MKS vapor source flow controller. This flow meter gave the flow reading directly in sccm and was not needed calibrated.

The way in which the calibration of the UNIT flow controllers was done is as follows. For a certain starting vacuum pressure of the reactor, and the valve open by certain percent, the gas was allowed to enter the reactor for a certain amount of time (Δt) and the final pressure of the reactor at the end of the time period was noted. The pressure increase (ΔP) was measured and used to calculate the volume of the gas corrected to the STP conditions (i.e. at T_0 = 273K and P_0 = 760 torr). The expression for flow rate (F.R.) in sccm corrected to STP was derived from the gas law and is as follows:

$$F.R. = 60(\Delta P/\Delta t)(T_0 V/P_0 T) \quad (3.1)$$

Where ΔP = pressure increase (torr)

Δt = time duration of addition of the gas (sec)

V_0 = volume of the reactor = 19557 cc

By carrying out this calculation for different percentages of the valve opening, a calibration plot was obtained of the actual flow vs. % valve value. This calibration plot was used to determine the percentage at which the valve should be kept open so as to give the desired flow rate and hence the desired flow ratio. These flow calibrations were done periodically to check for inconsistencies.

3.2.2 Leakage and Outgassing Check

Before starting the experiments, the reactor setup was for leakage and outgassing. With the reactor evacuated and the flow controllers fully open, the valves were closed and the flow controller reading was monitored for any change indicating valve leakage. Leakage of the reactor was checked using alcohol at all the potential points of leakage like the reactor entrance and the entry point of the reactants. A rapid increase in the pressure indicated leakage.

Finally the reactor was checked for outgassing, which is the volatilization of the deposited compounds on the inside of the reactor, due to extremely low pressure inside the reactor. To check for outgassing, the pressure in the reactor was lowered to the minimum steady value. Then all the inlet and outlet valves were closed and the pressure in the reactor was monitored. The increase in the pressure was noted. If this increase is very rapid, it implies that there is considerable outgassing. This is taken care of by keeping the reactor evacuated for a long time and even by heating it. But no matter what, there will always be a certain minimal outgassing in the reactor, which is not a problem during the experimentation and can be neglected.

3.3 Experimental Procedure

3.3.1 Wafer Loading

Single sided polished silicon wafers of type <111>, with a diameter of 100 mm and thickness of around 525 μm, were cut into four approximately equal parts (quarters). Along with these four quarters, whole wafers were introduced for the purpose of stress and thickness measurement. The wafer for stress measurement was placed back to back with another whole wafer so that deposition took place only on one side. For the whole wafer to be used for film thickness measurement by Dektak, a small wafer piece was kept face-to-face with it. Before loading into the reactor, the weights of all these pieces were measured using an electronic balance and noted. They were then loaded onto a clean quartz boat by placing them vertically in the slots provided on the boat. The reactor was brought to atmospheric pressure, by filling it with nitrogen, so as to open the door. The boat was then carefully kept inside the reactor at a distance of 65 cm. from the reactor inlet and the door was shut close.

3.3.2 Reactor Start-up

Once the wafers were loaded, the door of the reactor was shut and all the inlet valves were closed. Now the bypass valve was opened and the chamber pressure was reduced from atmospheric pressure to 5 torr. Then the outlet (main) valve was opened so that the pressure dropped down to as low as 50 mtorr. This two step procedure of reducing the chamber pressure ensured that the process wafers were not subjected to a sudden force and as a result they

didn't break. A low pressure was maintained inside the chamber using the vacuum pumps. At this point the reactor was checked for any possible leakage. The furnace was then switched on. The temperature of the reactor was increased in steps of 200°C till the final desired temperature was reached. The external cooling system (fans) was switched on to keep the pump end cool.

When the temperature and the pressure stabilized, the reaction was started. Before opening any of the reactant gas valves, the flow controllers for these valves were set to the desired level. The valves were then opened one after the other. The timer was started as the pressure of the reactor stabilized. The deposition was then allowed to take place for a certain period of time. Among the deposition parameters recorded were the pressure, reaction temperature, flow rates of the reactants and the deposition time.

3.3.3 Reactor Shutdown and Wafer Unloading

At the end of the given time period, the furnace and the turbo pump were shut off. The flows of the reactant gases were shut off one after the other. Here care was taken to see that the gases were evacuated from the lines as well. The reactor was then allowed to cool overnight.

After the reactor has cooled to room temperature, it was still under vacuum. So nitrogen was let into the reactor till the pressure became atmospheric. The door of the reactor was then opened and the boat was pulled out using a long rod with a hook at the other end. The weight of the wafers was measured and recorded.

3.3.4 Reactor Cleanup

During every run, the inside of the reactor also became coated and it was essential to clean the reactor so as to avoid outgassing during the next run. Alcohol and acetone, which are good solvents, were used to clean the reactor. Water was avoided since it, being not volatile, stays in the reactor. The boat was also cleaned and readied for the next run.

3.4 Characterization

(A) Film Weight: An electronic balance was used to measure the weight of the wafers, accurately to 0.1 milligram, before and after the deposition process. The difference gave the film weight.

(B) Thickness: The thickness of the deposited films was measured with the help of the Sloan II Dektak machine. To facilitate this measurement, the film had to be deposited on the wafer in such a way that a certain part of the wafer was obscured and didn't have the film, but the film was deposited on the surrounding portion. This was done by keeping a small piece of the wafer in face-to-face contact with the wafer on which the film was to be deposited. So that after the deposition, the portion of the wafer covered by the small piece was just the original silicon surface while the surrounding area was the deposited film. The wafer used for thickness determination was always kept at the same distance from the reactor inlet for all the runs. The Sloan Dektak machine had a mechanical stylus profilometer, which scanned and plotted the profile of the

surface as it went from the undeposited region into the deposited region. The thickness of the film could be obtained from this plot.

(C) Growth Rate: Growth rate was determined in terms of Å/min, by dividing thickness by the time of deposition. Growth rate was used as measure of the rate of reaction and was studied with respect to the temperature of deposition as well as the partial pressures of the reactant gases in order to establish the rate equation.

(D) Density: The titanium nitride films were deposited on just one side of the wafers by placing them back to back. The film was thus deposited on a known surface area of 78.5 sqcm and the thickness of the film was determined as described in section 3.4.2. Thus the volume of the film could be determined, and knowing the film weight, density could be determined as the ratio of mass (weight) to volume.

