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## Abstract

Title of Thesis: Control of Stress in Reactively Sputtered Silicon Nitride Films

Ajay Krishnan, Master of Science in Electrical Engineering, 1990

Thesis Directed by: Dr. Roy Cornely, Professor of Electrical Engineering.

Silicon nitride thin films of varying composition and thickness were deposited on silicon substrates by reactive rf diode sputtering of a silicon target using an argon/nitrogen gas mixture. Film stoichiometry could be controlled by varying the partial pressure of nitrogen, the total sputtering gas pressure and the target rf power. Films with refractive index of 2.01, the value for stoichiometric silicon nitride, could be obtained. Film stress was measured by wafer curvature; refractive index and thickness of deposited films were obtained by ellipsometry and interferometry measurements. The etch rate in buffered HF for films with refractive index 2.05 was 29A/min; as measured by IR spectroscopy these films had relatively low oxygen and hydrogen content. On increasing the film thickness from 300 A to 1900 A, the stress decreased from  $4.45 \times 10^9 \text{ N/m}^2$  to  $0.56 \times 10^9 \text{ N/m}^2$  for a film with a refractive index of 2.05. It was observed that films with silicon in excess of the stoichiometric value and films with greater thickness exhibited reduced stress. Films with higher refractive index were obtained on reducing the nitrogen partial pressure and increasing the applied rf power.

Since low temperature deposition is critical for reducing the stress developed in thin films, the substrate temperature during sputter deposition was maintained at  $140^{\circ}C(\pm 10^{\circ}C)$ . The stress content of the unannealed NJIT films was observed to be higher by about a factor of 10 than the lowest stress value  $(2 \times 10^8 N/m^2)$  obtained by plasma deposition followed by a 400°C postanneal for a 1000 A thick film. The lowest stress value obtained during this research was 0.98 x  $10^{9} N/m^{2}$ , with 2.24 being the refractive index for this silicon rich film with a thickness of 700 A. The value for a 730 A thick film with index of 1.702 was 2.036 x  $10^{9}N/m^{2}$ .

# <sup>2)</sup> Control of Stress in Silicon Nitride Thin Films

)) by Ajay Krishnan

Thesis submitted to the Faculty of the Graduate School of the New Jersey Institute of Technology in partial fulfillment of the requirement for the degree of Master of Science 1990

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# Approval Sheet

Title of Thesis: Control of Stress in Reactively Sputtered Silicon Nitride Films

Name of Candidate: Ajay Krishnan

Degree: Master of Science in Electrical Engineering

Thesis and Abstract Approved:

Dr Roy Cornely Thesis Advisor

Dr Kenneth Sohn Committee Member

Dr Marek Sosnowski Committee Member Date

Date

Date

## Vita

Name: Ajay Krishnan.

Degree and date to be conferred: M.S.E.E., 1990.

Secondary Education: Central School, Bhopal, India.

Collegiate institutions attended	Dates	Degree	Date of Degree
College of Engineering, Guindy.	1984-88	B.S.E.E.	May, 1988
New Jersey Institute of Technology	1988-90	M.S.E.E.	October, 1990

Major: Electrical Engineering.

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# Chapter 1 Introduction

The research reported in this thesis was a part of the joint research program between New Jersey Institute of Technology and Epitaxx, Inc.. The research was partially supported by the New Jersey State Commission on Science and Technology. All the experiments were carried out at the Drexler Microelectronics Laboratories at NJIT under the supervision of Dr. Roy H. Cornely and Dr. Kenneth Sohn, Professors of Electrical Engineering, NJIT.

The primary goals of this research were to control the stress silicon nitride films for applications in microelectronics and optoelectronic device passivation.. Silicon nitride thin films of varying composition were deposited by reactive rf sputtering. This was done by adjusting the various deposition parameters. Refractive index and thickness of the films were determined by ellipsometry, infrared spectrophotometry was used to determine the film composition and etch rate studies were used to study the structural and chemical properties of the film. Stress developed in the deposited films was determined by measuring the wafer curvature using laser reflectance technique.

Chapter 2 is a review of sputtering and sputter deposition, passivation, the different materials used for passivation, and the theoretical background of the various characterization techniques used in this study.

1

Chapter 3 discusses the deposition equipment, substrate preparation and the deposition procedure.

Experimental data and results obtained during this research as well as data obtained by other researchers are presented in chapter 4.

Chapter 5 discusses the results presented in chapter 4. The work of other researchers is also discussed and the results of this research are compared.

Concluding remarks and suggestions for future work are given in chapter 6.

## Chapter 2

#### Introduction

This chapter discusses the process of sputtering, passivation and the need for passivation of surfaces. Different types of passivating materials used in the industry are analysed, although emphasis has been placed on silicon nitride and its properties. Then the different techniques commonly used for thin film deposition are described, the advantages and drawbacks of each method are stated. Finally, the different characterization techniques used for sample analysis during this research are described.

### 2.1 Ion bombardment of a surface

When a solid, or liquid, at any temperature is subjected to bombardment, by suitably high energy particles (usually ions), it is possible for individual atoms to acquire adequate energy via the process of momentum transfer, due to collisions, to escape from the surface. This process of ejection of atoms from a surface is called *Sputtering*. The atoms ejected from the surface can be used to deposit a coating on a substrate by a process called sputter-deposition.

The exact mechanism by which atoms are ejected from a surface when the surface is subjected to ion bombardment is not very clear. According to Stuart [1], when an ion impinges against a surface, it suffers a collision with a surface atom. When the energy exchange between the impinging ion and the surface atom is much greater than the lattice energies or the vibrational energies of the lattice atoms, significant sputtering occurs. At these energies the collisions are purely binary, the neighbouring atoms do not become involved in the collision. Such a collision is called a "Primary collision". An ion incident on the bombarded surface in a direction perpendicular to the surface will bounce back from the surface after the collision. During the collision some energy will be imparted to the surface atom, which has been driven into the surface. When the mass of the incident ion is greater than the mass of the atom at the surface then both the ion and the atom will be driven into the surface, irrespective of the nature of the collision [2] (ie. whether the collision was head on or glancing). This is shown in Figure 2.1.

For the atom to be ejected from the surface, it must acquire a velocity component in a direction opposite to that of the original incident ion. The greatest possible angle between the original incident ion and the subsequent momentum vector of the struck atom is 90°. But in this case the velocity component perpendicular to the surface of the struck atom is zero. Hence it is not possible to eject an atom from the surface as the direct result of a primary collision. We need a second set of binary collisions to enable atoms to be ejected from the surface.

Another phenomenon which occurs ion bombardment is secondary electron emission. When an ion approaches a surface at any energy, it will be neutralized before impact due to interaction with lattice electrons of the surface. This interaction involves two lattice electrons and occurs within less than an atomic diameter of the surface. One electron is captured by the incident ion, thereby neutralizing the ion. The second electron acquires the excess energy and momentum given up by the other electron and may be ejected from the surface. This ejection process is referred to as secondary emission and the electrons ejected in this manner are



Figure 2.1: Representation of three types of collision between an incident ion and a surface atom. The mass of the incident ion is represented here as being less than the mass of the struck atom.

called "Secondary electrons".

### 2.1.1 Characteristics of sputtering

Some of the unique characteristics of sputtering are:

- 1. Deposition rates do not differ significantly for different metals, alloys, or even insulators. The compatibility and applicability to various materials make sputtering attractive in multilayer deposition.
- 2. Thickness control is very simple. After a calibration run has been made, thickness control is merely a matter of setting the time.
- 3. The lifetime of a sputtering target may be as long as 150-200 hours; it is seldom less than 10.
- 4. In sputtering alloys and other composite materials, the deposit maintains stoichiometry with the original target composition.

