OPTICAL PROPERTIES OF CHEMICAL VAPOR DEPOSITIONS
OF SILICON OXYNITRIDE FILMS

by

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ABSTRACT

This work deals with a chemical vapor deposition (CVD) process for deposition of amorphous silicon oxynitride films. The optical properties of these films are of specific interest.

Selected CVD process parameters affecting the optical and physical properties of the deposited films are varied over a limited temperature range. The optical and physical properties of the films are evaluated by ellipsometer and spectrophotometer measurements. Optimization of the process parameters and reproducibility of the films are studied.

The CVD process and evaluation techniques are explained and experimental results presented.
CHAPTER 1

INTRODUCTION

Industry and science have found many uses for a family of dielectrics called silicon oxynitrides. Historically, their most common use has been as antireflection coatings of optical surfaces. More recently, however, silicon oxynitride films (particularly $\text{SiO}_2$) have been used as passivating surfaces during integrated circuit fabrication. Particular Si-O-N polymers have been used successfully as radiation resistant films to protect vulnerable electronic equipment. Si-O-N films also are being used for the fabrication of optical wave guides.

It is apparent, then, that a study of silicon oxynitride films is a worthwhile undertaking. However, current research at The University of Arizona on the development of photothermal solar energy converters has made this study of immediate value.

A type of solar energy photothermal converter which currently shows considerable promise is a two-layered device. The top layer is silicon, and it must be designed to absorb as much solar energy (light) in the visible spectrum as possible. But, silicon has a relatively high coefficient of reflection in the visible. Thus, an antireflection coating on the silicon surface is necessary if this device is to be successful.
Silicon oxynitride films, though not ideal, are capable of satisfying most of the requirements for this coating.

1. The films are compatible with chemical vapor deposition.
2. They are adherent, stable, durable, inexpensive and relatively easy to manufacture.
3. A suitable range of refractive index is realizable with the Si-O-N family.

The data obtained and reported in this thesis will provide the basic information needed to produce the required antireflection coating. Specifically, the objective of this research is to:

1. Establish a procedure, using available equipment, to produce Si-O-N films with the desired optical and physical properties;
2. Confirm the optical properties of these films through ellipsometer and spectrophotometer measurements;
3. Confirm the reproducibility of specific films; and
4. To compare the data obtained with that in the literature.

It should be emphasized that, in this report, the term Si-O-N implies no specific stoichiometric relationship. Rather, it refers to the silicon oxynitride family of films in general. The films are amorphous polymers of silicon, oxygen and nitrogen. The amount of each element may be varied at will by controlling the amount of each reactant gas introduced into the reaction chamber. The Si-O-N composition does not appear to be a mixture of SiO\textsubscript{2} and Si\textsubscript{3}N\textsubscript{4} [Rand and Roberts, 1973], but rather a polymer of the three basic elements [Philipp, 1971].
The optical properties may be varied according to the ratios of the nitrogen and oxygen bearing gases introduced into the system.
CHAPTER 2

CHEMICAL VAPOR DEPOSITION

General Information

In chemical vapor deposition (CVD), the substrate to be coated is placed in a heated chamber and exposed to a gaseous mixture containing the appropriate reactants. The gaseous reactants are thermally decomposed at the surface of the hot substrate and, if all parameters are properly chosen, the desired elements are chemically recombined and deposited on the substrate surface. The chemical reactions which occur are described by the laws of chemical thermodynamics and reaction kinetics.

Figure 2.1 shows how the growth rate of a typical CVD reaction varies as a function of temperature. At lower temperatures, the deposition rate is strongly temperature-dependent and limited by adsorption and kinetics affects. At higher temperatures, interdiffusion of gaseous reactants and products becomes the rate limiting factor. At still higher temperatures, homogeneous nucleation can set in, resulting in precipitation of the solid reaction product ("snow") and a reduced deposition rate. It is in the range of gas-phase diffusion limitation that the highest possible deposition rates are obtained [Blocher, 1966].
Fig. 2.1 Effect of Temperature on a Typical CVD
Principles of Thermodynamics

The First and Second Laws of Thermodynamics state that energy must be conserved in a chemical reaction. However, its conversion from one form to another is possible, e.g., conversion of solar energy (light) to thermal energy (heat) to mechanical energy (work). Using thermochemical analysis, the likelihood of a reaction occurring is determined and expressed by the free energy ($\Delta F$).

$$\Delta F = \Delta H - T \Delta S$$  \hspace{1cm} (2.1)

$\Delta H$ is the heat of reaction, $T$ is temperature ($^\circ$K), and $\Delta S$ is entropy. At constant temperature, standard pressure and all substances in their standard state, the free energy of a reaction may be mathematically summed:

$$\Delta F_T^o = \sum (\Delta F_T^o)_{\text{products}} - \sum (\Delta F_T^o)_{\text{reactants}}$$  \hspace{1cm} (2.2)

If $\Delta F_T^o$ is positive, the reaction requires outside energy to be realized at that temperature, indicated by the subscript in Eq. (2.2). If $\Delta F_T^o$ is negative, the reaction goes spontaneously at the given temperature.