(E) Stress: The stress in the film was determined by a house-developed device, employing dual laser beam equipment, which measures change in radius of curvature of the wafer resulting from the film deposited on one side. Two fixed and parallel He-Ne laser beams were incident on the wafer surface before and after deposition. The reflected beams from the two surfaces were then projected by an angled plane mirror as two points onto a scale at a fixed distance and their separation was measured. The change in separation of these two points, D(mm),

before and after deposition of a film of thickness T(μm), was fed into the following equation, obtained by simplifying Stony's equation, to obtain actual stress value δ in MPa :

$$\delta = 12.3\ D/T \qquad (3.2)$$

(F) Resistivity: To determine the resistivity of the film, first the sheet resistance was determined using a standard four-point probe. The sheet resistance when multiplied by thickness of the film gave the resistivity of the film.

(G) Hardness: The hardness of the titanium nitride films deposited was measured using the nanoindentation technique. The data obtained gave the values for hardness at different indentations starting from zero to more than 200 nm. The hardness of the film was taken to be the value for an indentation of 200 nm since the value more or less stabilized at this depth.

(G) X-ray Diffraction: The films deposited were analyzed using X-ray diffraction (XRD), so as to determine the orientation of the lattice planes. The equipment used was a Phillips X-ray Diffractometer, which was operated using APD software. A 40 kV voltage was used at a current of 45 mA to do the XRD. The angle (2θ) range scanned was 5° to 110° in a duration of 6 hours.

(H) Optical Measurements: Optical measurements for the deposited films were carried out using a benchtop emmissometer. These measurements gave the spectral data for reflectance, transmittance and emittance of the films.

CHAPTER 4

RESULTS AND DISCUSSION

The results of titanium nitride thin film deposition on silicon substrates, under varying conditions of temperature and flow ratios of the reactant gases are discussed in this chapter. The changes in the film properties, electrical as well as mechanical, due to variation in the process parameters are also explained. In all the experiments, films deposited were uniform and without cracks. No peeling was observed indicating that the adhesion properties of titanium nitride on silicon substrate are excellent.

First, in the kinetic study of the reaction, the change in the growth rate due to variation in the deposition temperature is used to determine the activation energy for the reaction. The rate order of the reaction with respect to the reactant gases is determined by studying the change in the growth rate due to variation in the partial pressure of the reactant gases. The kinetic study is followed by the characterization study, in which the effect of varying the process parameters on the various mechanical and electrical properties of the film is studied.

4.1 Kinetic Study

The kinetic study of titanium nitride thin film deposition, using $TiCl_4$ and NH_3 as the precursors, was carried out by taking the growth rate as a measure of the reaction rate and studying it as a function of temperature and the partial pressures of the reactant gases.

4.1.1 Temperature Effects

The deposition was carried out at different temperatures while keeping all other parameters constant and the growth rate of the films in each case was determined. Two sets of data were obtained: (a) For a NH_3 /$TiCl_4$ flow ratio of 10, experiments were carried out at 450, 475, 500, 530, 550, 600 and 700 °C and (b) For a NH_3 /$TiCl_4$ flow ratio of 5, experiments were carried out at 600, 700, 800 and 850 °C. In both cases, the thickness data, knowing the time of deposition, was converted into growth rate data in terms of Å/min. This film growth rate is a measure of the rate of the chemical reaction and the rate of the chemical reaction can be expressed as follows:

$$\text{rate} = k(P_{NH3})^x(P_{TiCl4})^y \tag{4.1}$$

where P_A = partial pressure of species A

x,y = reaction rate orders

The constant k in the above reaction depends on the temperature according to the Arrhenius expression given below.

$$k = A_0{*}\exp(-1000E_a/RT) \tag{4.2}$$

where E_a = activation energy for the reaction, kcal mol^{-1}

R = gas constant, 1.987 cal K^{-1} mol^{-1}

T = temperature, K

A_0 = constant

Since the flow rates of the reactants and the total pressure was maintained constant, and only the temperature was varied, the growth rate for

each of these experiments was dependent only on the exponential term in equation 4.2.

$$rate = k'exp(-1000E_a/RT) \quad (4.3)$$

By taking natural logarithm (ln) on both sides of the above equation and plotting a graph of ln (growth rate) versus (1000/T), the following plot is obtained.

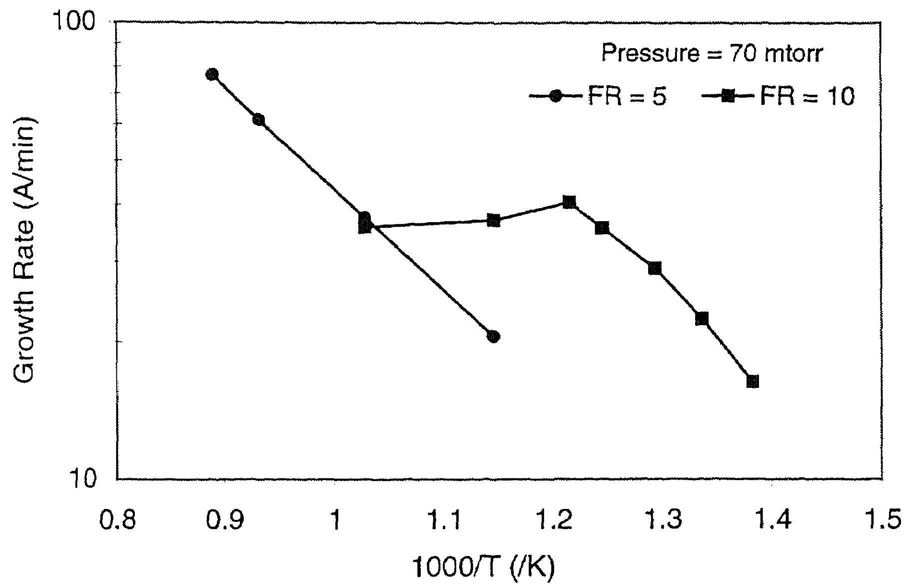


Figure 4.1 Plot of growth rate vs. 1000/T.

Neglecting the horizontal part of the plot, since that is for the diffusion controlled regime, the negative slope of the plot gives the ratio between the activation energy and the gas constant. By determining the slope of the curve, the activation energy for the reaction can be calculated. For the plot shown in Figure 4.1 above, the slopes of the two lines are almost equal and give an average value of 5150 for E_a/R, from which the activation energy can be calculated to be about 10 kcal/mol.