This can be explained by considering the mechanism of sputtering wherein the target atoms are dislodged from the target by momentum transfer from the impinging ion. Since there is no mass transport within the target, the composition of the sputtered constituents must be identical with the composition of the target; however, the composition of the deposit could vary if the sticking coefficient or the angular distribution is different for each ejected species.

- 5. Cleaning of parts and substrates can be achieved by a applying negative voltage to the anode (reverse sputtering is an advantage that can be gained with no other process).
- 6. The problem of ejection of large particles from sources, "Spitting", usually does not occur in sputtering. However, one has to be careful that particles do

not fall out of the target during sputter-down (this would occur, in a system in which the target is located at the top of the chamber, is used). Spitting does occur in evaporation, laser ablation and other methods.

- 7. The high ejection energy of sputtered atoms, average mean energy for diode sputtering is often suggested as a factor in improving the film structure and adhesion to the substrate. On the other hand, the high energy tail of the sputtered species, estimated to be 1 to 10 KeV, can cause surface defects and other undesirable effects.
- 8. There are different types of sputtering systems available, each having its own unique features and each capable of either dc or rf operation:
  - Planar diode sputtering;
  - Triode sputtering;
  - Ion beam sputtering;
  - Magnetically assisted sputtering.

Low pressure operation gives the triode technique several advantages over the typical diode system. They are:

- (a) The triode technique results in increased deposition rates due to higher ion density.
- (b) The decreased ratio of residual gas molecules to sputtered atoms means the film density and purity are enhanced.
- (c) Consistent straight line deposition from target to substrate, due to low pressure, makes it possible to use masks in front of the substrate to define film patterns.

(d) Independent control of the plasma density makes it possible to regulate film deposition more carefully.

As compared to the diode mode, the triode mode has its disadvantages too. The thermionic filaments (usually tungsten is used), make reactive sputtering with oxygen impractical because oxidation of tungsten makes the filament very brittle. The filament contributes to contamination. It is subject to burnout and its power dissipation adds heat to the chamber area.

The following are some of the advantages of RF induced plasma sputtering over the DC diode or triode modes:

- (a) It is possible to sputter insulators using RF sputtering because the RF prevents the charge buildup on the target surface.
- (b) At operating pressures as low as 2x10<sup>-4</sup>torr, two difficulties, gaseous impurity inclusions and nonreproducibility of film properties, inherent in higher pressure diode type of sputtering are reduced.
- (c) A heated filament to sustain the plasma is not required. Hence contamination from thermionic emission is eliminated and filament burnout is avoided.

## 2.2 An Overview of Semiconductor Surface Passivation

#### Introduction

The characteristics of an electronic device are subject to deterioration due to the incursion of moisture, impurities or diffusion of dopants. The device properties can be stabilized by deposition of a passivating coating over its surface. This is termed "Passivation". In the case of semiconductor device passivation, in addition to chemical stability, electrical stability is also required.

#### 2.2.1 Types of Passivation

Semiconductor surface passivation can be broadly classified into two categories:

- Primary passivation
- Secondary passivation

#### **Primary Passivation**

Passivation coatings may be classified as primary if they are directly in contact with single crystal silicon from which the device is fabricated [3,4]. Primary passivating coating serves to:

- 1. Control and stabilize semiconductor surface properties;
- 2. Provide good dielectric properties, low surface recombination velocity and control immobile charge density;
- 3. Improve device stability at elevated temperatures.

#### Secondary Passivation

When an underlying dielectric layer separates the passivating coating from silicon, it is termed secondary passivation [3,4]. The function of secondary passivation is to:

- 1. Protect and stabilize the primary passivating medium;
- 2. Insulate and protect the interconnections and terminal metallurgy;
- 3. Provide overall chemical and mechanical protection.

### 2.2.2 Electrical Requirements of an Ideal Passivating Layer

The electrical requirements of an ideal passivating layer are [4,5]:

- 1. The semiconductor surface potential must not change significantly with time, under the stress conditions encountered by the devices;
- 2. The semiconductor surface potential must be optimum for the particular device under consideration;
- 3. Device requirements of the surface state density and surface charge should be met by passivation.

#### 2.2.3 Passivation Mechanism

Surface states arise from the termination of a periodic array and are present on an ideal surface. On real surfaces the density and distribution of the surface states are affected by the impurities, structural defects and adsorbed molecules and ions. The formation of an oxide layer uses up most of the surface states through bond formation. A residual broken chemical bond at the surface is referred to as a "dangling bond".

The presence of charge, in an oxide layer on the surface of a crystal can give rise to a *surface potential* at the interface, which causes perturbation of the electron density inside the semiconductor. This perturbation region near the surface is called as the space charge region. It is a complex function of the surface potential, carrier density and the oxide semiconductor interface. Formation of the oxide layer generally results in positive interfacial charge, which causes an accumulation of electrons at the silicon surface. The excess carriers near the surface cause surface conductivity to vary from bulk value [6].

#### 2.2.4 Comparision of Passivating Materials

There are a number of materials that have passivating properties. Only some of the important and frequently used passivating materials such as silicon dioxide, phosphosilicate glass (PSG), borophosphosilicate glass (BPSG) and silicon nitride will be discussed here.

#### Silicon Dioxide

Amorphous  $SiO_2$  grown on silicon is the most widely used primary passivation layer, it can be grown thermally, chemical vapor deposited, directly sputtered or reactively sputtered. The best electrical properties are obtained with thermally grown films. A layer of undoped silicon dioxide is used to insulate multilevel metallization, to mask ion implantation, diffusion and to increase the thickness of thermally grown field oxides.

Silicon dioxide has a refractive index of 1.46 and very high resistivity  $(2x10^{15}$  ohm-cm). Oxides with lower refractive index are porous. The porous nature of the oxide is also responsible for the lower dielectric strength. The etch rates of the oxides in a hydrofluoric acid (HF) solution depend upon the deposition temperature, annealing history and dopant concentration. Usually higher quality oxides are etched at lower rates [7].

#### PSG and BPSG

Phosphorous doped silicon dioxide (usually called P-glass or PSG) inhibits the diffusion of sodium impurities. It softens and flows at  $950^{\circ}-1100^{\circ}C$ , creating a smoother topography which is useful for depositing metals.

Borophosphosilicate glass (BPSG) is formed when boron is added to phos-

phorous. It flows at even lower temperatures  $850^{\circ} - 950^{\circ}C$  [7].

#### Silicon Nitride

The bulk properties of silicon nitride show an interesting combination of chemical, mechanical and electrical properties for applications in silicon semiconductor technology. The applications of silicon nitride films for passivation are based on its properties as a barrier against atomic and ionic diffusion and its electrical properties. The major applications are: a) as a barrier against ionic contamination in FET applications, where it forms a part of the gate insulation and b) as a mask for diffusants in optoelectronic materials, eg. zinc in GaAs.

The advantages of silicon nitride are:

- Inhibitor of diffusion by many species;
- High dielectric constant;
- Chemically inert nature;
- Mechanical durability.

Due to the importance of silicon nitride in the processing industry, its properties are discussed at length in the following paragraphs.

#### Mechanical and Thermal properties

The main mechanical [8-14] and thermal [15-17] properties of thin film/substrate pairs are: adhesion of the film to the substrate, hardness and scratch resistance of the film, relative thermal expansion coefficients and thermal stresses at the interface.

The adhesion of a thin film to a substrate is controlled by the nature of the film-substrate interaction forces (particularly forces of the Van der Waals type or electrostatic forces). The adhesion also depends greatly upon the cleanliness and microstructure of the substrate, on the deposition process, the temperature during deposition and on the subsequent treatment. As a general rule, good adhesion is obtained with a clean substrate which has few structural flaws and which is heated to a temperature high enough to cause some interdiffusion at the interface during deposition. However, this last condition leads to an increase in the number and intensity of mechanical stresses of thermal origin in the film. Subsequent heat treatment conducted in vacuum or in inert atmospheres can also improve the adhesion between the sample and the support.