There are many chemical reactions for which $\Delta F$ shows promise of a successful reaction at reasonable temperatures. The chemical equations describing the overall nitride and oxide reactions used for this study are:
3SiH₄ + 4NH₃ → Si₃N₄ + 12H₂ \hspace{1cm} (2.3)

SiH₄ + 2N₂O → SiO₂ + 2H₂ + 2N₂ \hspace{1cm} (2.4)

Other reactions which are capable of producing the full range of Si-O-N include SiH₄ - CO₂ - H₂ - NH₃, SiH₄ - O₂ - NH₃, SiH₄ - NO - NH₃, and SiCl₄ - CO₂ - NH₃ [Rand and Roberts, 1973]. The SiH₄ - N₂O - NH₃ reaction was selected for this research based upon availability of reactants, future use of data, safety and ease of handling.

Although Equations (2.3) and (2.4) are the forms considered most probable, other chemical equations which describe the decomposition of the reactant gases into their respective chemical elements, are of greater interest in preliminary analysis of potential CVD reactions. Table 2.1 lists three basic equations considered critical to the overall reactions. The overall reactions, (2.3) and (2.4) are also listed. The values of $\Delta F^\circ_T$, for temperatures shown, were obtained from the JANAF Thermochemical Tables [Stull and Prophet, 1971], and plotted in Fig. 2.2. Equations (2.3) and (2.4) are also included in this plot. The relatively high negative values of $\Delta F^\circ_T$ for (2.3) and (2.4) indicate a potentially successfully overall reaction. The similarity of $\Delta F$ values (especially at higher temperatures) indicate a potential for both the oxide and nitride reactions to go simultaneously, e.g., the deposition of silicon oxynitrides. The data plots linearly, as expected, since only thermodynamic principles are considered. Note the linear rate versus temperature plot of Fig. 2.1 at lower temperatures where reaction kinetics (thermodynamic considerations) predominate.
<table>
<thead>
<tr>
<th>Chemical Reaction</th>
<th>Temperature °K</th>
</tr>
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<tbody>
<tr>
<td>NH$_3$ $\rightarrow$ 1/2 N$_2$ + 3/2 H$_2$</td>
<td>+3.91, -3.79, -9.24, -14.8, -23.2</td>
</tr>
<tr>
<td>N$_2$O $\rightarrow$ 1/2 N$_2$ + NO</td>
<td>-4.20, -10.5, -14.7, -18.8, -24.9</td>
</tr>
<tr>
<td>N$_2$O $\rightarrow$ N$_2$ + 1/2 O$_2$</td>
<td>-24.9, -30.3, -33.9, -37.4, -42.6</td>
</tr>
<tr>
<td>SiH$_4$ + 4/3 NH$_3$ $\rightarrow$</td>
<td>-178, -205, -224, -244, -276</td>
</tr>
<tr>
<td>$\quad$ 1/3 Si$_3$N$_4$ + 4H$_2$</td>
<td></td>
</tr>
<tr>
<td>SiH$_4$ + 2 N$_2$O $\rightarrow$</td>
<td>-267, -272, -275, -278, -283</td>
</tr>
<tr>
<td>$\quad$ SiO$_2$ + 2H$_2$ + 2N$_2$</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 2.2 Plot of $\Delta F^\circ$ vs. Temperature for the Principal Reactions in the Si-O-N Process.
Once $\Delta F^o_T$ is known, the next logical step is to determine the extent to which the reaction may be expected to go to completion. A measure of this is the equilibrium constant ($K_T$), which is a function of $\Delta F$ and temperature.

$$K_T = e^{-\frac{\Delta F^o_T}{RT}}$$

(2.5)

$R$ is the universal gas constant and $T$ is absolute temperature. Table 2.2 tabulates $K_T$ for the indicated temperatures for Equations (2.3) and (2.4). The high values of $K_T$ indicate a tendency for the reactions to go to completion. This may be somewhat deceptive, however, since it is presumed that the decomposition of reactant gases into a reactive form is sufficient to sustain the overall reaction. Table 2.1 and Fig. 2.2 show that the decomposition of both $NH_3$ and $N_2O$ into a reactive form cannot be asserted as strongly as it would appear from $\Delta F$ calculations for the overall reactions. In fact, the decomposition of $NH_3$ does not appear probable until around 800°K. Also shown in Fig. 2.2 is that the decomposition of $N_2O$ into $N_2$ and $O_2$ is more probable than its decomposition into $N_2$ and NO.

The values of $\Delta F$ and $K_T$ are unique for a given reaction at constant pressure and given temperature. As $\Delta F$ becomes less negative and $K_T$ becomes smaller, the prospects for a successful CVD reaction becomes less. Thus, the more highly favored reactions for CVD are those with $\Delta F^o_T$ highly negative and $K_T$ large. It should also be noted that although Equations (2.3) and (2.4) are the most probable reactions,
Table 2.2 Free Energies and Equilibrium Constants Computed for Specific Temperatures of the Reactions Shown

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>ΔF° <em>T</em> (cal/mole)</th>
<th>ln K° <em>T</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>973</td>
<td>-275,000</td>
<td>142</td>
</tr>
<tr>
<td>1073</td>
<td>-280,000</td>
<td>131</td>
</tr>
<tr>
<td>1158</td>
<td>-281,000</td>
<td>122</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>ΔF° <em>T</em> (cal/mole)</th>
<th>ln K° <em>T</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>973</td>
<td>-235,000</td>
<td>122</td>
</tr>
<tr>
<td>1073</td>
<td>-255,000</td>
<td>119</td>
</tr>
<tr>
<td>1158</td>
<td>-267,000</td>
<td>116</td>
</tr>
</tbody>
</table>
other chemical combinations are possible as products. A computer assisted analysis, such as that found in CHIMEQ [Wells, 1972], could be used to determine the actual concentration of products, if such were of primary interest.