4.1.2 Partial Pressure of $TiCl_4$

To study the effect of partial pressure of $TiCl_4$ on the growth rate, $TiCl_4$ flow rate was changed while keeping flow rate of NH_3 constant at 50 sccm. The reactor temperature and pressure were also maintained constant. Since the mole fraction of NH_3 varied, its partial pressure also changed, but these changes were relatively small enough, compared to the changes in the partial pressure of $TiCl_4$, to be neglected. The growth rate was then plotted versus the partial pressure of $TiCl_4$ on a double logarithmic plot as shown in Figure 4.2 below. All other parameters being constant in equation 4.1, the growth rate is proportional to the partial pressure of $TiCl_4$. If x is the order of proportionality, then we have,

$$\text{rate} = k'(P_{TiCl4})^{x} \tag{4.4}$$

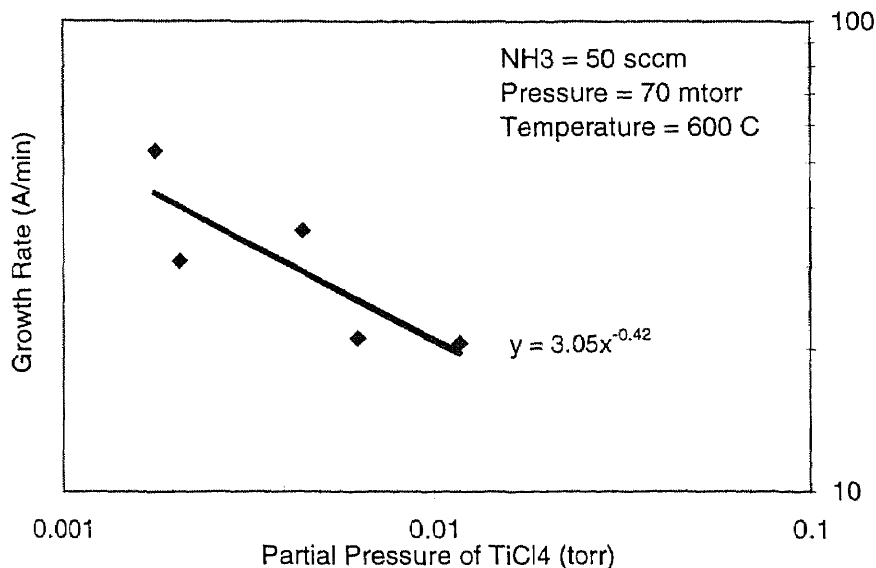


Figure 4.2 Plot of growth rate as a function of partial pressure of $TiCl_4$.

4.1.3 Partial Pressure of NH_3

To study the effect of partial pressure of NH_3 on the growth rate, argon had to be introduced into the reactor for the following reason. Unlike in the case of$TiCl_4$, changing the flow rate of NH_3 while maintaining constant, the flow rate of $TiCl_4$ and reactor pressure, changed partial pressures of both the gases significantly. Hence, if only partial pressure of NH_3 was to be changed, another gas (argon) was needed to compensate for this change and thus maintain partial pressure of $TiCl_4$ constant. Argon being an inert gas did not participate in the reaction.

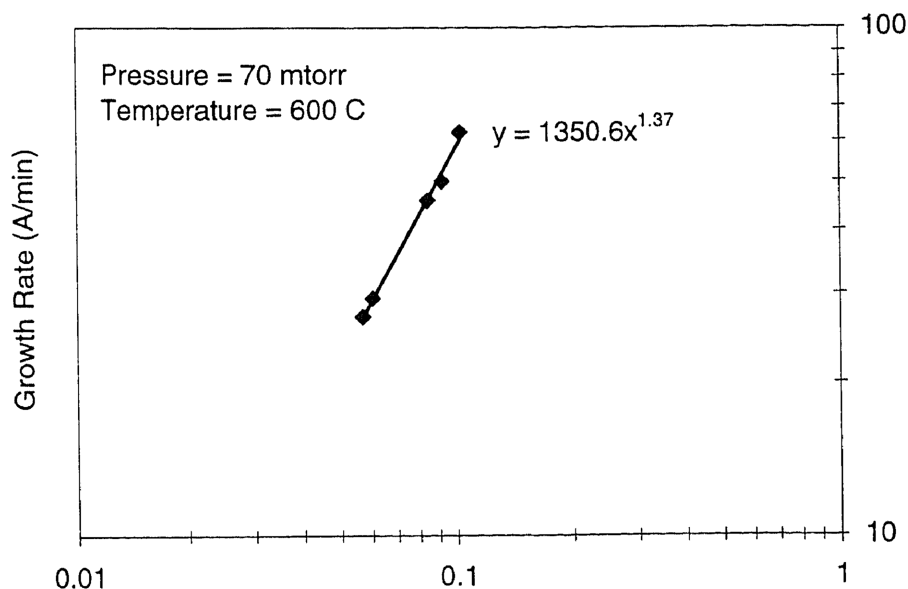


Figure 4.3 Plot of growth rate as a function of partial pressure of NH_3.

As in the case of $TiCl_4$, the growth rate was plotted versus the partial pressure of ammonia on a double logarithmic plot (Figure 4.3) and the slope of this plot gave the order of the reaction with respect to ammonia as 1.37.

4.1.4 Rate Equation

Knowing the values of the activation energy and the rate orders with respect to ammonia and titanium tetrachloride, the following rate equation can be established using equations 4.1 and 4.2, where rate is in mol/min.

$$rate = 4.35*10^{-5}\exp(-5150/T)*(P_{NH3})^{1.37}(P_{TiCl4})^{-0.42} \quad (4.5)$$

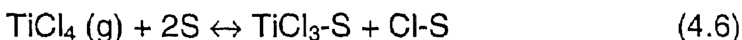
4.1.5 Reaction Mechanism

In the gaseous phase at lower temperatures, NH_3 and $TiCl_4$ are known to form a $TiCl_4.nNH_3$ complex [19]. In accordance with this, a yellow powder, presumably to be of $TiCl_4.2NH_3$, was observed at the cooler pumping-side exhaust in the experiments carried out. At higher temperatures, the complex is believed to finally decompose into TiN.

The rate equation obtained in section 4.1.4 can be explained with the help of the theory put forth by Imhoff et. al. [19] using Langmuir-Hinshelwood model for the case of competitive adsorption. As explained in section 1.3.4, this model states that the growth rate vs. reactant partial pressure plot shows a maximum. At low partial pressure of the reactant, the growth rate increases with the partial pressure of the reactant and the reaction order is positive. At high partial pressures of this reactant, growth rate decreases with increasing reactant partial pressure and reaction order is negative. In the present study, even though $TiCl_4$ partial pressure was low, since $TiCl_4$ was introduced in the reactor closer to the wafers (see Figure 3.1), its local partial pressure was high as compared to that of NH_3 and this is why the rate order is negative for $TiCl_4$ and positive for NH_3.