Density determinations have been made by weighing the wafers on a semimicrobalance with and without the deposited silicon nitride film, measuring the film thickness and wafer diameter and using the values thus found, to compute the density value.

Mechanical stresses developed in the films generally have two components:

- An intrinsic component which is characteristic of the layer and is controlled by structural imperfections, impurities etc.
- A thermal component which originates from a difference in the thermal coefficient of expansion of the substrate and the layer.

Silicon nitride films deposited by CVD processes are generally under tensile stress while those deposited by plasma sputtering have been found to be under compressive stress (about 2-4x10<sup>9</sup> dynes/ $cm^2$ ). There are different techniques to determine the stress developed between the substrate and the deposited film. In this thesis, laser reflectance technique was used. This is discussed in detail in section 2.4.4.

#### **Optical properties**

Investigations into the optical properties [18-24] of thin silicon nitride layers have led to important conclusions about their structure and composition. Among these optical properties, absorption and reflection of light and the refractive index have been widely studied.

The refractive index of thin films can be obtained using ellipsometry and interferometry among other techniques. The use of an ellipsometer to determine the refractive index and thickness is discussed in section 2.4.1.

The absorption spectra in the IR range are particularly important for silicon nitride since they provide information on the molecular structure of the layers. The absorption peak due to Si-N bond occurs at  $11.5\mu m$ . Absorption peaks for Si-O  $(9.4\mu m)$ , O-N  $(2.9\mu m)$  and Si-H  $(4\mu m)$  and N-H  $(7.2\mu m)$  have seldom been found in high quality films, but are often observed in non stoichiometric silicon nitride films.

#### **Chemical Properties**

Silicon nitride is highly resistant to many chemicals. However, it can be etched at room temperature by fluoride solutions (conc. HF, Buffered HF), non fluoride solutions  $(H_3PO_4 \text{ at } 140 - 180^{\circ}C)$  and by gaseous HCl [25], according to the following reactions:

 $Si_{3}N_{4} + 18 \text{ HF} = H_{2}SiF_{6} + 2(NH_{4})_{2}SiF_{6}$   $Si_{3}N_{4} + 27H_{2}O + 4H_{3}PO_{4} = 4(NH_{4})_{3}PO_{4} + 9H_{2}SiO_{3}$  $Si_{3}N_{4} + 16 \text{ HCl} = 3SiCl_{4} + NH_{4}Cl.$ 

The etch rate of silicon nitride film is controlled by:

• the density of the film;

- film stoichiometry;
- bond strain;
- impurities.

#### **Electrical properties**

Silicon nitride films are electrical insulators. The breakdown voltage, dielectric constant and electric conductance of silicon nitride have been widely studied [26-30].

The electrical characteristics of silicon nitride films on Si are obtained from Metal-Nitride-Semiconductor (MNS) capacitors. A MNS capacitor has two electrodes, one is connected to the metal layer deposited over the nitride and is called the "grid" and the other is the ohmic contact to the semiconductor. The capacitance "C" between the electrodes is measured and it's dependance on the d.c voltage  $V_g$ applied to the grid i.e the C- $V_g$  characteristic is plotted. Fig. 2.2 gives the typical curves.

The capacitance of MNS devices varies from a maximum  $(C_o)$  to a minimum  $(C_{min})$  according to the relation:

$$\frac{C}{C_N} = 1 + \frac{2\epsilon_n \epsilon_0 V_g}{q N_A \epsilon_{Si} X_N^2}$$

where  $\epsilon_n, \epsilon_{si}$  represent the relative dielectric constant of the nitride and silicon resp.,

 $\epsilon_o$  is the permittivity of free space (8.85x10<sup>-14</sup> F/cm),  $C_N$  is the capacitance per unit area of the nitride film,  $N_A$  is the concentration of acceptor impurities,  $X_N$  is the thickness of the nitride layer,



Figure 2.2: Typical C-V curves for a MNS capacitor: A, theoretical curve; B,C curves showing hysteresis of an MNS capacitor; D, curve for an MNS capacitor as-deposited: G,H, curves for an MNS capacitor after a bias-temperature stress test; I, curve for an MNOS capacitor. [14].

and  $V_g$  is the Grid voltage.

To determine the breakdown voltage, an MNS capacitor is biased in the accumulation region by increasing the d.c voltage. Breakdown occurs when the leakage current exceeds certain limits. The breakdown field  $(10^7 \text{ v/cm})$  of high quality silicon nitride is independent of the contact area or film thickness.

The dielectric constant " $\epsilon$ " can be obtained from the relation:

$$\epsilon = Cd/\epsilon_0 A$$

where C is the measured capacitance, d is the thickness of the silicon nitride layer,  $\epsilon_0$  is the permitivity of free space, and A is the area of the capacitor.

#### Electrical Conductance:

In silicon nitride films conduction is not governed by ohm's law; Poole-Frenkel mechanism is obeyed. The Poole-Frenkel effect is the lowering of the potential barrier due to interaction with an external electric field. This can also be described as a field enhanced thermal excitation of the trapped electrons into the conduction band [31]. In short, it is the mechanism by which electrical conduction takes place by means of electrons/holes which are generated by electric field ionization of trapping levels in silicon nitride films. The current density equation governing the Poole-Frenkel mechanism is:

$$J = C_2 Eexp[-q(\phi_B - \sqrt{(qE/\pi\epsilon_i)})/kT]$$

where  $C_2$  is a constant depending on the trapping density in the insulator  $\phi_B$  is the barrier height,  $\epsilon_i$  the dynamic permittivity and E is the field.

### 2.3 Characterization techniques

#### 2.3.1 Ellipsometry

Ellipsometry is the art of measuring and analysing the elliptical polarization of light. Ellipsometry is based on the classic theory of Paul Drude, concerning the change in the state of polarization of light upon reflection from a bare surface or a surface with a film on it. By measuring the change in the state of polarization, it is possible to measure the thickness and refractive index of the film [32].

The Fresnel formulae are the foundations of ellipsometry. These indicate that when light is reflected, the two components vibrating in and perpendicular to the plane of incidence, which can be referred to as  $r_p$  and  $r_s$ , undergo a phase shift of 180° or 0°. Also  $r_p$  becomes zero at a certain angle called Brewster angle. If the incident light is plane polarized at 45° to the principal planes, after reflection at the Brewster angle, the ratio K of the reflected amplitudes in the plane of incidence and perpendicular to the plane of incidence is called "Ellipticity". In the proximity of the Brewsterian angle, the reflection of light deviates from fresnel's law and an appreciable amount of ellipticity is present. The two parameters characterizing the ellipse representing the reflected light are:

the ratio  $tan\psi = \rho^p / \rho^s$  and  $\Delta = \delta^p - \delta^s$ .

where  $\rho^p$ ,  $\rho^s$  are the reflection coefficients of the components in and perpendicular to the plane of incidence after reflection.  $\delta^p$ ,  $\delta s$  are the absolute phase shifts of the same two components.



Figure 2.3: Schematic of an ellipsometer

$$tan\psi e^{i\Delta} = \frac{(r_{f}^{p} + r_{m}^{p} e^{-ix})(1 + r_{f}^{s} r_{m}^{s} e^{-ix})}{(1 + r_{f}^{s} r_{m}^{p} e^{-ix})(r_{f}^{s} + r_{m}^{s} e^{-ix})}$$

where  $r_f^{p,s}, r_m^{p,s}$  are the fresnel coefficients for reflection at the film and the surface.