**Kinetic Principles**

The actual condensation step of a CVD process is preceded and/or followed by diffusion, adsorption, reaction and desorption steps [Lydtin, 1972]. These steps complicate the theoretical analysis of a CVD reaction and it becomes impossible to predict a CVD reaction using only chemical equilibrium. For example, consider the CVD formation of SiO$_2$ in accordance with Eq. (2.4). The SiO$_2$ is to be grown on a heated substrate within an atmosphere of helium containing controlled amounts of reactant gases (SiH$_4$ and N$_2$O). As the gases flow across the substrate, a diffusion boundary layer of a few millimeters thickness is formed through which the SiH$_4$ and N$_2$O must diffuse. At, or very near the surface, SiH$_4$ and N$_2$O decompose and recombine as SiO$_2$ on the substrate surface. The average distance from the surface that SiH$_4$ and N$_2$O break up is called the mean free path and is normally very small compared to the diffusion boundary layer thickness. The H$_2$ and N$_2$ must now diffuse back into the main gas stream. Figure 2.3 shows the reactant concentration profile (n) as a function of the distance (x) from the substrate surface (x=0). At lower deposition temperatures, the process is reaction rate limited represented in Fig. 2.3 by the discontinuity (n$_s$/n') at the solid/gas interface, and in Fig. 2.1 by that portion of the curve labeled "surface kinetics variations". As temperature is
Dashed line represents a reaction rate limited reaction.

Fig. 2.3 Concentration Profile of Reactants as a Function of the Distance from the Substrate Surface
increased, the reaction rate also increases until no excess reactant atoms are available at the interface. Further increases in temperature have little affect on the deposition rate as reflected in the flattened portion of the curve in Fig. 2.1. Still further increases in temperature causes a decomposition of reactants and condensation away from the substrate surface. The products then literally "snow" throughout the reactor tube resulting in a drastic decrease in deposition rate on the substrate.

The complications introduced by the kinetic aspects of a CVD process renders any attempt to theoretically predict a reaction very complex. Simplifying assumptions permit calculations of reasonable accuracy for very low deposition rates. However, such rates are too slow to be of any practical value and recourse is therefore made to empirical data.
CHAPTER 3

EXPERIMENTAL EQUIPMENT AND SUBSTRATE DATA

CVD System

The CVD system used to deposit the films used for this research study is depicted in Fig. 3.1. Reactor grade helium and electronic grade reactant gases were metered and mixed in a manifold before introduction into a horizontal, quartz reaction tube. An additional diffusion baffle was found necessary to eliminate laminar gas flow. It was placed in the first few inches of the tube. Although previous work with this reactor had indicated an inclined susceptor produced good results, comparative analysis indicates little, if any, advantage to the inclined susceptor for this work. Very good results were realized by using a horizontal susceptor and two substrates in tandem. The second substrate, which was used for analysis, was placed in the center of the heating coil. This resulted in more uniform film thickness. The reactor tube was room vented as the SiH₄ concentration of the total gas flow was very low and prevented no danger.

The RF generator is rated at 10 KW and was operated at 425 KHz. It is water cooled and provides adequate coupling into the graphite susceptor block for temperatures exceeding 900°C.

Infrared emittance from the wafer is monitored by the in-process growth monitor subsystem. A lead sulfide detector is the basic component; the output is amplified by a tunable microvoltmeter. To obtain
In-Process Growth Monitor Subsystem
IR Detector
Microvoltmeter
Y-T Recorder

Diffusion Baffles

Gas Flow

Exhaust

Substrates

Susceptor
Quartz Spacer

RF Induction Coils

Temperature Monitor Subsystem

Key:
- Shut off Valve
- Metering Valve
- Pressure Gauge
- Regulator

Silane SiH₄
Dinitrogen Monoxide N₂O
N-Gas or Ammonia (NH₃)
Helium

Fig. 3.1 CVD System Used in this Research
monochromatic radiation, a narrow-pass filter is located between the detector and the substrate. Output variations produced by emittance changes from the wafer due to film growth are displayed on a y-t recorder. (See Appendix C for operating details.)

Ellipsometer Theory

The ellipsometer is a valuable tool in evaluating the optical properties of thin films. When used in conjunction with a digital computer algorithm, tedious calculations and gross approximations are reduced to a few simple measurements which yield very accurate data.

The ellipsometer measures the effect of reflection on the state of polarization of light. These measurements are then interpreted to yield the optical constants and thickness of the film or surface being studied. The optical constants are defined by the equation:

\[ N = n - jk \]  

where both \( N \) and \( n \) are referred to as the refractive index, and \( k \) is the extinction coefficient.

The state of polarization is defined by phase and magnitude relationships between the "p" and "s" components of the complex light wave. The p component lies in the plane of incidence and the s component is normal to it. When both are in phase, the resulting wave is plane-polarized. Any difference in the phase represents elliptical polarization. Reflecting a light beam from a surface causes phase changes in the p and s components called DEL (\( \Delta \)) and magnitude changes called
PSI (ψ). It is the objective of ellipsometry to measure Δ and ψ. With these values, it is then possible to calculate the optical constants and film thickness, if present.