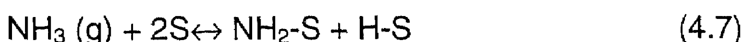
To study the reaction mechanism in detail, consider the following elementary reactions:

(1) $TiCl_4$ adsorption: Because of the sp^3 hybridization of the Ti atom in the $TiCl_4$ molecule, direct adsorption of $TiCl_4$ on one site is less probable. Instead it adsorbs dissociatively on 2 adjacent sites [19], according to,



$$TiCl_4\,(g) + 2S \leftrightarrow TiCl_3\text{-}S + Cl\text{-}S \qquad (4.6)$$

(2) NH_3 adsorption: On hot surface, NH_3 adsorption is dissociative according to the following steps,

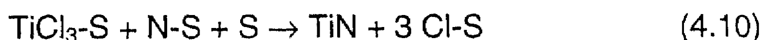


$$NH_3\,(g) + 2S \leftrightarrow NH_2\text{-}S + H\text{-}S \qquad (4.7)$$

$$NH_2\text{-}S + S \leftrightarrow NH\text{-}S + H\text{-}S \qquad (4.8)$$

$$NH_3\text{-}S + S \leftrightarrow N\text{-}S + H\text{-}S \qquad (4.9)$$

(3) Surface reaction: $TiCl_3$-S reacts with either of NH_2-S, NH-S and N-S to give TiN, according to the following reaction [17]:



$$TiCl_3\text{-}S + N\text{-}S + S \rightarrow TiN + 3\,Cl\text{-}S \qquad (4.10)$$

$$TiCl_3\text{-}S + NH\text{-}S \rightarrow TiN + 2\,Cl\text{-}S + HCl\,(g) \qquad (4.11)$$

$$TiCl_3\text{-}S + NH_2\text{-}S \rightarrow TiN + Cl\text{-}S + S + HCl\,(g) \qquad (4.12)$$

Of these, last reaction is by far most probable since it involves and one step for NH_3 dissociation and two sites for the reaction.

According to the Langmuir-Hinshelwood theory, the numerator of the growth rate expression is related to the adsorption phenomena, leading to TiN formation, while the denominator is related to the adsorption phenomena, which inhibit TiN deposition by poisoning surface sites [19]. Thus at a fixed temperature the growth rate can be given as,

$$\text{rate} = k' \theta_{TiCl3} \theta_{NH2} \tag{4.13}$$

Since $TiCl_4$ adsorbs dissociatively, $\theta_{TiCl3} \alpha P_{TiCl4}^{1/2}$. NH_3 also adsorbs dissociatively, but its adsorption is inhibited by $TiCl_4$. Moreover, local partial pressure of NH_3 is much lower than the partial pressure at which it enters. Thus $\theta_{NH2} \alpha P_{NH3}$. Thus using the expression given by Laidler [5] for bimolecular adsorption, we have,

$$\text{rate} = k P_{TiCl4}^{1/2} P_{NH3} / (1 + K_{TiCl3\text{-}S} P_{TiCl4}^{1/2} + K_{NH2\text{-}S} P_{NH3})^2 \tag{4.14}$$

Since $TiCl_4$ is introduced near the substrate, a high value for adsorption term for $TiCl_4$ (i.e. $K_{TiCl3\text{-}S} P_{TiCl4}^{1/2}$) can be expected, so as to neglect other additive terms in the denominator.

$$\text{rate} \; \alpha \; P_{TiCl4}^{1/2} P_{NH3} / (P_{TiCl4}^{1/2})^2 \tag{4.15}$$

$$\text{rate} \; \alpha \; P_{TiCl4}^{-1/2} P_{NH3} \tag{4.16}$$

Thus the rate order with respect to $TiCl_4$ is near the experimental value of -0.42.

Since NH_3 was introduced far from the wafers, and impinges a $TiCl_4$ poisoned surface, an attenuating component α' needs to be introduced as explained by Imhoff et. al. [19], in order to lead to a reaction order of 1.37 for NH_3.

As Imhoff et. al. have concluded, the reactor geometry as well as the location of entrance of the reactants are important factors in determining the dependence of the growth rate on the partial pressure of the reactants. Buiting et. al. have proposed that increasing P_{TiCl4} results in more complex formation, which in turn results in the decrease in TiN formation as less NH_3 is available. This is another possible explanation for the negative order for $TiCl_4$.

4.2 Characterization Study

4.2.1 Temperature Effects

(A) Color: The color of pure TiN films has been reported to be golden [1]. In the experiments carried out in this study, the color of the films deposited was found to be dependent on the deposition temperature. The color was brilliantly golden at deposition temperatures greater than 750°C. For deposition temperatures in the range 550-750 °C the color became brownish, while for still lower temperatures (<550°C) the films were grayish in color.

(B) Density: A series of experiments was carried out at a constant $NH_3:TiCl_4$ flow ratio of 5 and pressure of 70 mtorr at 600, 700, 800 and 850 °C. The density of the films deposited was determined by dividing the film weight by film volume as calculated from the product of film thickness and known area of the wafer.

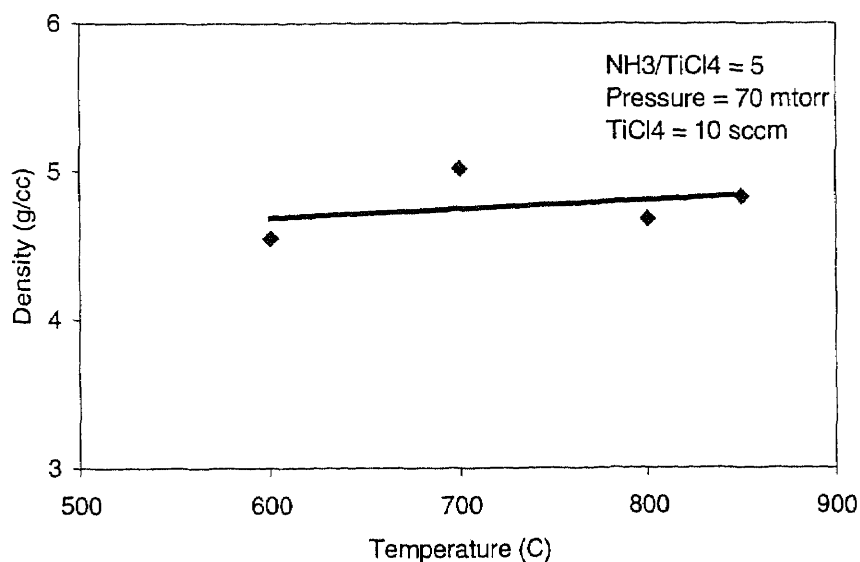


Figure 4.4 Variation in film density with deposition temperature.