 $\psi$  and  $\Delta$  are obtained experimentally from ellipsometric measurements, ie. by measuring the orientation of the amplitude vectors.

The plane of the paper is perpendicular to the light beam. The plane of polarization is perpendicular to the plane of vibration of the electric vector. A light beam is plane polarized at  $45^{\circ}$  to the plane of incidence. Before reflection, the two components in the plane of incidence and perpendicular to it, are equal in magnitude and are in phase. After reflection each of them suffers a phase shift ( $\delta^{p}$  and  $\delta^{s}$ ), and the ratio  $\psi$  of their amplitudes which is now equal to  $tan\psi$  is decreased.

#### 2.3.2 Chemical Etching of Thin Films

Chemical etching in thin film technology plays a prominent role in both the preparation and utilization of thin films. The substrate must be first suitably prepared prior to film deposition. Once the film has been deposited, chemical etching is often used again, to create patterns in appropriately masked films. Another important application of chemical etching is in characterization of materials, especially in the detection of lattice defects in semiconductors, the study of distribution of localized impurities and the determination of composition [25].

The variations in the etch rate of a specific material in a given etchant are the function of :

- Chemical composition;
- Film density;

- Residual stress;
- Defect density; and
- Microstructure.

In general insulating and dielectric materials are relatively inert chemically and hence require highly reactive media for etching.

#### Chemical Etching of Silicon Nitride

The silicon nitride films deposited in this research were found to be amorphous. This is in agreement with the results obtained by other researchers [5,25]. Low substrate deposition temperature  $(100 - 150^{\circ}C)$  was used. Since the structure is found to be amorphous, the etching proceeds isotropically [33].

The commonly used etchants for silicon nitride are :

- Concentrated Hydrofluoric acid (49% HF);
- Buffered HF (7:1);
- Phosphoric acid (at  $140^{\circ}C 200^{\circ}C$ ).

The etch rate of silicon nitride is different in the different etchants. Depending upon factors such as the type of the substrate on which the silicon nitride is deposited and the thickness of the nitride layer etc., the etchant is chosen. Fig. 2.7 gives the etch rates of silicon nitride in refluxed boiling phosphoric acid at atmospheric pressure as a function of boiling temperature and acid concentration. . The table also gives the etch rates for CVD deposited silicon nitride for comparison purposes.



Figure 2.4: Etch rates of silicon nitride in refluxed phosphoric acid at atmospheric pressure [Van Gelder and Hauser].

Silicon nitride films deposited by sputtering techniques generally have lower etch rates than CVD deposited silicon nitride. If they are less dense, they most probably contain large quantities of gases and/or are nonstoichiometric.

#### Infrared Spectroscopy

The physical and electrical properties of silicon nitride depend on the stoichiometry of the film. As discussed earlier, film composition depends on the deposition parameters. Infrared spectroscopy is one of the techniques used to determine film composition [18-24].

In this work, an infrared spectrophotometer (Perkin-Elmer type 1600 FTIR) was used. An interferometer utilizing Fourier Transform (FTIR) method was used to determine the absorption spectrum (fig. 2.8). A beam of incident IR radiation is split by a semitransparent mirror into two spatially separated beams (A, B) which follow their respective paths shown by the respective dashed and dotted lines. The two beams interfere with each other at the detector. If, one of the mirrors is uniformly translated, the path difference will change continuously. If the source is monochromatic, then the combined beams will go in and out of phase with each other, resulting in a sinusoidal modulation at the detector. The fourier transform of such a function will be a delta function, proportional in strength to the incident intensity at the source frequency. If the source is polychromatic, the fourier transforms are calculated by the computer. Then on inserting the sample, an absorption signal is obtained. By absorption spectrum can then be obtained from the fourier transforms of the sample and the instrument background.

The results obtained are presented in chapter 4 and discussed in chapter 5.



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Figure 2.8: Fourier Transform Infrared Spectrophotometer (FTIR).

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#### **Stress Measurement**

The measurement of stress in thin films is of interest in many areas of microfabrication. Nearly all films, by whatever means they are produced are found to be in a state of internal stress. The stress may be compressive (ie., the film would like to expand parallel to the surface). Alternatively, the film may be in tensile stress (ie., the film would like to contract).

High stress causes lateral diffusion (*Winging*) during doping processes when silicon nitride is used as a mask [34-40]. High stress can also cause cracking of the nitride film during bonding operations. Intrinsic stress plays a key role in altering the mechanical, electrical, optical and electron-transport properties of a film.

In this work, laser reflectance measurements of wafer curvature was used to compute film stress. Stress may also be measured by x-ray or electron diffraction techniques.

#### Laser Reflectance

The stress of a film on a thick substrate, assuming uniform film thickness and otherwise isotropic film stress, is given as

$$\sigma = \frac{ED^2}{6(1-\nu)Rt}$$

where E and  $\nu$  are the Young's modulus and Poisson's ratio of the substrate. D, t are the substrate and film thicknesses respectively, R is the radius of curvature of the composite. By convention R is negative for a convex wafer surface (compressive film stress) and positive for a concave wafer surface (tensile film stress).

The radius R can be determined by measuring the deflection of a light beam reflected off a wafer surface as the wafer is moved a fixed distance perpendicular to the beam. This method uses a collimated laser beam which reflects from a wafer surface and projects on a screen about 5 m away. The wafer is moved a known and


Figure 2.9: Schematic of laser reflectance measurement apparatus

# SUBSTRATE CURVATURE TECHNIQUE FOR STUDYING MECHANICAL PROPERTIES OF THIN FILMS ON SUBSTRATES



STRESS IN FILM =  $\frac{E_s d^2}{6(1 - V_s)Rt}$ 

 $E_s$  = Young's Modulus of Substrate

- $\mathcal{V}_{s}$  = Poisson's Ratio of Substrate
  - d = Thickness of Substrate
  - t = Thickness of Film
- R = Radius of Curvature

fixed distance while being illuminated by the incident laser beam. Wafer curvature causes the image of the beam to appear shifted on the screen. A measure of the wafer translation x, the corresponding translation of the position of the reflected beam d, and the reflected beam path length L gives the radius of curvature R:

$$R = 2L_{d}^{\mathbf{x}}$$

A sample calculation is presented here:

For x = 1 cm  $d = 2.8 \times 10^{-3}$  L = 5.08 m.

Hence, R = 36.38 m

Substituting  $\nu = 0.42$ ; E = 10.89 x 9.81 x 10<sup>9</sup> N/m<sup>2</sup>; D = 355.6 x 10<sup>-6</sup> m and t = 1.9 x 10<sup>-7</sup> m,

We get, film stress  $\sigma = 0.56 \ge 10^9 \text{ N}/m^2$ .

# Chapter 3

# **Experimental Procedure**

#### Introduction

In this chapter the sputter deposition equipment is described and the experimental procedure followed in this research work given. The cleaning of silicon substrates by chemical etching prior to film deposition is also discussed.

# 3.1 Sputtering system

A modified version of the MRC 8800 sputtering system (Triode system 18120) was used for the deposition of silicon nitride thin films. A schematic representation of the sputtering system is shown in fig. 5.1. The RF generator which operates at 13.56 MHz supplies voltage to an intrinsic silicon target of 99.999% purity, 5.0 inch diameter and 0.25 inch thickness. The rotating target head can accommodate four targets fitted with ground shields. The anode cathode spacing can be varied between 1.0 to 4.0 inches. The substrates are placed on a plate in the intervac chamber and then transported, without breaking the vacuum, into the main chamber through a connecting door. This is done using a pneumatic plunger arrangement. The background vacuum pressure, which is an important parameter in any vacuum deposition process, must be in the  $10^{-6}$  torr region to be considered low enough for sputtering. The gases for sputtering are supplied from high pressure cylinders through a micrometer valve provided at the top edge of the deposition chamber.

