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Hydrogen redistribution in annealed silicon nitride thin films deposited by PECVD

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HYDROGEN REDISTRIBUTION IN ANNEALED
SILICON NITRIDE THIN FILMS DEPOSITED BY PECVD

A Thesis

Presented to

The Faculty of the Department of Materials Engineering
San Jose State University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by

Ferenc A. Nagy

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ABSTRACT

HYDROGEN REDISTRIBUTION IN ANNEALED SILICON NITRIDE THIN FILMS DEPOSITED BY PECVD

by Ferenc A. Nagy

Amorphous silicon nitride films were deposited under systematically varied process conditions in a PECVD reactor. All of the films were found to contain nominally 20 atomic percent total hydrogen, but the Si-H/N-H bond concentration ratio varied over a range from 0.4 to 8. Thermal stability of the films was evaluated by ramp annealing from room temperature to 500°C. Films with the lowest concentrations of Si-H were found to undergo the least stress change upon annealing. None of the films exhibited any experimentally significant change in the as-deposited bond absorption peaks after annealing. However, all of the films developed an additional peak at $\sim 630\text{ cm}^{-1}$. Two distinct hydrogen outgassing peaks were observed, but the absolute amount of desorbed hydrogen was very small. The presence of "loosely bound" hydrogen is suggested to explain these phenomena. When vacuum annealed to 1000°C, each of the films exhibited either blistering, crystallization, or no apparent change.

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1. Introduction

1.1 Application of Plasma-Deposited SiN Films

Silicon nitride (SiN) deposited by Plasma Enhanced Chemical Vapor Deposition (PECVD) is a dielectric material of substantial importance in the manufacture of integrated circuits (ICs). SiN is a hard, dense film which is scratch resistant and impervious to moisture and alkali metal ions which are abundant environmental contaminants. Silicon nitride is most commonly used as the final passivation layer to encapsulate the finished devices. The first widely circulated report of plasma deposited SiN as an encapsulant material for electronic devices on silicon was published in 1965 [1]. Commercial equipment for PECVD of silicon nitride was introduced in 1976 [2,3] and since that time SiN has been commonly used for IC passivation.

In silicon-based IC technology SiN has also been used in many applications: as a gate dielectric in non-volatile memories (so-called MNOS devices), as an interlayer insulator, as an etch-stop layer, and as a barrier layer to prevent oxidation of silicon and to prevent diffusion of dopants from silicate flow glasses. In all of these applications the distribution of hydrogen, a process byproduct, within the silicon nitride films is important. The bonding states of hydrogen play a major role in the

thermal stability of the films and the reliability of the finished product. Control of the hydrogen content of SiN through process optimization is therefore desirable to ensure the production of consistently reliable devices.

1.2 Project Hypothesis and Objectives

The hypothesis of this project was that thermally driven stress changes in PECVD silicon nitride films are a function of both the *total* quantity of hydrogen incorporated and the *partitioning* of hydrogen among variously bound species.

With the hypothesis thereby established, there were two goals of this research project:

- (1) To study the effect of varying deposition parameters on the incorporation of hydrogen and its bonding according to specie.
- (2) To formulate a descriptive model that describes how the physical characteristics of the film change during thermal cycling as a function of hydrogen distribution and total hydrogen content.

It is important to know the fraction of hydrogen present in each possible form, both before and after temperature cycling, because the different species of hydrogen existing in the film will begin to out-diffuse at different

temperatures and thereby determine the film's ultimate thermal stability. The analysis of experimental data generated from this project is expected to provide insight into the parameters necessary to control hydrogen content in SiN films and the mechanism of hydrogen redistribution in silicon nitride films due to annealing.

2. Background

2.1 Physical Description of SiN Films

PECVD silicon nitride is an amorphous solid material. It can be considered a random network of silicon and nitrogen atoms. However, the material does have short range order. The atoms are tetrahedrally oriented with covalent bonding and the first few nearest neighbors (up to the third or fourth) [4] generally obey coordination rules. The network structure of the material maintains bond angles and bond lengths between atoms in a narrow distribution around the ideal values of the stoichiometric crystalline compound Si_3N_4 .

A material very closely related to PECVD silicon nitride is plasma-deposited hydrogenated amorphous silicon. It too exhibits tetrahedral bonding and shares many of the defect states of silicon nitride. Amorphous silicon has been extensively studied for various electronics applications. The vast literature base on the subject of amorphous silicon has provided a useful source of relevant information.