In theory, ellipsometry can be applied to surface films of partial monoatomic coverage to thickness of several microns [Archer, 1969]. However, difficulties arise in interpreting data from films approaching 100 Å or less due to the non-ideal optical surfaces of the substrate. In this research, it was found that possible errors in the refractive index existed for films of a few hundred angstroms or less. It was also found that the extinction coefficient (k) was not reproducible, nor interpretable, except by an order-of-magnitude approximation for any thickness. This is due to the fact that surface films tend to swamp the effect of k, when k is small. For example, consider a film with |k| ≈ 0.03, deposited on a silicon substrate. The effect of k on the measured change in phase angle would be about 1°. However, a SiO₂ surface film of only 10 Å would cause a change in phase angle of nearly 3° in the same film, entirely swamping out the effect of k [Archer, 1969]. Thus, it is ordinarily only possible to obtain order-of-magnitude approximations for the value of k in films where |k| is small. Fortunately, an order-of-magnitude approximation for k is sufficient for this research.

In Fig. 3.2 the principle components of the ellipsometer are shown. Any light source in the visible spectral range is suitable. The band pass filter used for this research is centered at 5467 Å with a bandwidth of 85 Å. The collimator eliminates parallax error and
Fig. 3.2 Principal Components of the Ellipsometer Setup
also permits adjustment for the amount of light and size of the reflecting surface to be sampled. The polarizer is mounted in a rotatable support with a vernier scale readable to .01°. The compensator is an adjustable quarter wave plate also mounted in a rotatable support similar to the polarizer. The telescope is pre-focussed on the iris diaphragm of the collimator. (See Appendix B for operating details.)

The polarizer (P) and compensator (Q) are oriented such that compensation is realized for the phase difference introduced by the subsequent reflection from the substrate. With Q set at 45°, P may be adjusted so that an incident light beam is precisely elliptically polarized so that the reflected beam is plane polarized. Then, A may be adjusted to provide extinction at the detector. The settings are first approximated visually and then refined with the aid of photometer [Whitmer, 1973]. Δ and ψ are related to P and A by:

\[ \Delta = (360 - Q) - 2P \quad (3.2) \]

\[ \psi = A \quad (3.3) \]

With Q = 45°, and by limiting the P and A readings to those between 0° and 180° which produce extinction, Δ will have a value between 0° and 360° and ψ between 0° and 180°. This eliminates any ambiguity in Δ and ψ due to their cyclic nature.

Once Δ and ψ are known as well as the optical constants of the substrate, it is possible to determine the refactive index and thickness of the film on the substrate. The theoretical equations to accomplish this are mathematically cumbersome and cannot be solved in closed form.
This leads to a situation for which the digital computer is ideally suited. An available FORTRAN IV program [McCrackin, 1969] was adapted to the CDC 6400 at the University for this calculation [Whitmer, 1973]. It was utilized for the data reported in this thesis.

Substrate Data

The substrates used in this research were chemically polished, n-doped, silicon wafers of from .001 to .015 ohm-cm. Prior to use, each wafer was degreased, etched in HF-HNO₃, and the optical constants ellipsometrically measured. A specific sequence was established for these preliminaries in order to minimize the effect of surface contamination and natural surface films (see Appendix A). Archer [1969] has reported some success in minimizing the growth of natural SiO₂ by quenching the HF-HNO₃ etchant with HNO₃ rather than H₂O. In attempting this procedure, optical degradation of the substrate surface resulted. It, therefore, was not used. Quenching was accomplished by H₂O only, followed immediately by an ellipsometric measurement of the substrate.

The precision with which thin film optical properties can be measured depends heavily upon the accuracy of substrate data. For this reason, a standard, average or normal value of refractive index for the silicon substrate was not used. The specific value was measured for each individual wafer. Figure 3.3 shows the spread of refractive index values encountered. An average value of N = 4.074 - j.073 (5467 Å) is indicated which compares to a literature value of 4.05 - j.028 (5890 Å) for bulk silicon [Archer, 1969].
Average value is 4.074-\(0.074\) (\(\otimes\) in the figure).

Ellips represents 85% assurance limits.

Fig. 3.3 Distribution of N for all Substrates Measured in this Research
The index of refraction, as found in most of the literature, is expressed in the form \( N = n - jk \), or very often only the real portion, \( n \), is printed. The index may also be expressed as \( N = n(1 - jk) \), which is the form most easily handled by the computer. It is in this form that McCrackin [1969] has written the FORTRAN program. Therefore, care must be exercised in comparing data obtained through the use of this program with that from the literature. All index data in this report will be in the form \( n - jk \), which is the more common usage.

The value of \( k \) is an extremely elusive quantity to measure when its magnitude is small as has been shown for the case of SiO\(_2\). For this reason, except to note that \( k \) is small for all films measured, no further attempts to quantify \( k \) will be made.
CHAPTER 4

CHEMICAL VAPOR DEPOSITION RESULTS

General Film Data

All CVD runs were made with a constant flow of carrier gas (helium) of 55 liters per minute. Total reactant gas flow was maintained initially at 200 cc/min and later increased to 400 cc/min. This increase was made to permit adequate reactant control in the preparation of the nitride heavy Si-O-N polymers. Silane flowrate was maintained at 4 cc/min. The first runs were to obtain nitride films using N-gas (1% SiH$_4$ in NH$_3$) and helium only. Oxide films were then made using N$_2$O, SiH$_4$, and helium. Finally, the oxynitride runs were accomplished. A coating series going from oxygen-rich to nitrogen-rich was made at a set temperature and then repeated for a new temperature.