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The deposition chamber is heated externally prior to deposition for about 4-5 hours, to remove any moisture that may be present in the chamber. This is crucial for obtaining good films since the presence of even traces of water vapor in the chamber will cause a deterioration of the film properties.

# 3.2 Substrates

Silicon substrates of low resistivity (14-16 ohm-cm), (100) orientation and n-type doping were used for deposition. Silicon nitride was also deposited on indium phosphide substrates provided by Epitaxx, Inc., Princeton, New Jersey.

## 3.2.1 Etching of Substrates

#### Introduction

Silicon substrates carry approximately a 5-10 nm thick layer of native oxide which must be etched prior to deposition of silicon nitride. This would also remove any impurities or contamination that might be present on the substrate surface. Organic residues can be removed by treating with a series of appropriate organic solvents.

#### Substrate Preparation

The following procedure was adopted during this research, for cleaning the substrate surface prior to film deposition:

 The samples were first ultrasonically cleaned in deionized water for about 20 minutes;



Figure 3.1: MRC 8800 sputtering system

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- 2. They were then dipped into 48% Hydrofluoric acid (HF) solution for 40 seconds.
- 3. The samples were then rinsed with DI water to remove any acid and then treated with 2- propanol for about 2 minutes.
- 4. They were then treated in 1-1-1 Trichloroethane for about 2-3 minutes.
- 5. The next step was a 3 minute dip in methanol.
- The samples were treated with 1-1-1 Trichloroethane for 1 minute followed by a rinse in DI water.
- 7. The final step was to blow the samples dry with a jet of  $N_2$  gas.

After this process was complete the samples were immediately transferred into the intervac chamber which was pumped down to a pressure of 30 - 40 mTorr in about 25 minutes, after which they were inserted into the deposition chamber as discussed earlier. This was done in order to minimize the probability of any impurities from being absorbed into the substrate surface.

# 3.3 Deposition Process

#### Introduction

This section focuses on presputtering of the target, the formation of an altered surface layer on the target and the subsequent film deposition on the substrate.

#### 3.3.1 Presputtering

Presputtering of targets is done in order to clean and equilibrate the target surface prior to film deposition and to outgas the vacuum chamber. During presputtering, the substrates are sheilded with a shutter located close to the substrates. If the shutter facility is absent, then the substrates are introduced into the chamber after presputtering. Presputtering results in the formation of an altered surface layer on the target. During this research, the presputtering time used ranged between 15 to 60 minutes and was typically 30 minutes for most cases.

To aid the removal of moisture from the interior of the chamber, the external walls of the chamber were heated for a period of 3-4 hours prior to presputtering.

## 3.3.2 Sputter Deposition

The substrate samples were placed on the anode plate, which was then reintroduced into the deposition chamber from the intervac. Nitrogen gas (99.95% pure) was introduced into the chamber, then argon gas (99.95% pure) was added to obtain the required ratio of the gas mixture in the chamber. The ratio of the gases introduced into the chamber determines the film composition. When the desired ratio of the mixture is attained at the required deposition pressure, the plasma is ignited. The typical chamber pressure during deposition is in the range of  $10^{-3}$  torr. If the plasma fails to ignite at this deposition pressure, the pressure is increased to the  $10^{-2}$  torr range by increasing the argon flow into the deposition chamber. This however should be done only for a short period of time (less than about 10 seconds) until a plasma is obtained. The tuning circuit is then adjusted to obtain the forward power of 220 W and a reflected power of 0-10W. During deposition, the measured substrate temperature ranged from  $100-150^{\circ}C$ . The ability to deposit high quality thin films at low temperatures is crucial in the fabrication of semiconductor and optoelectronic devices. Sputter deposition time depends upon the film thickness required. The deposition parameters recorded were: Background pressure, Deposition gas pressure, partial pressures of the reactant gases, anode-cathode separation, cathode voltage, deposition time and the target power. The experimental data are given at the end of chapter 4.

After deposition was completed, the power to the circuit and the gas mixture supply to the chamber were turned off. The samples were then allowed to cool down for a period of 1-2 hours before removing them for analysis. The samples were then subjected to ellipsometric analysis to determine the refractive index and thickness of the film. The film composition was determined by infrared spectrophotometry. One sample from each experiment was used to fabricate a Metal-Nitride-Semiconductor (M-N-S) structure and the capacitance-voltage (C-V) characteristics studied. Chemical etching of one sample per experiment was also done to determine the the etch rate. Etch rate was also used as an indicator of the composition of the film. Stress analysis was conducted on many films. These techniques are presented and discussed in detail in section 2.4.

# Chapter 4 Experimental results

#### Introduction

Experimental data obtained by reactive sputter deposition of silicon nitride thin films on silicon and indium phosphide substrates are presented in this chapter. The variation of film properties with different deposition parameters are shown. A summary of the results has been given in table 4.1. The IR absorption spectra obtained for a representative set of samples are also presented.

The effects of the following deposition parameters on the refractive index, stress, C-V characteristics and etch rate were studied:

- Nitrogen partial pressure;
- Total gas pressure;
- Deposition time;
- RF power density;
- Cathode voltage.

# 4.1 Refractive Index

#### Introduction

The change in the refractive index of the films was studied as a function of the different deposition parameters. Refractive index of the films was measured using an ellipsometer (Rudolph type 43603-200E).

#### 4.1.1 Effect of $N_2$ Partial Pressure on Refractive Index

The variation in the refractive index of the silicon nitride with the partial pressure of nitrogen is shown in fig. 4.1. It is observed that the refractive index decreases with an increase in nitrogen partial pressure.

#### 4.1.2 Effect of Total Gas Pressure on Refractive Index

As observed in fig. 4.2, at low gas pressures the refractive index is low and increases with an increase in pressure. It exhibits a peak at 5 mTorr and then decreases.

#### 4.1.3 Variation of Etch Rate with Refractive Index

The variation of etch rate with refractive index is shown in fig. 4.3. It is observed that the etch rate drops with an increase in the refractive index of the film. The experimental data obtained are in general agreement with data obtained by other researchers [33].

It is interesting to observe the correlation obtainted by Gregor between film density and power density (fig. 4.4) [4].

### 4.1.4 Effect of Power Density on Refractive Index

It has been seen earlier that an increase in the power density leads to the deposition of denser films fig 4.4. It was also observed that the etch rate drops with an increase in the refractive index of the films. On comparing the data from fig. 4.5 (refractive index vs power density) with those in fig. 4.3 (etch rate vs refractive index) and taking into account that denser films have a higher refractive index, a relationship between the refractive index and the film density is observed.

# 4.2 Deposition and Etch Rates

#### Introduction

Deposition rates depend upon the geometry of the system, particularly upon the diameter of the target and the spacing between the target and substrate.

Etch rate is a very sensitive indicator of both chemical and structural properties. In this research, etch rates were found in buffered HF solution (7 parts 40%  $NH_4F$  aqueous solution and 1 part 49% HF aqueous solution).

#### 4.2.1 Effect of Power Density on Deposition and Etch Rates

A plot of the variation in the deposition rate with power density is shown in fig. 4.6. At fixed  $N_2$  pressure, the deposition rate is observed to increase linearly with power density.

This result is consistent with those obtained by other researchers [5,7]. The variation of etch rate of the films with power density is shown in fig. 4.6. Below a power density of  $1.5 \text{ W/}cm^2$  a sharp rise in etch rate is observed.