The formation of silicon nitride can be described in terms of chains of silicon atoms being cross-linked by nitrogen atoms, which has led to it being called an inorganic polymer [5,6]. For the material to exist at all,

at least metastably, the network structure of the atoms must contain defects to relieve excessive strain. Creation of dangling bonds, microvoids, and incorporation of hydrogen are examples of such defects.

The structure of silicon nitride is a strong function of deposition conditions. In the case of PECVD, the process environment of a glow discharge with its many ionized and neutral species, combined with low substrate temperature (300 - 400°C), results in an amorphous condensed film with an abundance of point defects. This feature is common to other plasma-deposited materials, namely amorphous semiconductors and dielectrics. The nature of the defects, in terms of their charge states and stability, has much to do with the incorporation and movement of hydrogen and has been the focus of ongoing research [7,8,9].

The purely thermally activated low pressure CVD (LPCVD) processes done at high temperature (700 - 900°C), also produce amorphous films but yield a silicon nitride with the stoichiometric composition of Si_3N_4 . Neither the PECVD or LPCVD technique used in the semiconductor industry is kinetically capable of producing thermodynamically stable crystalline films of silicon nitride due to the relatively complex structural arrangement required. Temperatures of

over 1300°C are required to obtain crystalline layers of Si_3N_4 by CVD [10]. Two crystalline phases are known: hexagonal α -phase and rhombohedral β -phase [10,11,12,13].

PECVD films of silicon nitride are generally "silicon-rich" ($\text{Si}/\text{N} \approx 1$) compared to the stoichiometric LPCVD films ($\text{Si}/\text{N} = 0.75$). Hence, the notation SiN or $\text{SiN}_x\text{:H}$ (indicating a significant atomic fraction of H), is used to refer to these films, as opposed to the stoichiometric formula Si_3N_4 . This means that each silicon atom in the PECVD film is coordinated, on average, by less than four nitrogen atoms. In this case silicon atoms can instead be coordinated by either other silicon atoms or by hydrogen atoms. The excess silicon content leads to silicon dangling bonds which are in turn compensated by the incorporation of large amounts of hydrogen. More unusual defect states are said to exist such as an over-coordination of the silicon atom, which can also capture or hold hydrogen [4]. However, the relative number of these sites is far fewer (by several orders of magnitude) than that of the simpler dangling bonds.

Threefold coordination of nitrogen is readily satisfied by silicon atoms due to the Si/N ratio typically being greater than unity. Therefore nitrogen-rich (silicon-poor)

silicon nitride is less commonly produced than the silicon-rich variety, although it can be produced by the method of PECVD under suitable process conditions [7,14].

2.2 Methods of Thin Film Synthesis

The method of PECVD allows deposition of SiN films at low enough temperatures ($\leq 400^{\circ}\text{C}$) so that the underlying layers (especially aluminum-based metallizations) do not undergo any structural or compositional transformations. Plasma deposition, in the appropriate biasing configuration, also provides the option of tuning the intrinsic stress of a film by controlling ion bombardment during deposition.

The chemistry involved in producing silicon nitride films by vapor deposition processes (with or without plasma) is expected to have some influence on the incorporation of hydrogen into the films. A number of different precursor systems have been characterized, at least superficially if not completely, by the amount of hydrogen they introduce into the resulting film. These include $\text{SiH}_4\text{-NH}_3$ and $\text{SiH}_2\text{Cl}_2\text{-NH}_3$ for LPCVD [15], and $\text{SiH}_4\text{-N}_2$, $\text{SiH}_4\text{-NH}_3\text{-N}_2$, $\text{SiH}_4\text{-NH}_3\text{-H}_2$, $\text{SiH}_4\text{-NH}_3\text{-Ar}$, $\text{SiH}_4\text{-N}_2\text{-He}$, $\text{SiF}_4\text{-N}_2\text{-H}_2$ for PECVD [16,17,18]. Reactive sputtering has also been proposed and evaluated as a method of deposition in an effort to eliminate or minimize

the incorporation of hydrogen into silicon nitride thin films (to reduce its perceived negative effects) [19].

The non-equilibrium nature of the synthesis of silicon nitride by CVD methods from hydrogen-bearing gas source reactants implies the inevitable incorporation of hydrogen into the end product in some form. Most papers on the subject of silicon nitride deposition allude to this fact, e.g., [16,20].