Throughout the entire series of runs, the single largest problem was that of obtaining film uniformity. Although this problem was never completely solved, several measures were taken to minimize the effect. It was believed that fluid dynamics in the reactor tube was the major contributor. Therefore, a diffusion baffle was introduced to discourage laminar flow and to affect better mixing of the gases. Similarly, it was hoped that the large volume of helium would help mix the reactant gases. It became apparent that thicker films only magnified the problem, therefore, films were produced only thick enough to provide accurate data, usually 1000-2000 Å.
Oxide Film Data

Figure 4.1 graphically depicts the deposition rate (DR) of SiO$_2$ as a function of temperature. It shows an effective zero growth rate at 650°C or less and the reaction is rate limited to about 725°C whereupon it becomes diffusion rate limited. The activation energy ($E_A$) may be computed from the slope of the rate limited portion of the curve and Arrhenius' Equation:

$$\frac{-E_A}{RT} = \ln \frac{\text{DR}}{A}$$  \hspace{1cm} (4.1)

where

- $A$ is a constant unique to the system
- $R$ is the universal gas constant = 1.987
- $T$ is temperature (°K)

By taking two points from the graph and substituting into Eq. (4.1) and subtracting:

$$E_A = \frac{R(\ln \text{DR}_1 - \ln \text{DR}_2)}{(1/T_2 - 1/T_1)}$$

$$E_A = 1.987 \left(\ln 20 - \ln 100\right) \frac{10^{-3}(1.030 - 1.076)}{}$$

$$E_A = 70 \text{ Kcal/mole}$$

Strater [1968] reported 32 kcal/mole for the SiH$_4$-N$_2$O reaction. This would have produced the dashed line shown in Fig. 4.1. Additional runs
Fig. 4.1 Deposition Rate vs. Temperature for Oxides
in the temperature range of 600-700°C may have disclosed a threshold
temperature similar to that found by Baliga and Ghandi [1973] in their
study on the pyrolysis of silane in oxygen. This possibility was not
pursued, since the lower deposition rates were not of primary interest.
Strater used much heavier concentrations of reactants than were used
for the research reported here. This may have caused some differences
in the apparent activation energy.

The oxide refractive index remained constant for all deposition
temperatures and reactant flowrates (see lowest curve on Fig. 4.2). The
value of \( n = 1.47 \) compares favorably with Rand and Roberts [1973], and
the normally accepted index for \( \text{SiO}_2 \). The value of \( k \) was very small, as
expected; on the order of .0015 to .015.

**Nitride Film Data**

Figure 4.3 shows the deposition rate of \( \text{Si}_3\text{N}_4 \) as a function of
temperature. It reflects a zero growth rate at 650°C or less and is
reaction rate limited to about 700°C whereupon it becomes diffusion
rate limited. The apparent activation energy computed from this curve
is 80 kcal/mole. This is higher than anticipated. Kohler [1970]
reported 40 kcal/mole and Goursat, Lortholary, Tetard, and Billy [1972]
reported 70 kcal/mole. Kohler's data, as published in Milek [1971] is
shown as the dashed line in Fig. 4.2. Kohler's gas flow parameters were
considerably different from that used in this research:

\[
\text{SiH}_4 \quad - \quad 1 \text{ ml/min}
\]
\[
\text{NH}_3 \quad - \quad 20 \text{ ml/min}
\]
Fig. 4.2 Room Temperature Refractive Index (n) vs. Growth Temperature (°K)
Fig. 4.3 Deposition Rate vs. Temperature for Nitrides
\[ \text{N}_2 \text{ (carrier) } = 30 \text{ l/min} \]

The relatively low reactant flowrate is reflected in a correspondingly slow growth rate which was not considered acceptable for this research. Goursat et al. studied the kinetics of the reaction

\[ \text{Si}_3\text{N}_4 + 3\text{O}_2 \rightarrow 3\text{SiO}_2 + 2\text{N}_2 \]

by using a thermogravimetric apparatus at high temperatures under vacuum. The variations in activation energies suggest that the different parameters used highlight different mechanisms in the reaction process.

The nitride refractive index drops sharply from a value of \( n \sim 1.98 \) at a deposition temperature of \( 950^\circ \text{K} \) as shown in Fig. 4.2. This is the same temperature at which the deposition rate drops to near zero. It is suspected that this change in \( n \) is a result of

1. the failure or \( \text{NH}_3 \) to decompose, and
2. traces of oxygen in the system.

In Fig. 2.2 it is shown that the decomposition of \( \text{NH}_3 \) becomes marginal in this temperature range. Traces of oxygen would naturally result in an oxynitride film rather than a pure nitride. Even a very small amount of oxygen is sufficient to cause a marked drop in the value of \( n \) (see Fig. 4.2). Below \( 850^\circ \text{K} \), the deposition rate is effectively zero. When the deposited film becomes very thin, its optical constants become swamped by the surface films of \( \text{SiO}_2 \). This, of course, causes the refractive index of the film to approach that of \( \text{SiO}_2 \).
Again, $k$ was measured as a very small quantity. Its value was between .005 - .112. Although small, $k$'s effect is not negligible in ellipsometric calculations. It must be included when refining optical data.

**Oxynitride Film Data**

Figure 4.4 shows the deposition rate of one member of the Si-O-N family as a function of temperature. NH$_3$ and N$_2$O gases were mixed in a ratio of 1:1. Zero growth rate is shown at 650°C or less and the reaction is rate limited to about 800°C. Note that the reactant flow-rates were doubled for the oxynitride runs. This was necessary to allow control of the nitrogen-rich film compositions. As expected, the deposition rate is increased as is the temperature at which the reaction becomes diffusion limited. This is due to the increased concentration of reactants available at the substrate surface.