### 4.2.2 Effect of N<sub>2</sub> Partial Pressure on Deposition Rate

The deposition rate is observed to increase marginally with an increase in nitrogen partial pressure. A plot of data obtained in six separate experiments is shown in fig. 4.7.

## 4.2.3 Effect of Total Gas Pressure on Deposition Rate

It is observed that the deposition rate was almost constant for varying total gas pressures (fig.4.8). Deposition was done at 5, 6, 6.5 m Torr at constant nitrogen partial pressure and power density. Deposition was also done at 8 mTorr and 1.2626  $W/cm^2$  power density. It is seen that, at reduced power density, there is a drop in the deposition rate.

#### 4.2.4 Effect of Deposition Time on Deposition Rate

The deposition rate was more or less the same with time of deposition. This is a useful feature of sputter deposition. Getting the required film thickness is only a matter of setting the time once the deposition rate for a particular material is known (at a fixed power density and partial pressure). This is shown in fig. 4.9.

# 4.3 Stress

#### Introduction

Stress developed in the deposited film has been studied with variation in film composition and thickness. The stress measurement in the deposited film was done by using a laser reflectance (LR) apparatus specifically setup for the purpose at Drexler Microelectronics and Surface Modification Laboratory, NJIT.

#### 4.3.1 Effect of N<sub>2</sub> Partial Pressure on Stress

An analysis of the data obtained showed that there was a variation in the stress induced in the deposited film with a change in the nitrogen partial pressure (ie. with composition). Samples of varying composition were deposited and their stress calculated using LR. The data obtained are shown in fig. 4.10. The data indicate an increase in stress with an increase in the nitrogen partial pressure.

## 4.3.2 Effect of Thickness on Stress

It is observed that the stress in the deposited silicon nitride film reduced with an increase in film thickness. Films of varying thickness were deposited The variation of stress measured in these films is shown in fig. 4.11.

# 4.4 IR absorption spectra

FTIR absorption spectra were obtained for a representative set of the samples. Figures 4.12-4.16 show the absorption spectra. The characteristic absorption bands are at 1100  $cm^{-1}$  for Si-O, 880  $cm^{-1}$  for Si-H and 840  $cm^{-1}$  for Si-N.







Figure 4.2: Variation of refractive index with total gas pressure.



Figure 4.3: Variation of etch rate with refractive index.



Figure 4.4: Variation of film density with power density.[Gregor]







Figure 4.6: Variation of deposition and etch rates with power density.







Figure 4.8: Variation of deposition rate with total gas pressure.



Figure 4.9: Variation of deposition rate with deposition time.



Figure 4.10: Variation of compressive stress with nitrogen partial pressure.







X: 1 scan, 4.0cm-1

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Figure 4.12: Infrared absorption spectrum.



69/11/20 16:16 X: 1 scan, 4.0cm-1





89/11/20 16:00 X: 1 scan 4.0cm-1

Figure 4.14: Infrared absorption spectrum.

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Figure 4.15: Infrared absorption spectrum.



Figure 4.16: Lorentz-Lorenz correlation curves for reactive plasma deposited silicon nitride films (after Sinha [48]).

EXPT.	DEP. TIME MIN	BASE PRESS X10 <sup>-5</sup>	DEP. PRESS	8 м <u>-</u>	CATHODE VOLTAGE KVOLTS	FORWARD POWER WATTS	REFLECTED POWER WATTS	REF. INDEX	FILM THICK A <sup>O</sup>
13JUN	30	4	2	16.5	2.5	500	8	1.456	
14JUN	30	4	2	15.5	1.8	160	0	1.555	
21JUN	30	4	2	25	1.6	125	8	1.424	
21JUN	20	4	2	10	2.1	300	25	1.410	
22JUN	30	4	3	15	1.5	160	0	1.669	1000
22JUN	30	4	7	15	1.5	125	8	1.602	830
13JUL .	25	4	5 I	15	1.5	160	8	1.458	780
17JUL :	20	4	<b>;</b> (	15	1.5	220	4	1.334	200
26JUL ;	15	4	5.5	16.51	1.5	220	9	1.7401	
J6AUG .	15	2 :	5	15.21	2.1	220	8	1.9201	860
06AUG	15	2	5.5	15.1:	2.0	220	12.5	1.8941	
LEAUG :	15	2 !	5	15	1.6	220	0	1.320	
13AUG '	15	2	-5 ·	14.6	2.0	220	6	1.3771	
13AUG :	15	2	ŝ	14.31	1.7	220	11	1.7801	
LANUG .	15	2	5	15	2.0	220	12.5	1.8401	850
15AUG	15	0.8	6.8 I	15.2:	1.9	220	12.5	1.7901	
L6AUG	15	1	5.5	15.1;	1.9	220	13	1.3201	930
TAUG	15	2	5	15	2.0	220	8	1.3471	
llaug	15	0.8	3	15.2:	1.8	220	3	1.3601	
CAUG	15	2 ,	5	16.01	1.9	220	3	1.840)	930
CAUG	15	2 :	473	15.2:	2.3 !	400	10	1.852	1200
DAUG -	10	2	5	15.21	2.4	400	8	1.9201	
4AUG	15	2 *	10	15.61	1.9	220	5	1.850	770
5AUG	13	0.8	5	15.2;	2.0	220	õ	1.9161	770
SSEP	15	.52	5	10.01	2.0	220	10	1.4341	
SSEP 1	15	.8	5	10.01	1.5	220	10	1.6091	
20CT !	15	.2	-5	10.01	2.1	220	10	;	
40CT '	15	.2	3	10.01	2.0	220	ŝ	2.2501	70 <b>0</b>
50CT :	15	.2	5	12.01	2.0	220	õ	2.06	300
4MAR	30	.45	ŝ	12.01	2.1	220	7	1.7041	1500
2APR	15	.4 :	3	12.01	1.9	220	7	1.702	730
OAPR I	45	.35	3	12.01	2.0	350	ő	2.401/	2100
4APR I	45	.35	5	8.01	1.9	150	7	2.050	1900

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# Chapter 5 Discussion of Results

#### Introduction

Silicon nitride films were deposited in an  $Ar-N_2$  plasma by reactive rf sputtering using a Si target of 99.99% purity. It was seen in chapter 4 that precise control of the deposition parameters was critical for obtaining films of desired composition and characteristics. This chapter presents a discussion of the experimental data obtained.

# 5.1 Refractive Index

The refractive indices of stoichiometric silicon nitride  $(Si_3N_4)$  and bulk silicon are 2.01 and 4.05 respectively at 5461 A. Silicon nitride films that have a refractive index higher than 2.01 are expected to have excess silicon. A refractive index of less than 2.01 can be caused either by nitrogen in excess of the stoichiometric amount or by oxygen impurities incorporated into the film.

# 5.1.1 Effect of Nitrogen Partial Pressure on Refractive Index

The refractive index of silicon nitride films deposited during this research was found to be inversely proportional to the  $N_2$  partial pressure in the Ar- $N_2$  mixture in the deposition chamber (fig.4.1). This can be attributed to the change in nitrogen content at the target surface, ie. the formation of an altered layer.

An increase in the nitrogen partial pressure results in an increase in the number of nitrogen ions bombarding the silicon target. This leads to the formation of a nitrogen rich altered layer which results in the deposition of a film with higher nitrogen content thereby lowering the refractive index. In addition, since the total gas pressure is kept constant, increasing the partial pressure of nitrogen reduces the number of argon ions impinging at the target surface. Argon has a higher sputtering yield than nitrogen hence a decrease in the number of argon ions could also lead to a decrease in the number of silicon atoms sputtered from the target leading to lower refractive indices.