The thickness in this case was obtained using Sloan Dektak as mentioned in section 3.4.2. There is a sight increase in the density with temperature. Higher density at higher deposition temperatures might be an indication that films were becoming purer and thus achieving a density closer to that of bulk TiN.

(C) Stress: Stress was determined for the films deposited at a pressure of 70 mtorr at four different temperatures for each of the flow ratios of 5 and 10. It was found to be tensile. This means that the film causes the wafer to be concave on the side it is deposited. Figure 4.5 shows the results plotted for the two different flow ratios. The stress decreased with the increase in temperature. The lowest stress was observed to be 40 MPa at a deposition temperature of 850°C, for a flow ratio of 5. Since it is not desirable of films to exert stress on the wafer, either tensile or compressive, low stress means better film quality

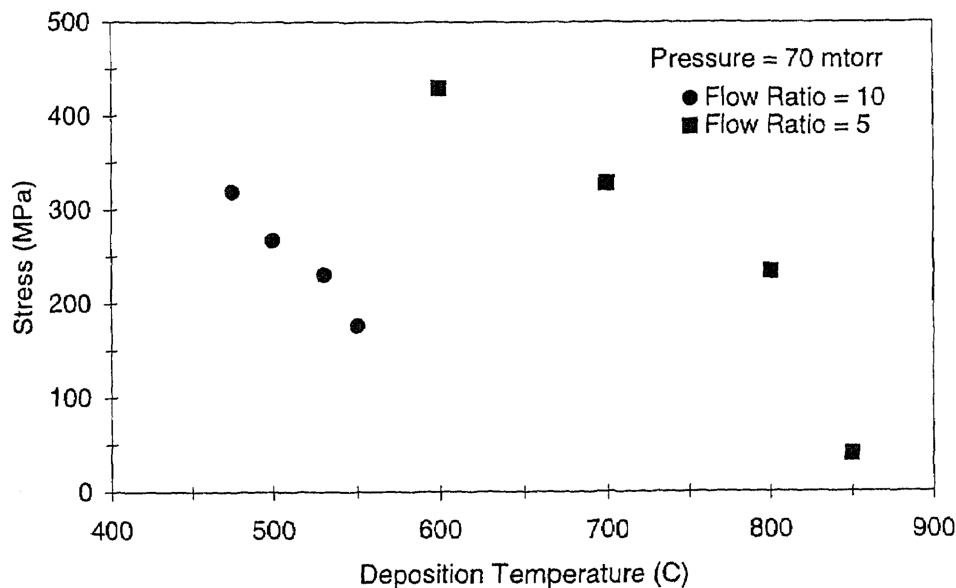


Figure 4.5 Variation in film stress with deposition temperature.

(D) Resistivity: The variation in resistivity with temperature was also studied at 2 different flow ratios. Figure 4.6 shows the results. Resistivity was found to decrease with increasing temperature. All the experiments were carried out at a pressure of 70 mtorr. The lowest resistivity obtained was 86 μohm-cm at a temperature of 850°C and flow ratio of 10. Since TiN is used in the microelectronics industry as a diffusion barrier, low film resistivity is an important characteristic, and again, high temperature leads to this desirable film quality.

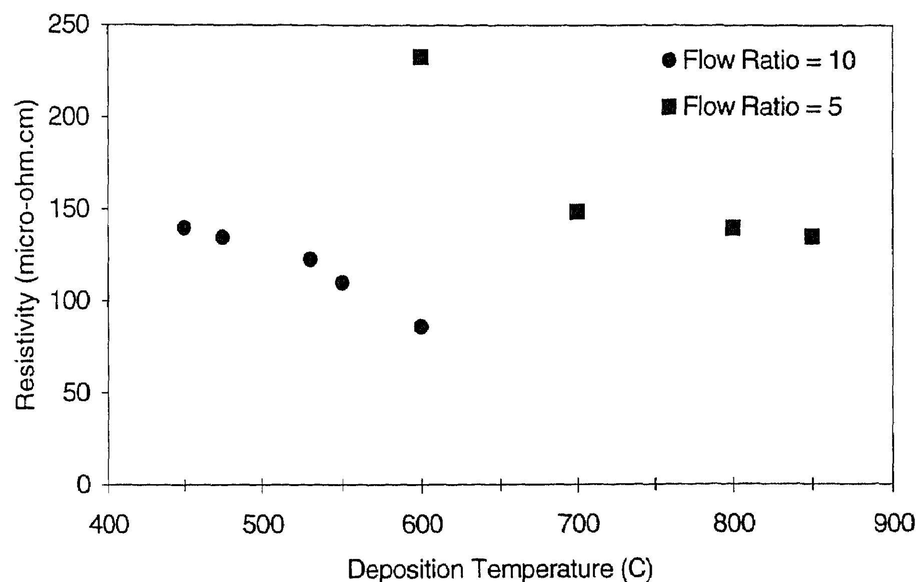


Figure 4.6 Variation in film resistivity with deposition temperature.

(E) Hardness: On an average, the titanium nitride films were 50% harder than silicon. At an indentation of 200 nm, the value of the hardness ranged from 13 to 17 GPa depending on the film deposition process parameters while the hardness

for silicon was found to be about 10 GPa. Study of the variation in the film hardness with the deposition temperature (Figure 4.7) showed that the film hardness decreased with increasing film deposition temperature, for a NH_3:$TiCl_4$ ratio of 5.