The apparent activation energy computed from this curve is 44 kcal/mole. This value does not agree with what would be expected from the oxide and nitride activation energies. It suggests that the activation energy may have a concentration dependence.

The index of refraction remained constant for temperatures of 975°K-1150°K as shown in Fig. 4.4. The index also remained constant for variations in flowrate, if the NH$_3$:N$_2$O ratio was not varied. The value of $k$, as with oxides and nitrides, is small.
**Fig. 4.4** Deposition Rate vs. Temperature for Stoichiometric SiON
Summary of Experimental Data

Over a temperature range of 975°K-1250°K, the refractive index (n) is a function of only the ratio of NH\textsubscript{3}:N\textsubscript{2}O. Sensitivity to temperature and total reactant flow appears to be slight. Figure 4.5 confirms this, as the data points used for this plot include runs of different temperatures and flowrates, yet n varied only with the NH\textsubscript{3}:N\textsubscript{2}O ratio. Data points extracted from Rand and Roberts are also included in Fig. 4.5. Their work at Bell Laboratories was done with the SiH\textsubscript{4} - NH\textsubscript{3} - NO reaction. The plots are identical which suggests that the reaction N\textsubscript{2}O $\rightarrow$ NO + 1/2 N\textsubscript{2} is not limiting. This might have been inferred from Fig. 2.2, since the reaction N\textsubscript{2}O $\rightarrow$ N\textsubscript{2} + 1/2 O\textsubscript{2} would be thermodynamically favored. It appears that little, if any, advantage is gained by using the more highly reactive NO instead of N\textsubscript{2}O.

The data in Fig. 4.5 confirms that the oxynitride composition may be inferred from n; and, conversely, a film of a desired index may be prepared by using the proper reactant ratio.

The steep slope in the nitrogen-rich area of Fig. 4.5 clearly indicates the requirement for carefully monitoring the amount of oxygen in the reactor. The reactor must be leak-free, for even a trace of oxygen can drastically alter the stoichometric composition and n.

Rand and Roberts reported an index (n only) reproducibility of $\pm$ .01. With equipment available in this laboratory, assurance of any better than $\pm$ .05 would be difficult. This can be improved, however, with more accurate flow meters. By repeating a run, without readjusting the flow meters, reproducibility of n, $\pm$ .01 was accomplished in our system.
Silicon oxynitride

He  55,000 cc/min
NH₃  400 cc/min (total)
N₂O
SiH₄ 0.00725%

Temp. 700°C to 885°C

Fig. 4.5 Refractive Index vs. Reactant Ratio

× Rand and Roberts, 1973
○ Experimental Data
CHAPTER 5

ERROR SOURCE ANALYSIS

The largest source of error was in film nonuniformities. The nonuniformities resulted from gas flow dynamics and temperature gradients within the reactor tube. The effects were dramatic, yet, by their very nature, unpredictable and difficult to control.

In attempting to control flow dynamics, a mixing baffle was used at the entrance to the reactor tube. The objective was to mix the reactants and break up any laminar flow characteristics. An inclined susceptor was also tried with the same objectives in mind. The inclined susceptor caused problems of wafer positioning and temperature uniformity. Later runs showed improvement by positioning two or three wafers in tandem with the second wafer being used for data (see Fig. 5.1). The lead wafer probably precipitated out excess reactants, providing for a more consistent and uniform flow over the second. The third wafer, if used, produced a thinner film, indicating a decreasing concentration of reactants and/or a decreasing temperature gradient.

The nonuniform film thickness also presented a measurements problem on the ellipsometer. Careful placement of the wafer on the ellipsometer chuck and precise angular orientation reduced this to a minor problem.
Fig. 5.1 Position of Wafers in CVD Reactor
Ellipsometric measurement errors are insignificant when compared with the mentioned errors. The computer, of course, is only as accurate as the data introduced.

For a given film on a previously measured substrate, $n$ can be measured to within 1% and thickness to within 10%. An approximate range in thickness must be known before the computer can zero in on a solution due to the cyclic nature of $\Delta$ and $\psi$. This presents no serious difficulty since color charts, growth monitors, and expected growth rates can be used to approximate this range of thickness.

The largest source of measurement error is the uncompensated natural $\text{SiO}_2$ grown on the substrate between the final HF dip and substrate measurement. Allowing for a natural growth of up to 100 Å, this would introduce a thickness error of about 5-10% for the CVD film. The effect on $n$ would be less than 5%, however, even for the worst case analysis where a nitride ($n = 1.98$) is grown over natural $\text{SiO}_2$ ($n = 1.46$). As the nitride thickness becomes an order of magnitude thicker than the $\text{SiO}_2$, the error becomes negligible. An oxide grown over natural $\text{SiO}_2$ introduces no error in $n$, $n = 1.46$ for both films.

More complicated and more prone to error is the problem of growing a film of specified thickness and index. This combines the errors of production with the errors of measurement. It was very difficult to get accuracy for film thicknesses >3000 Å. Occasionally an initial period of non-growth would result in unexpectedly thin films. This initial period was probably a combination of several factors:
1. the finite period of time required to transport the reactants from shut-off valves to substrate;
2. improper mixing of reactants;
3. variations in substrate surfaces (numbers of nucleation sites), and
4. variations in substrate doping.