2.3 Hydrogen in SiN Films

Hydrogen is the most important impurity component of silicon nitride. Hydrogen is incorporated as a by-product of the reactants, typically silane (SiH_4) and ammonia (NH_3). For PECVD films of SiN the hydrogen content can range from 10 to 30 atomic percent [1,2]. Hydrogen can exist various ways in the film, both in bound forms (as Si-H and N-H bonds) and the unbound molecular form (i.e., not bound to the matrix) as H_2 . Hydrogen is believed to have a large influence on many of the properties of SiN thin films including structure, density, intrinsic stress, dielectric constant, extinction coefficient, electrical conductivity, and thermal stability.

Stress and refractive index, two easily measured properties of SiN films, are usually good indicators of the film density and composition. Denser films of a nominally fixed composition generally have both higher compressive stress and higher refractive index. The more silicon-rich films have higher refractive indices; for a fixed value of stress, variation of the Si/N ratio corresponds to different refractive indices [16,20,21,22]. The correlation of the Si-N ratios of some silicon nitride films to their refractive indices provides a convenient rough measurement of their composition. The stoichiometry of silicon nitride films is most commonly analyzed by Rutherford Backscattering Spectrometry (RBS) [5,15,23].

Hydrogen manifests itself in silicon nitride by altering the bonding and short-range order in the film. As mentioned above, hydrogen can be bound to silicon or nitrogen, or to itself in molecular form. Generally there should be some distribution among all of these different forms. It is interesting to note that most published papers make the assumption, either explicitly or implicitly, that all of the hydrogen in the film is distributed only between N-H and Si-H bonds, e.g., [5,18,23,24]. Seldom is there mention of unbound or molecular hydrogen [25,26]. This appears to be a

major weakness of most of the studies that have been published to date.

To lend support to the existence of unbound hydrogen in silicon nitride films, porosity of the films, which could contain "free" hydrogen, has been acknowledged [27,28]. Pertinent results from the literature of monocrystalline and amorphous silicon, based both on theoretical calculations and on data from Nuclear Magnetic Resonance (NMR) studies, indicate that molecules or clusters of hydrogen are thermodynamically stable entities and their existence is expected to be favored over isolated (so-called "interstitial") atoms of hydrogen [29,30].

Heating of silicon nitride films to temperatures slightly above the deposition temperature (typically $> 400^{\circ}\text{C}$) has been shown to alter the stress of the film while the N-H and Si-H peaks in the FTIR spectra remain largely unchanged (except for a slight shift in peak location corresponding to the stress change) [26]. The temperature at which this phenomenon occurs ($< 500^{\circ}\text{C}$) is much too low for long range diffusion of the film's constituent atoms to proceed readily by vacancy exchange, although some local rearrangement might occur. However, hydrogen can move very easily due to its small size, low mass, and interstitial transport path. It

is possible that the measured change in stress can be accounted for by the evolution of molecular hydrogen from the film causing densification of the film at the atomic level accompanied by an increase in tensile strain [31].

Partial attempts to determine the partitioning of hydrogen among all of its different forms in SiN films have been carried out. For example, Budhani et al. [26], studied the IR absorption and stress changes in silicon-rich and nitrogen-rich SiN films on silicon substrates ramp-annealed to various temperatures between 600 and 800°C. They found no measurable changes in the absorption peak areas up to 600°C while there were significant changes in stress in the tensile direction. They suggested that molecular hydrogen evolved from the film causing densification and shrinkage. Pearce et al. [23], on the other hand, observed an increase in Si-H bond peak area along with a decrease in N-H bond peak area when they isochronally annealed their silicon nitride films at various temperatures between 330 and 540°C. They proposed a kinetic mechanism whereby hydrogen from N-H₂ structures dissociates and moves to passivate a dangling bond of silicon, creating an Si-H bond.

2.4 Effects of Hydrogen on ICs

The evolution of hydrogen from SiN films during thermal cycles (up to $\sim 450^{\circ}\text{C}$) encountered in the final stages of IC processing has been widely reported to have deleterious effects on device performance, e.g., [18,23,32,33]. Diffusion of hydrogen into the active regions of the device has been tied to electrical effects, including threshold voltage shifts in field effect transistors, hot carrier degradation, and change in resistance of polysilicon load resistors [32]. The negative aspects of hydrogen on the long term integrity of back-end metal interconnects in ICs have also been elucidated. The mechanical effects include blister formation at interfaces [33] and failure due to void growth and crack formation [34]. These are relevant because of the proximity of the hydrogen-laden SiN passivation film to metallization structures.