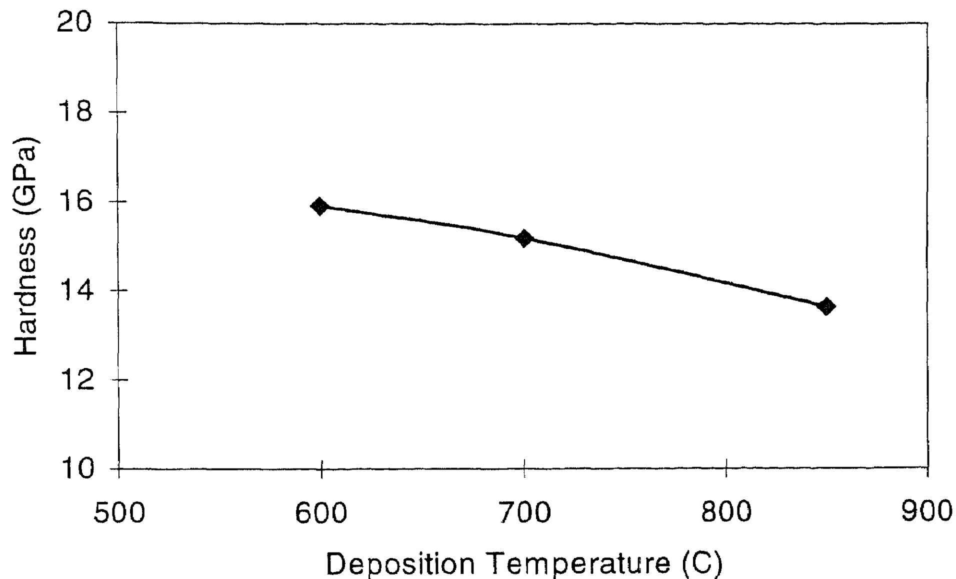


Figure 4.7 Variation in film hardness with deposition temperature.

4.2.2 Flow Ratio Effects

(A) Growth Rate: The growth rate was measured for a series of experiments carried out at 600°C at a pressure of 70 mtorr for different flow ratios: 5, 7,10, 25 and 50. The results are plotted in Figure 4.8 below. It can be seen that the growth rate increases almost proportionally with the flow ratio.

The results of the kinetic study can be used to explain this behavior. Since the pressure as well as flow rate of NH_3 was maintained constant, NH_3:$TiCl_4$ flow

ratio was increased by decreasing the flow rate of $TiCl_4$. This increased the partial pressure of NH_3 and decreased that of $TiCl_4$. From the kinetic study, we have found out that the growth rate is directly proportional to the partial pressure of NH_3 and inversely proportional to the partial pressure of $TiCl_4$. This explains the increase in the growth rate with increase in the flow ratio.

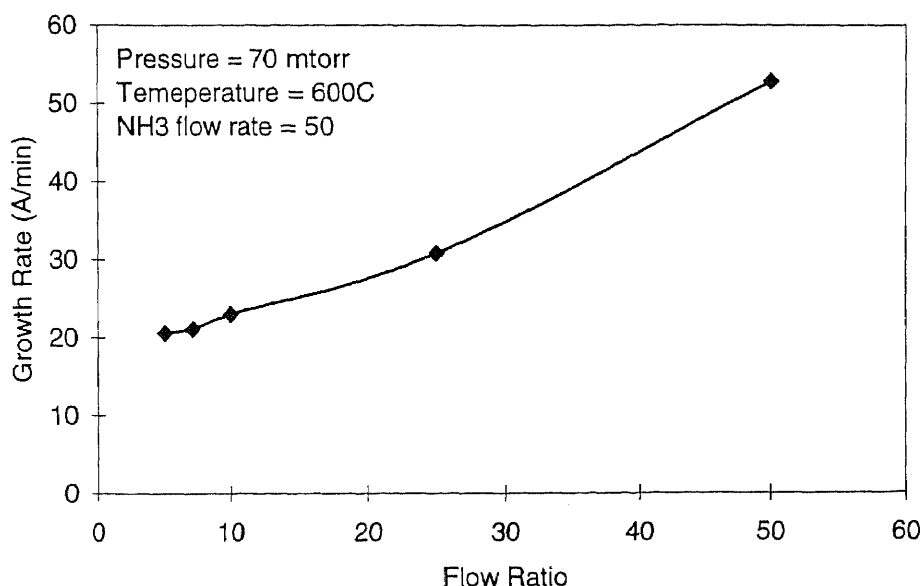


Figure 4.8 Variation in growth rate with flow ratio.

(B) Density: As the flow ratio was increased, the density increased at first but then became constant at a value of around 4.9 gm/cc (Figure 4.9). The films in this case were deposited at a temperature of 600 °C and pressure of 70 mtorr. This variation in the density might be due to the change in the composition of the film.

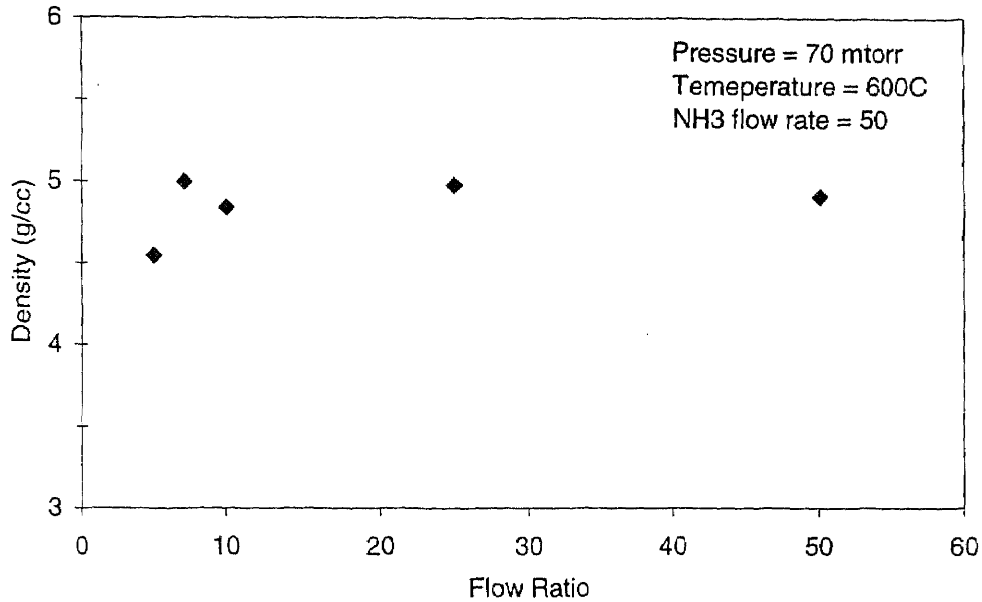


Figure 4.9 Variation in film density with flow ratio.