All things considered, with equipment available, a variation of ± 15% should be allowed in the thickness tolerances for a one time film. Subsequent identical runs could reduce that to ± 10% easily.

Since a one-to-one correlation exists between the reactant gas ratio (NH₃:N₂O) and n, the only limitation on the accuracy obtainable for a specified index is the accuracy and readability of the flowmeters. For example, a requirement existed for a film of about 6000 Å having an index of 1.50 ≤ n ≤ 1.60. The NH₃:N₂O ratio was adjusted for appropriate flowrates corresponding to n = 1.55 and the readout from the in-process growth monitor (IR detector) was used to approximate thickness. The results of two runs are as shown in Table 5.1. The results show a better than expected tolerance on n, and a thickness tolerance about as expected. The films exhibited the expected problem of nonuniform thickness.
Table 5.1 Results of Two Runs Aimed at Producing $n = 1.55$ and Thickness of About 6000 Å

<table>
<thead>
<tr>
<th>Run Number</th>
<th>Index</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>CVD 74</td>
<td>1.55</td>
<td>6000 Å</td>
</tr>
<tr>
<td>CVD 76</td>
<td>1.54</td>
<td>6800 Å</td>
</tr>
</tbody>
</table>
CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

In this work, the following conclusions were reached:

1. The CVD System, as presently configured, can be used to deposit amorphous Si-O-N films with a specified index of refraction.
2. Strict adherence to the appropriate parameters will result in good reproducibility.
3. The use of ellipsometric measurements and computer assisted analysis of data results in accurate, usable data.
4. The SiH$_4$-NH$_3$-N$_2$O reaction, with helium carrier, is capable of producing the entire family of Si-O-N films safely, accurately and at moderate temperatures (975-1275°K).
5. The optical constants of the films produced for this work closely agree with those published by Rand and Roberts [1973].

Recommendations

The following recommendations have been mentioned or implied in the main text of this report. They will only be summarized here.

Reactor System

A better system of mixing the reactant gases prior to their introduction into the reaction chamber should have a pronounced effect on improving film uniformity. Such a system should provide for on-off
control between the mixing manifold and the reactor tube. This would reduce the time required by the reactant gases to flow from the control valve to the substrate. Also necessary is a by-pass of the reaction chamber. This would provide a way of adjusting flowrates and then switching into the reactor. Together, these improvements would reduce system time transients and enable more accurate study of deposition rates, especially for very thin films.

The Brooks Rotameters should be replaced with more accurate mass flowmeters.

The growth monitor subsystem needs improvement in order to get a more accurate output. An example system is described by Sugawara, et al. [1973].

Study of Surface Films

The problem of surface films, particularly SiO$_2$, on "clean" substrates needs further study. A method of either eliminating the film or compensating for it must be devised if the inherent precision and accuracy of the ellipsometer is to be realized. This would also permit a more accurate study of the extinction coefficient.

Ellipsometer

A phase-lock-loop system should be installed on the ellipsometer photo-detector system to eliminate the noise problem. This would permit final adjustment regardless of ambient light. It would also greatly improve efficiency from a human engineering point of view.
Computer Program

During the course of this work, the software package for the CDC 6400 was changed. The FORTRAN program used for ellipsometric data calculations would not function properly under the new software package. Additional refinements need to be made on this program to make it compatible with the CDC 6400.
APPENDIX A

SUBSTRATE PREPARATION

The substrates were prepared using the initial clean procedure as standardized for The University of Arizona Solid State Engineering Laboratory. The procedure is as follows:

1. Ultrasonic in acetone, 5 minutes.
2. Rinse in deionized (DI) water until run-off resistance measures 2 megohm or greater.
3. Dip in hot chromic solution (90-100°C), 10 minutes.
4. Ultrasonic in DI water, 3 minutes.
5. Dip in HF solution, 10 seconds.
6. Rinse in DI water as above.
7. Dip in hot chromic solution (80-87°C), 10 minutes.
8. Ultrasonic in DI water, 3 minutes.
9. Rinse in DI water as above.
10. Dip in HF solution, 10 seconds.
11. Rinse in DI water as above.
12. Dry with dry nitrogen.

The chromic solution is made up of 400 ml of Cr₂O₃ crystals dissolved in 1600 ml of H₂O and 90 ml of H₂SO₄ (95-98%). The HF solution is made up of 25 ml of ammonium fluoride (40%), 30 ml of HF, and 50 ml of H₂O.
The substrates are stored in individual covered containers until used. Prior to use, each substrate is processed as follows:

13. Dip in HF solution, 10 seconds.

14. Rinse in DI water, as above.

15. Dry with dry nitrogen.

16. Immediately measure the optical constants of the substrate on the ellipsometer.

17. Repeat steps 13-15 (HF dip only 2-3 seconds).

18. Insert substrate into the reactor tube for film deposition.
APPENDIX B

ELLIPSOMETER OPERATION

The operation of the ellipsometer is relatively simple. The sample to be measured is centered on the vacuum chuck mount and angularly oriented in the same manner for both substrate and film measurements. Then while viewing through the port on the telescope, P and A are rotated until extinction occurs. Once extinction has been visually determined, the overhead lights must be turned off and the P and A extinction angles refined through the use of the photomultiplier detector and its associated DC milliammeter. A sensitivity control is provided to permit compensation for various levels of reflectance and/or absorption. Noise within the electronic circuit becomes significant when in HIGH sensitivity mode. Normally, however, MED sensitivity will allow for good extinction refinement. The sensitivity switch must be returned to LOW when the room lights are on or damage may result to the detector or meter.