Reliability issues associated with thin films of silicon nitride continue to be investigated and re-examined. Fracture of aluminum lines has been attributed by one group of researchers [35] to hydrogen embrittlement, challenging the widely held belief that purely mechanical stresses due to the silicon nitride are to blame for the failures [33]. Kikkawa and Endo [34] sought to characterize the effect of thermally evolved hydrogen from silicon nitride films on the

generation of defects in underlying aluminum films. They attempted to relate the final stress state of an SiN passivation film after 800°C heat treatment to elastic/plastic deformation in the encapsulated aluminum metallization.

Hydrogen might also help to maintain a compressive stress component in the PECVD film which would otherwise be tensile due to a less dense structure [21,36]. Very low hydrogen content films might then be more prone to cracking like the LPCVD films which inherently have low levels of hydrogen [37] and are always in a tensile state of stress.

The same mechanism of dangling bond passivation that is detrimental to load resistors can be used beneficially to improve the yield of microfabricated, polycrystalline silicon devices by taking advantage of a layer of PECVD silicon nitride as a hydrogen source [38]. Likewise, hydrogen passivation of defects within silicon nitride films themselves appears to be responsible for improving the dielectric properties of the films by reducing their electrical conductance [17].

2.5 Measurement of Hydrogen Content

Measurement of hydrogen content in silicon nitride films is difficult due to hydrogen's small atomic size and low mass. A number of techniques are used, each with its own inherent advantages and limitations.

Semi-quantitative information can be obtained quickly and easily by Fourier Transform Infrared spectroscopy (FTIR). It is the most frequently cited analysis technique. Although FTIR is the most commonly used method, it is also probably the most abused method of assessing hydrogen content of silicon nitride thin films. Reasons for this are discussed later in this report.

Accurate quantitative measurement of the hydrogen contained in SiN films requires sophisticated techniques such as Nuclear Reaction Analysis (NRA), Prompt Gamma Activation Analysis (PGAA), and Hydrogen Forward Scattering (HFS). Nuclear Magnetic Resonance (NMR) and FTIR provide information primarily about the state of hydrogen. However, measurement of the absolute hydrogen content of SiN films is especially problematic. In addition to NRA and HFS, Thermal Desorption Analysis (TDA), also known as Thermal Desorption Spectroscopy (TDS), is a physical method which can be used for this purpose. The specific techniques used for this

study (FTIR, NRA, HFS, and TDA) are described in more detail in the Principles and Experimental sections which follow.

3. Principles

3.1 Statistical Design of Experiments

The first goal of the project was to understand the effect of varying the deposition process parameters on the incorporation of hydrogen and its distribution according to specie. There are several process parameters which can be controlled, including gas flow, gas ratio, process pressure, radio frequency (RF) power, RF power ratio, RF frequency, and temperature. Based both on experience and historical data from a literature survey, a subset of the readily controllable process parameters believed most important was chosen to be the set of experimental variables called "factors." The four factors chosen for evaluation in the experiment were silane flow, pressure, total RF power, and fraction of low frequency (LF) RF power. Process temperature was fixed by choice at a standard value of 400°C. Ammonia and nitrogen gas flows were also fixed.

In order to determine the range of the experimental variables which allowed stable process conditions a

preliminary screening test was done. The screening was done by varying each of the chosen factors to the extremes of its range while holding the others fixed. At this stage only the process itself was observed for plasma stability and no films were analyzed. This lead to the settings used for the high and low levels of each factor in the final experimental design, which are symmetrical about the standard process condition for the reactor.

Statistical Design of Experiments (DOE) techniques provide a framework for systematically and economically arranging experimental runs. The overall concept is to maximize the information obtained while minimizing the experimental overhead. Collection of sufficient data allows the development of a model by statistical analysis which may later be used as the basis for process optimization.