4.2.3 Optical Properties

Figure 4.10 shows the optical characterization of a Tin film deposited at 600°C and 70 mtorr pressure, using a NH_3:$TiCl_4$ flow ratio of 5. From the reflectance, emittance and transmittance spectra in the IR region, it can be concluded that TiN films can act as a good reflector of IR radiation (i. e. heat), since they reflect more than 80% of the radiation. It is for this heat reflecting property of TiN films that they have been used as heat mirrors in architectural applications [1]. Almost zero radiation is transmitted while a very small percent is emitted. However this behavior was found to change at a deposition temperature of around 750°C, where the reflectance went down considerably and the emittance increased; the transmittance remained unchanged. The probable cause for this was formation of some kind of oxide that had different optical properties.

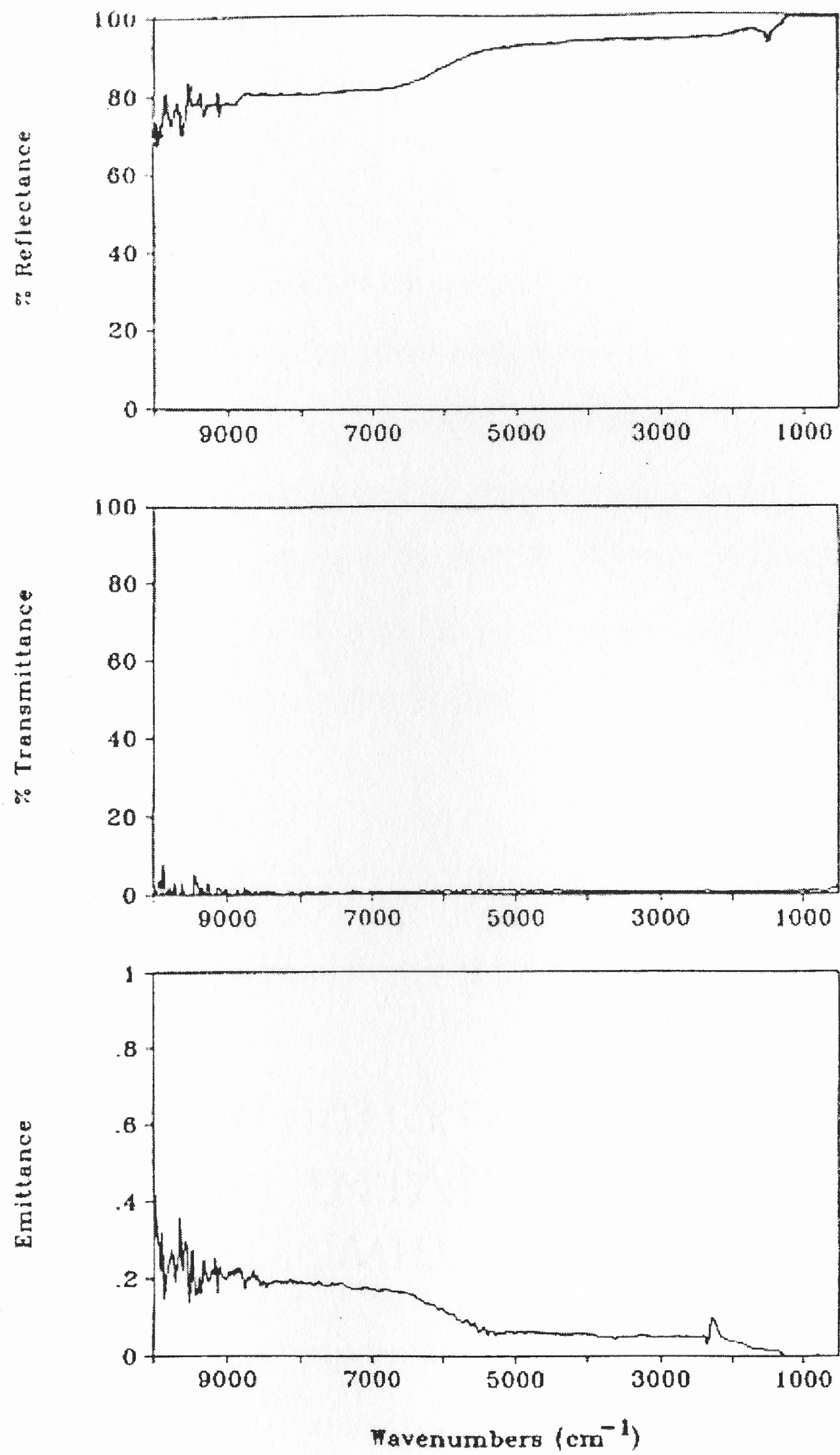


Figure 4.10 Optical Properties of TiN.

4.2.4 X-ray Diffraction (XRD)

X-ray diffraction analysis was carried out for a TiN film of thickness 2578 Å deposited at 600°C and 70 mtorr, using a NH_3:$TiCl_4$ flow ratio of 5. The corresponding X-ray diffraction plot is shown in Figure 4.11. From the d-value of 2.13 Å for the (200) plane, the lattice constant was calculated as 4.26 Å.

Table 4.1 compares the relative intensities of different orientations for the above film with those given in the diffraction data card for TiN. Looking at the minimal relative intensities of the peaks for orientations other than (200), we can safely say that the orientation of the film is (200). This is in agreement with the findings of Oh et. al. [22], who have confirmed that for lower thickness (<5900Å), TiN films exhibit a preferred orientation of (200).

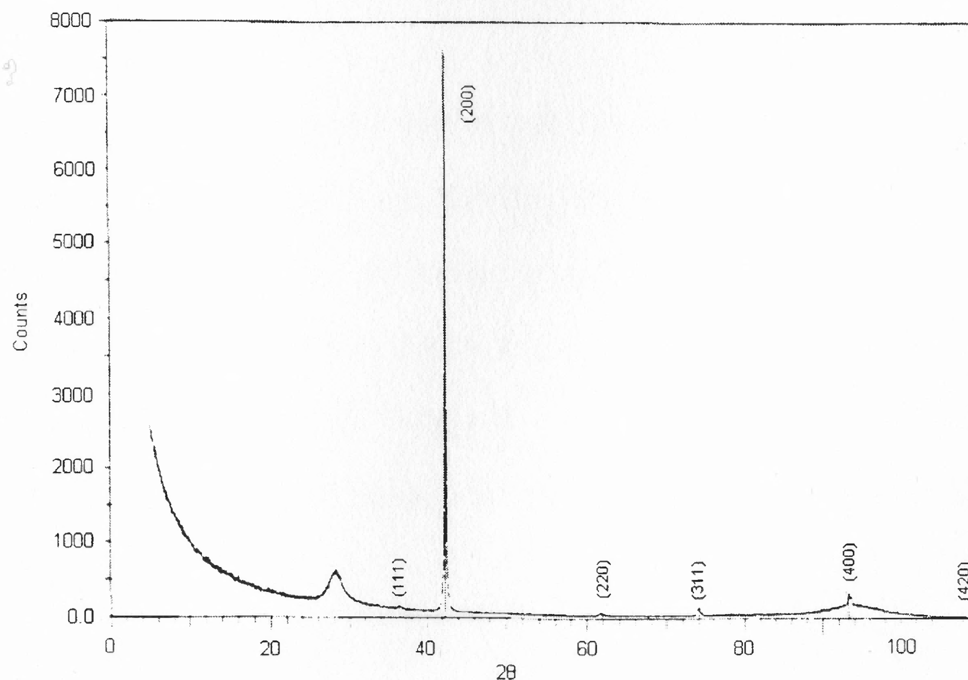


Figure 4.11 X-ray Diffraction plot for TiN.