There will be four combinations of P and A settings which produce extinction. Those settings between 0° and 180°, only, should be used in order to prevent ambiguity in computed read-out data.

Upon completion, a set of readings will include two polarizer angle settings (P₁ and P₂) and two analyzer angle settings (A₁ and A₂). In addition, the wave plate has a preset value (Q) which must be included with the data to be entered into the computer. This data, together with
appropriate code words to delineate which specific calculations are desired, are then read into the computer with the program deck to obtain the desired optical constants or physical data [Whitmer, 1973].
This appendix is not a comprehensive operator's guide. The magnitude of such a comprehensive endeavor precludes its inclusion in this thesis. Additionally, modifications and additions to the system will quickly render a detailed set of instructions obsolete.

Before an operator can effectively operate the reactor, a general understanding of the function of the system and subsystems is requisite. The first part of this appendix gives a brief preview of the entire CVD system. The second part briefly describes the sequence followed in obtaining the films used in this research.

The CVD Reactor and Subsystem

The CVD reactor is a complex entity consisting of the RF generator and reaction chamber and three subsystems:

1. the gas metering subsystem,
2. the temperature monitoring subsystem, and
3. the in-process thickness monitoring subsystem.

The success of a CVD process depends upon the proper interrelationships of the system and its subsystems.

The RF generator and reaction chamber are the heart of the system. The RF generator is capable of producing up to 10 KW of energy.
This energy is coupled into a graphite susceptor block located inside the reaction chamber and upon which the substrates are placed. The substrates are heated to the temperature necessary for the chemical reaction and the desired film is grown on the substrate.

The RF generator is water cooled. A ten gallon reservoir stores the cooling (DI) water which is pumped through the power tube filaments, RF coil, and heat exchanger. The reservoir must be checked and filled daily. External plumbing carries normal tap water through the heat exchanger and carries off excess heat.

When power is applied to the filaments of the power tube, wait 15-20 minutes before applying DC voltage to the plate. This allows the tube to temperature stabilize and prolongs tube life.

The gas metering subsystem is a bank of Brooks Rotameters for all gases except silane which has a Matheson mass flow meter. Adequate plumbing and appropriate valving is provided for metering eight different gases simultaneously. Various metering tubes are available to handle a wide range of flow rates. Graphs have been prepared [Edgar, 1973] to aid in associating rotameter readings with flow rates. Graph data must be modified to compensate for different line pressure and the specific gravity of the gas being metered.

The temperature monitoring subsystem reads temperature from a chromel-alumel thermocouple. The thermocouple is centered in the susceptor block, thus some temperature gradient must be expected between the thermocouple and the substrate surface. This will be small to negligible, however, depending upon substrate thickness and magnitude of
gas flow over the substrate. The thermocouple output is read from a microvoltmeter and converted to temperature on appropriate tables. Correction should be made for room temperature for this conversion.

The in-process thickness monitor operation is based upon thermal radiation properties and the physical and optical properties of the monitored film. Radiated energy from the substrate is chopped, detected, amplified and recorded. The number of peaks and valleys on the recorder provides a measure of the film thickness according to the equation [Whitmer, 1972]

\[ d = \frac{\lambda(N)}{4n} \]  

where

\[ d = \text{physical thickness} \]
\[ \lambda = \text{wavelength of detected radiation} \]
\[ N = \text{integer sum of the peaks and valleys on the yt recorder} \]
\[ n = \text{film index of refraction (real part only)} \]

CVD Reactor Operation

A specific sequence of events, based upon the desired results, must be established before operating the CVD reactor. Failure to do this could result in an unsuccessful deposition, equipment failure and/or personal injury. The following sequence was established for the work in this paper. It may be used as a general guide for other similar work. However, the operator should carefully preview the desired results to insure operational compatibility.
About four consecutive hours was established as a minimum period of time within which profitable work could be realized. A maximum of twelve hours of continuous operation is the upper limit. Beyond this, operator fatigue reduces profitable output to marginal limits.

1. Apply AC power to all equipment and measuring instruments. Turn on filament voltage to RF power tube.
2. Turn on water valves to the heat exchanger.
3. Switch from nitrogen to helium carrier gas. Turn off dehydrator. Adjust helium line pressure.
4. Open N₂O and NH₃ tanks; adjust line pressure.
5. Adjust all gas flow meters as needed for the next run. Check line pressures and adjust as needed. Readjust flow meters.
6. Close reactant gas line valves.
7. Reduce carrier flow as an economic measure.
9. Insert the substrate(s) into the reaction chamber.
10. Apply RF power (START) and adjust the powerstat to obtain the desired temperature.
11. Adjust carrier flow; readjust powerstat; repeat as necessary until temperature has stabilized.
12. Set timer and open reactor gas valves.
13. After the run, turn off the RF power (STOP) and shut reactant gas valves. Reduce carrier flow rate. Allow 5 minutes to cool and then extract the sample.
14. Repeat steps 5-13 if desired.

15. Measure film optical constants on the ellipsometer.

16. Shut down reactor in reverse sequence of steps 1-4. Allow 15-20 minutes between turning off filament voltage and turning off master power switch (cooling pump).
LIST OF REFERENCES