The experiment for this study was run as a so-called two level, full factorial design. This design is the simplest of DOEs and yields data that are relatively easily analyzed. The two level full factorial entails running all

combinations of all the factors at both their low and high settings (hence the term "two level"); a centerpoint condition (the "standard" process for the reactor) was added for purposes of validation and comparison. Each run condition (combination of factors) was replicated once, i.e., run twice, to allow a mean value to be obtained for some of the film properties (refractive index, thickness, as-deposited stress). Thus a total of 34 runs were made (2×2^4 [factorial] + 2 [centerpoint] = 34). The matrix of run conditions is listed in Table 1 in standard run order, the customary layout for factorial designs. However, the actual runs were carried out in random order to minimize systematic error, with the exception that the replicates were run in pairs for practicality owing to the reactor design.

The effects of each of the factors were determined from the rate of change in the responses (properties of interest) as the given factor varied from the low level to the high level. If a response increased as the factor increased the effect is considered "positive" in the algebraic sense. If

Table 1: Design matrix of deposition conditions used for the experiment

Standard Run Order	A: Silane Flow (sccm)	B: Pressure (Torr)	C: Total RF Power (Watts)	D: LF RF Power (%)	Actual HF RF Power (Watts)	Actual LF RF Power (Watts)
0	500	2.60	1000	50	500	500
1	300	2.00	1200	80	240	960
2	300	2.00	1200	20	960	240
3	300	5.00	800	20	640	160
4	700	5.00	1200	80	240	960
5	700	5.00	800	80	160	640
6	700	2.00	800	20	640	160
7	700	2.00	1200	20	960	240
8	700	2.00	800	80	160	640
9	300	2.00	800	80	160	640
10	700	5.00	1200	20	960	240
11	300	5.00	1200	20	960	240
12	300	5.00	1200	80	240	960
13	300	5.00	800	80	160	640
14	300	2.00	800	20	640	160
15	700	2.00	1200	80	240	960
16	700	5.00	800	20	640	160

a response decreased as the factor increased the effect is considered algebraically "negative." The main effects (due to the factors only) and the interactions (effects due to combinations of the factors) can be normalized and plotted on a normal probability percentage graph to obtain a measure of their relative significances to each other and to the error, or noise, in the experiment [38]. In addition, statistical tests of the results are used to validate assumptions about the error distribution (constant variance, normally distributed error, independence of errors, and additive treatment effects). The method used is known as Analysis of Variance (ANOVA) [39]. Comparison of the F-statistic with the critical F-value determined from ANOVA reveals whether an effect can be considered statistically significant (at a chosen confidence level; 95% for this work). Statistical calculations were cross-checked with graphical methods to verify consistency.

3.2 Measurement of Hydrogen Content

The most accurate techniques for measurement of hydrogen content involve the use of ion beams and nuclear methods. By their nature such methods are complicated and expensive to employ. A technique known as Nuclear Reaction Analysis (NRA) has been in use since its introduction in 1978 [40]. This method utilizes a resonant nuclear reaction of hydrogen with nitrogen. High energy beams of nitrogen (~6MeV) impinge on the specimen and gamma rays from the nuclear reaction are detected. The resonant character of the reaction gives a depth profile of hydrogen in a layer. The concentration versus depth can be integrated to obtain a value of total hydrogen content. The total hydrogen in this sense includes the bonded species detected by FTIR and any additional unbound, or molecular, hydrogen in the film.

NRA has been used to characterize SiN and other thin film dielectrics and semiconductors [41,42]. The drawbacks of NRA are the sophisticated facilities required (of which there are only a few in the U.S.) and the destructive nature of the test due to high ion beam currents used which

irreversibly alter the film [6]. The accuracy of NRA is about $\pm 8\%$ [43].

An easier technique to carry out is Hydrogen Forward-recoil Scattering (HFS). It is based on the Rutherford Backscattering Spectrometry (RBS) method and uses the same equipment with some modifications [44]. For RBS, an ion beam is directed at the specimen in an inclination of about 15° above the surface and beam ions scattered in the reverse direction by heavy atoms in the specimen are collected and analyzed. In the case of HFS, the equipment is also designed to detect the lighter hydrogen atoms and protons which are scattered forward by the incident ions in the same direction as the analysis beam. When used in conjunction with sputtering, HFS can provide depth profiles of hydrogen concentration, as does NRA. This allows for specifically measuring the total hydrogen content in a film as opposed to the combined amount in both the film and substrate. The accuracy of HFS is about $\pm 10\%$ [45]. HFS has been used, and is increasingly being used, for determining hydrogen concentration in silicon nitride films [22,46]. HFS is

commercially available from major providers of materials analysis services, e.g., [45]. However, this technique is still expensive and impractical for routine, inline characterization of production films.