Table 4.1: Comparison of experimental XRD data with standard data.

Orientation (hkl)	Standard Data for TiN		Experimental Data	
	d (Å)	Rel. int. (%)	d (Å)	Rel. int. (%)
111	2.44	77	2.46	0.5
200	2.12	100	2.13	100
220	1.496	56	1.498	0.4
311	1.277	26	1.278	0.1
222	1.223	16	No peak	
400	1.059	7	1.0598	2.2
331	0.972	11	0.9475	0.6
420	0.948	22	No peak	
422	0.865	21	No peak	

4.3 Additional Studies

4.3.1 Etching Study

In many applications of thin film deposition, etching of the film is an important aspect. In wet etching, mostly hydrogen fluoride (HF) is used for etching of thin films. However, HF is a very dangerous chemical and is notorious for causing skin burns. Thus finding an alternative to HF for etching becomes essential. In the case of TiN thin films, Buiting et. al. [13] have reported that the mixture of ammonium hydroxide, hydrogen peroxide and water is effective in etching the film.

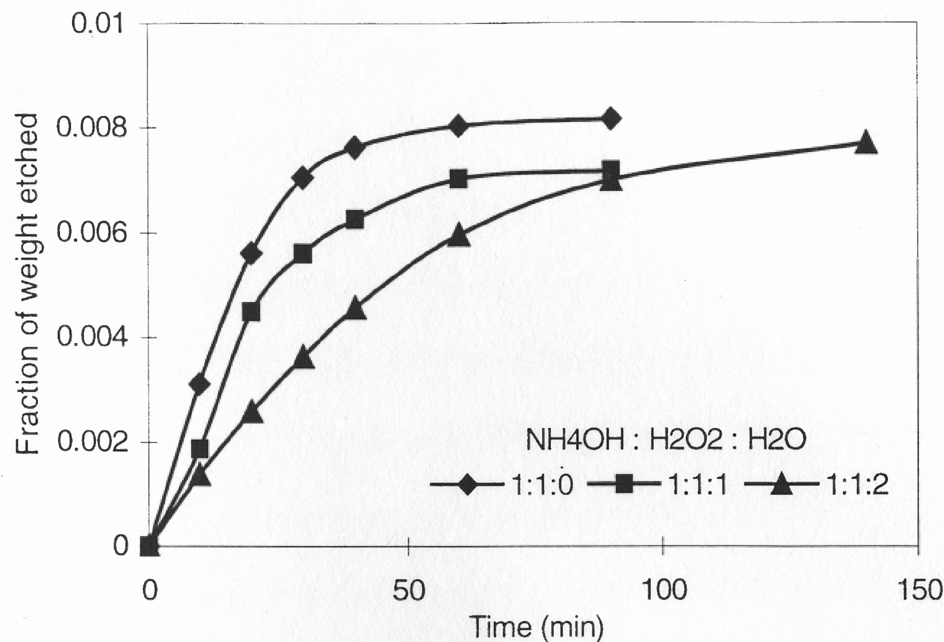


Figure 4.12 Etching characteristics.

Etching experiments were carried out using an etching solution containing NH_4OH, H_2O_2 and H_2O in different proportions. The wafers etched were all from the same experiment. NH_4OH used was concentrated while H_2O_2 was used as a 30% solution. The different NH_4OH:H_2O_2:H_2O ratios at which the experiments were carried were 1:1:2, 1:1:1 and 1:1:0.

Figure 4.12 shows the results of the etching experiments. The rate of etching (given by the slope of the plot during the initial stages of etching) decreased as the proportion of water was increased, i.e. as the etching solution was diluted. In the case where no water was added, the film etched almost completely within just half an hour, while it took more than 2 hours in the case

where dilution was maximum. In all the cases, the etching was complete and uniform, thus proving the ammonium hydroxide-hydrogen peroxide mixture as an efficient etching solution for etching of TiN thin films.

4.3.2 Effect of Aluminum on LPCVD of TiN

During one of the experiments, it was observed that the presence of aluminum in the reactor altered the color of the TiN film deposited. In the case of deposition carried out at 600°C, in the presence of aluminum, the color of the film deposited was found to be brilliant golden, which is characteristic of pure TiN films [14]. However for the deposition carried out under the same process conditions but in the absence of aluminum, the color of the film deposited was observed to be reddish brown. This implied that the presence of aluminum was affecting the composition of the deposited film.

However, the same golden color of the film is observed for deposition carried out at higher temperatures (~850°C). This implies that there is some similarity between the composition of the film deposited at 600°C in the presence of aluminum and the one deposited at 850°C in the absence of aluminum. This similarity was presumed to be low chlorine content in both the films. The chlorine content in the case of film deposited at 850°C is low since the chlorine content decreases with increase in the deposition temperature [13]. So it was suggested that the low chlorine content of the film deposited in the presence of aluminum was a result of the fact that aluminum reacted with the chlorine to form $AlCl_3$. Thus lesser chlorine went into the film, thereby imparting a golden color to the

film. This inference was further strengthened by the fact that the resistivity of this film was very low (21 $\mu\Omega$).

This aspect of TiN deposition might be particularly useful in the applications where TiN coating is used for decorative purposes or as a low resistivity film and the substrate on which the film is deposited cannot tolerate the temperature at which a pure TiN film is deposited. By carrying out the deposition in the presence of aluminum, this might be achieved at considerably lower temperature, which the substrate can survive. Apart from making the process feasible, this also results in huge savings in energy and time. Essentially, an entire separate study can be carried on the LPCVD of TiN in the presence of aluminum.

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