Hu and Gregor [4] also obtained similar results on measuring the refractive indices while depositing silicon nitride films by reactive rf sputtering in nitrogen. They observed lower refractive indices (indicating excess nitrogen incorporation) at higher nitrogen concentrations.

# 5.1.2 Variation of Refractive Index with Sputtering Gas Pressure

It is observed from fig.4.2 that the refractive index initially increases with an increase in sputtering gas pressure (at constant  $\operatorname{Ar}-N_2$  gas ratio in the deposition chamber). On increasing the gas pressure beyond a "Critical pressure" a drop in refractive index is observed. This occurs due to the variation of refractive index with composition. There are two possible explanations for pressure affecting composition, that have been considered. The first is that pressure changes cause the impact rate of nitrogen and argon bombarding ions to change. When one considers the sputtering yields for nitrogen and silicon atoms in a silicon nitride matrix (which are different for argon and nitrogen bombardment) one can see that the rate at which nitrogen and silicon atoms are sputtered off the target will be a sensitive function of pressure. The second possible explanation is the scattering of the sputtered species as they pass from the target to the substrate. This could affect the composition of the depositing film.

The Lorentz-Lorenz relation [42]<sup>1</sup> states that the film density and refractive index are directly proportional. At low pressures (2 mTorr), the energy with which the sputtered atoms from the target arrive at the substrate might be high enough to cause damage to the depositing film. The film thus formed would be less dense. Increasing the gas pressure would reduce the energies of the sputtered atoms (since the ions impinging at the target would now possess lower energy due an increase in the number of collisions) and thereby change the sticking coefficients of the arriving species. Denser films would thus be obtained (resulting in a higher refractive index). On increasing the pressure beyond the "critical pressure" (5 mTorr in this research), a decrease in refractive index is observed. The refractive index is lowered because of further reduction in the energy (due to increase in the number of collisions by the ions) with which the sputtered atoms reach the substrate, leading to the formation of porous (less dense) films.

The mean free paths (m.f.p) <sup>2</sup> for argon and nitrogen at varying deposition pressures was calculated. At 2 mTorr deposition pressure (for a fixed ratio of the reactant gases, say 12.5%  $N_2$  and 87.5% Ar) the m.f.p for argon and nitrogen are 5.68 cm and 4.748 cm respectively. which reduce to 2.272 cm and 1.899 cm respectively on increasing the pressure to 5 mTorr. Since the target-substrate spacing

<sup>&</sup>lt;sup>1</sup>Dielectric constant  $\epsilon = \frac{1 + (8\pi/3)N\alpha}{1 - (4\pi/3)N\alpha}$ , where N is the number of molecules per unit volume and  $\alpha$  represents the mean polarizibility.

<sup>&</sup>lt;sup>2</sup>Mean free path  $\lambda$  (in m) =  $\frac{kT}{\sqrt{2\pi Pd^2}}$ , P - pressure in Pascal; d - molecular diameter in meters ( $d_{Ar} = 2.88 \text{ A}$ ;  $d_{Nitrogen} = 3.17 \text{ A}$ ).

is approximately 9 cm, the reduction in mean free path (with increasing gas pressure) indicates a reduction in the energy (of particles causing sputtering) due to an increase in the number of collisions. Thus it is observed that energetic particle bombardment can lead to film densification in at least two ways: (i) enhancement of surface mobility of surface atoms and (ii) reemission of weakly bound atoms or clusters which are in unfavorable positions for achieving optimum density. Both these effects will be attenuated due to scattering collisions as the pressure is increased.

The film density, composition and refractive index of plasma silicon nitride have been correlated by Sinha [48] using Lorentz-Lorenz relationship. This is shown in fig. 4.16.

The number of ions bombarding the cathode increases on increasing the power density (this would cause an increased number of secondary electrons to be emitted from the cathode). At low nitrogen partial pressures, the film deposited would tend to be silicon rich resulting in a higher refractive index. At higher nitrogen partial pressures the altered layer at the target would have a higher nitrogen content hence the depositing film would have a lower refractive index. But it is observed from the experimental data that the refractive index increases. This could probably be due to resputtering of nitrogen from the depositing film preferentially, by energetic particles, which results in an increase in the film refractive index. Other workers have also obtained similar results. Jones *et al* [43] observed that insulating films of  $Si0_2$  deposited by rf sputtering could develop a substantial floating potential at the surface (approximately 100 V). Ions accelerated out of the plasma could then cause considerable resputtering.

An additional effect could be substrate heating due to the substantial number of secondary electrons generated at the cathode. This could lead to the formation of denser films (thereby increasing the refractive index) due to enhanced mobility of the surface atoms.

# 5.2 Deposition and Etch Rates

The variation of deposition and etch rates with power density is shown in fig.4.6. It is seen that the deposition rate is proportional to the target power density, whereas the etch rate decreases with increasing power density.

The glow discharge adjusts to an increase in the target power density by increasing the current density, ie. the number of particles bombarding the target increases. Therefore, increasing power density results in higher deposition rates.

Etch rate is a very sensitive indicator of the chemical and structural properties of an amorphous solid. The etch rate of amorphous silicon nitride varies over a wide range. It increases drastically at lower power densities where the films are appreciably off stoichiometry and there are many broken bonds available for chemical reactions. Films deposited by sputtering frequently have lower etch rates than films deposited by other techniques. This is mostly due to the presence of traces of water vapor in the deposition chamber which use up the Si bonds leading to the formation of Si-H. The presence of traces of water vapor in the chamber can be observed from the IR spectroscopic analysis of the samples shown in figures 4.12-4.15. Along with the change in stoichiometry the lowering of film density could also be due to entrapped gas species. This was suggested by Cordes [49] where he discussed the effect of neutral  $N_2$  molecules driven into the films. Trapping of energetic argon in sputtered Ni films has been observed by Winters and Kay [50].

## 5.3 Stress

#### Introduction

In this section the variation of stress with film refractive index and thickness has been discussed. The results obtained by other researchers have also been presented.

#### 5.3.1 Effect of Deposition Parameters on Stress

The variation of stress in the film with change in refractive index and thickness are shown in figures 4.10 and 4.11 respectively.

Experimental data obtained indicate that stress in the film increased with an increase in nitrogen partial pressure. Silicon nitride films, with silicon in excess of the stoichiometric value, exhibited reduced stress. This reduction in stress in silicon-rich silicon nitride films is most likely due to a reduction in lattice mismatch between the substrate and the deposited film.

Stress developed in the deposited film also depends upon the deposition temperature. Claassen *et al* [40] studied the influence of deposition temperature on plasma deposited silicon nitride and found that the stress developed in films deposited at low temperatures ( $< 550^{\circ}$ C) was compressive. The stress was observed to be tensile in films deposited at higher temperatures. The temperature during sputter deposition was recorded to be close to 140°C ( $^{+}_{-}10^{\circ}$ ). Due to the low deposition temperature, the stress developed in the NJIT films are compressive.

During this research it was observed that increasing film thickness reduced the stress in the deposited film. Blaauw *et al* [45, 46] examined plasma deposited  $Si_3N_4$  films and found that the stress in  $Si_3N_4$  decreased with increasing the thickness (as in this research). Roedel *et al* [34] employed sputtered dielectrics ( $Si_3N_4$ ,  $Si0_2$  and  $Al_20_3$  as masks for localized zinc diffusion into GaAs. Zinc diffusion was carried out for 60 minutes at 600°C. They observed diminishing stress with increasing thickness for  $Si_3N_4$  films, which implies that stress relief occurs during sputter deposition. This stress relief possibly occurs due to the exposure of the film to energetic particle bombardment for an increased length of time (since increased thicknesses require increased deposition time) causing nitrogen from the depositing film to get reemitted. This increases the silicon content of the film resulting in reduced lattice mismatch between the substrate and the deposited film. At this point, it is interesting to note that in the case of  $Si0_2$  films the stress increased with increasing thickness contrary to the behaviour of silicon nitride films. The stress variation of both  $Si_3N_4$  and  $Si0_2$  films is shown in fig.5.1.