Yet another method for determining hydrogen content is neutron scattering. Again, a sophisticated facility is required, namely one which can generate a collimated, nearly monochromatic neutron source. The specimens require little preparation and can be used in bulk form. Despite its light mass, hydrogen has a much larger scattering cross-section for neutrons than silicon and nitrogen. This scattering power enables the detection of hydrogen in many materials by radiography techniques. The average concentration of hydrogen through a material's total thickness is determined (including any underlying substrate in the case of thin films).

In principle, neutron scattering could be used in conjunction with other techniques, such as FTIR, to allow determination of the partitioning of hydrogen in a material

between chemically bound and unbound forms. Neutron scattering has been used successfully for characterization studies of metal hydrides [47] and organic liquids [48]. In addition to its very limited availability, other drawbacks of this test method are the long set up time and the long post-processing time required to obtain a useful quantitative interpretation of the data. A summary of the capabilities of each of the hydrogen measurement techniques discussed here is contained in Table 2.

3.3 Interpretation of FTIR Spectra

Fourier Transform Infrared spectroscopy (FTIR) plots the vibrational spectrum of a material's response to broadband IR illumination. Chemically bound species are detected through the absorption or transmission of energy by their characteristic vibrational modes. The species of interest must possess a dipole moment to be detectable. The most important absorption peaks in plasma deposited silicon nitride are the Si-H stretch mode at $\sim 2200\text{ cm}^{-1}$ and the N-H stretch mode at $\sim 3300\text{ cm}^{-1}$ [49]. Minor peaks include the Si-H wagging mode at $\sim 630\text{ cm}^{-1}$, the N-H₂ stretch mode at 1500

Table 2: Hydrogen measurement techniques covered in this study

Method Name (<i>Abbreviation</i>)	Approximate Resolution	Measurement Turnaround Time
Hydrogen Forward Recoil Scattering (<i>HFS</i>)	0.01 at. %	Hours
Nuclear Reaction Analysis (<i>NRA</i>)	100 ppm	Hours - Days
Fourier Transform Infrared Spectroscopy (<i>FTIR</i>)	1 ppm *	Minutes
Thermal Desorption Analysis (<i>TDA</i>)	0.1 wt. % *	Hours
Neutron Transmission/ Scattering	50 ppm	Hours - Days

* Semi-quantitative

cm^{-1} , and the N-H bending mode at $\sim 1200 \text{ cm}^{-1}$ [50,51]. A large absorption peak visible in the range of $820 \sim 890 \text{ cm}^{-1}$ is due to Si-N interaction and is actually a convolution of many vibrational modes [11], hence absorption band is a better term for this feature [6]. The Si-N absorption band was not treated as a distinct peak in this study except for tabulation of its location for the sake of completeness.

In principle, it is also possible to observe IR absorption peaks due to the interaction of hydrogen molecules with the SiN matrix. Such peaks have been reported for spinel (MgO) and some amorphous silicon alloys [52,53], but there is no published account of detecting H_2 in SiN this way. Furthermore, few instruments are capable of these measurements (including the one used in this study) because the resulting signals are very weak and outside of the mid-infrared spectral window usually examined (wavenumbers greater than 4000 cm^{-1}).

One problem with FTIR analysis of the plasma deposited SiN films is the assumption of many previous researchers and

authors that all of the hydrogen in the film is necessarily bound in some way to either silicon or nitrogen, because only these peaks are typically visible. This view discounts the existence of measurable quantities of unbound forms of hydrogen. The other difficulty with FTIR is that quantitative concentration determination is subjective due to the way in which peak areas are calculated. Attenuation of the IR signal by the film means that the spectra obtained will be thickness dependent; for this work a thickness correction algorithm was unavailable and consequently not used. An additional problem is that a baseline-procedure must be used to cancel interference effects and normalize the spectra. This involves drawing a baseline, either manually or using a computer algorithm, and then measuring the area under the selected peak(s) with respect to the baseline. The area measurement itself can also be done either manually or by computer and requires the analyst to define the peak width. The peak width can be defined in several different ways yielding different results thereby contributing another source of error. The algorithm used in the FTIR instrument for this work carries out the

calculation based on formulas developed by W.R. Knolle [54]. FTIR determination of hydrogen concentration can have uncertainties as large as 50%, especially for low hydrogen content films (~ 5 atomic percent or less) [43].