#### 5.3.2 Variation of Lateral Diffusion with Stress

The diffusion of impurities into semiconductor materials is an important step in device fabrication. Most diffusions are performed through masks for selected area junction formation. In many instances, the diffusion mask interacts with the diffusing species so that enhanced diffusion along the substrate-mask interface takes place. This excess lateral diffusion can have deleterious effects on device performance and characteristics. In the first place, design rules are violated and accurate control of lateral device dimensions becomes extremely difficult. In addition, any parameter that depends on area, such as device capacitance, will be adversely affected. A typical example of this phenomenon is shown in fig. 5.3 for zinc diffusion in GaAs through a silicon nitride mask [34].

In general, diffusion of impurity atoms into a substrate can be understood from defect-impurity interactions as explained by the atomistic theory. This involves interaction between vacancies, interstitials and impurity atoms for diffusion to occur. Studies [51, 52] for Si- $Si0_2$  systems have shown that Si interstitials are generated at the  $Si-Si0_2$  interface during oxidation. Assuming that vacancy concentration remained constant during oxidation, the enhancement of boron and phosphorous diffusivities could be explained by excess interstitials diffusing away from the oxide-silicon interface.

The search for a correlation between the extent of lateral diffusion and mechanical stress in sputter deposited silicon nitride films was conducted by Roedel et al [34]. Their data are shown in fig. 5.2. which is a plot of the ratio of lateral diffusion to junction depth, r, for silicon nitride films of varying thickness. This shows a clear dependence on the extent of lateral diffusion upon the thickness of the diffusion mask, a dependence which is reminiscent of that of the stress on the film thickness. It was also seen that two films of different composition but of equal stress value produced lateral diffusions of the same size. This further indicates a strong correlation between the stress content of the masking film and the extent of lateral diffusion. Baliga and Gandhi [47], reached a similar conclusion for  $SiO_2$ diffusion masks. They obtained a strong connection between phosphorous doped silicon dioxide diffusion masks and the lateral diffusion and minimized the extent of lateral diffusion by controlling the phosphorous content of the film.

During this research an attempt is being made to study the effect of interface trapped densities on stress. A study is in progress at NJIT in conjunction with Epitaxx, Inc., Princeton. The results of this study will be published at a later date.



Figure 5.1: Variation of Stress with Thickness. Roedel [34]

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Figure 5.2: Ratio of Lateral Diffusion to Junction Depth 'r' for  $Si_3N_4$  films of varying thickness. Roedel [34]



Figure 5.3: Zinc Diffusion in GaAs with  $Si_3N_4$  Mask. Roedel [34]

# Chapter 6

# Conclusions and Suggestions for Future Work

# 6.1 Conclusions

Films with a refractive index of 2.01, corresponding to stoichiometric silicon nitride, were obtained with very specific parameters by reactive argon/nitrogen diode sputtering. The deposition parameters for obtaining stoichiometric silicon nitride films were : Base vacuum pressure,  $2 \times 10^{-6}$  torr; cathode voltage, 1.8 - 2.0 kV; 12.5%  $N_2$ (in the  $N_2$ -Ar mixture); sputtering gas pressure, 5 mTorr; substrate temperature,  $140^{\circ}$ C  $^+_{-1}10^{\circ}$ C; target power 220 W. The etch rate of these films (29-31 A/min) compare well with published results of 35 A/min obtained by rf sputtering [44]. Silicon nitride films deposited by sputtering frequently have lower etch rates than the  $Si_3N_4$ deposited by other techniques if they contain gaseous impurities, eg. traces of water vapor which use up broken Si bonds (forming Si-H bonds) [Milek;33]. Films of  $Si_3N_4$  deposited by LPCVD at low temperature have higher etch rates (150 A/min) than high temperature CVD  $Si_3N_4$  (50-60 A/min). In spite of the higher etch rates the advantage of the films deposited by LPCVD/CVD is that better control over film composition can be exercised as compared to sputter deposited films.

The film composition as determined by IR spectroscopy exhibits a strong

absorption band centered at  $840cm^{-1}$  (Si-N) and weak absorption bands centered at  $880cm^{-1}$  and  $1100 \text{ cm}^{-1}$  for Si-H and Si-0 respectively. IR spectroscopic analysis of films deposited by CVD, plasma deposition techniques also show a prominent absorption for Si-N bonds.

The minimum stress obtained during this research for silicon nitride films deposited on silicon substrates was  $0.57 \ge 10^9 N/m^2$  for a film with a refractive index of 2.05 and 1900 A thickness. Assuming that stress decreases with thickness, the stress in this film at 730 A thickness would be about 1.6  $\ge 10^9 N/m^2$ . The measured stress for a film with refractive index 2.24 was  $0.98 \ge 10^9 N/m^2$  for a 730 A thick film. Thus one can notice that the stress decreases with increasing silicon content. These values compare well with the stress values (2.08  $\ge 10^8 N/m^2$ ) in plasma deposited annealed stoichiometric silicon nitride films extrapolated to the same thickness. Stress is thus seen to be a function of the silicon content of the deposited film. It is suggested by the writer that the decrease in stress with the silicon content was caused by a reduction in lattice mismatch between the substrate and the deposited film.

Stress has also been observed to vary with film thickness. Unlike  $Si0_2$ , the stress reduces with greater thickness for a nitride film. This reduction in thickness is possibly due to reemission of nitrogen from the depositing film (caused by the energetic particle bombardment) resulting in a silicon rich film. Roedel *et al* [34] also observed reduction in stress with increasing film thickness for sputter deposited silicon nitride films. Therefore, by suitably controlling the film composition and thickness, the film stress could be "tuned" to the required values.

It is expected that this research will be useful in solving the problem of lateral diffusion of dopants in silicon nitride on silicon and possibly silicon nitride on GaAs and other semiconductors. The stress results are promising because comparable stress values  $(2 \ge 10^9 \text{N}/m^2)$  of silicon nitride on silicon by LPCVD, PECVD have been obtained, but at much higher deposition temperatures  $(750 - 850^{\circ}\text{C} \& 300 - 450^{\circ}\text{C} \text{ respectively})$ , which are unsuitable for Al/Au metallization.

# 6.2 Suggestions for Future Work

The author would like to make the following suggestions for future work:

- 1. The effect of substrate bias on the film properties should be studied. Bias can possibly affect the energy of the ions hitting the substrate and influence the stoichiometry and purity of the growing films. Also stress developed in the films can be affected during growth.
- 2. The accuracy of the laser reflectance apparatus can be improved by incorporating a position sensitive detector. This would remove any inaccuracies resulting from the present technique. It is also evident that the accuracy of the present system could be increased by increasing the sample-screen distance (presently 5.08 meters).
- 3. The LR technique currently used to determine the substrate curvature is tedious. It would be possible to expedite the time required for measurement by moving the beam rather than the sample. The beam movement technique has the advantage of *in-situ* measurement. Also the beam intensity data could be inputted to a computer for faster stress calculations.
- 4. Sputtering should be tried in the triode mode. Sputtering can then be conducted at lower voltages which might reduce the deleterious effects due to high energy particle bombardment of the substrate by the sputtered species and secondary electrons. Since triode sputtering can be done at lower pressures,
there would also be a lower concentration of entrapped argon and contaminants in the sputtering gas source and films with better purity could be obtained.

5. Incorporating a liquid nitrogen trap in the vacuum chamber to reduce any traces of water vapor which could increase the conductivity of the insulating film.

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