4. Experimental

4.1 Materials and Equipment

Standard test grade 200 mm silicon wafers (single-side polished, > 5 ohm-cm resistivity, <100> orientation) were used as substrates for the silicon nitride films. The process equipment consisted of a Novellus Concept Two [55] commercial PECVD reactor using nitrogen, ammonia, and monosilane as source gases. Two radio frequency (RF) power generators, one at 13.56 Mhz and the other at 280 kHz, supplied the energy for the plasma discharge.

The film characterization equipment consisted of: a Prometrix (Model SM-200) [56] photoreflectometer film thickness measuring instrument, Tencor optical cantilever stress gauges (Models FLX-5200h and FLX-2320) [56], a Metricon prism coupler (Model PC-2000) [57] for refractive index measurement, a Bio-Rad FTIR instrument (Model QS-300) [58] for hydrogen bond concentration measurements, and an MTM Engineering Thermal Desorption Analyzer (Model WT-268) [59] for characterizing hydrogen evolution.

4.2 Thermal Analyses

One whole wafer, from the pair of wafers representing each process condition, was subjected to a stress hysteresis temperature cycle using the Tencor FLX-2320. The thermal cycle for this test consisted of ramping from room temperature to 500°C at a rate of 4°C/min, holding at 500 for 10 minutes, then ramping back down to room temperature at 4°C/minute.

The stress change during temperature cycling, as well as the as-deposited film stress, were measured by instruments using the optical lever technique [21,37]. This method relies on measuring the substrate curvature by scanning a laser beam first across the surface of a bare wafer, then across the same wafer coated with film. By obtaining the differences in substrate curvature with respect to the bare substrate, and by using the known substrate and film thicknesses, the stress can be calculated. Assumptions include complete film adherence, nearly perfect thickness uniformity, spherical bending of the substrate, and the thin

film approximation, i.e., the substrate is much thicker than the film ($\geq 100X$). The stress thus determined consists of a thermal component due to the mismatch in coefficients of thermal expansion between the substrate and film materials, and an intrinsic component of the film which is a function of its defect density.

FTIR spectra were collected before and after the stress hysteresis temperature cycle. The wafer deposited with the film from centerpoint ("standard") process condition was taken through the additional steps of weighing before deposition, after deposition/before thermal cycle, and after thermal cycle. This allowed determination of the as-deposited film density and then the change in mass after the stress hysteresis temperature cycle.

The other wafer processed under the same condition was cleaved for Thermal Desorption Analysis in the RGA mode. A piece of the wafer with film (about 2 X 8 cm in size) was placed into the machine's high vacuum chamber and the temperature was ramped from room temperature to 1000°C at a

rate of 5°C/minute; the ramp rate was selected to nearly match that used for the stress hysteresis cycle. The RGA mode of operation gives the partial pressure of selected molecular species, or their fragments, measured by Quadrupole Mass Spectrometry (QMS) as a function of the time. A plot of the partial pressure of selected species versus temperature is generated. Each of the wafer specimens used for TDA was approximately the same size in terms of surface area but no attempt was made to make them identical. The magnitudes of the peaks observed will depend on the amount of material present, hence the emphasis here is on comparing the peak positions of the films, and the relative magnitudes of the peaks for a given specimen. Although the vacuum chamber is continuously pumped, it has no purge flow to eliminate differences in diffusion rates of different species. This means separation of gas evolution peaks in time or temperature might be affected by diffusion limitations in the gas phase. This effect was neglected for interpretation of the desorption spectra in this study since the focus was on the single specie H₂.

TDA can also provide information to determine the total amount of hydrogen contained in a specimen if it is heated until outgassing is complete. The chamber is kept closed during the process after initial pumpdown. The final pressure and temperature is used to calculate the amount of gas present by application of the Ideal Gas Law using the known volume of the chamber. This procedure was carried out with a film specimen from the centerpoint process condition to independently cross-check against the weight change data.

5. Results and Discussion

Measurements of the film properties taken from the matrix of experimental conditions were compiled for statistical and graphical analysis by computer [60,61,62]. The film property data collected from all of the wafers is summarized in Tables 3 and 4. There were several conditions which produced very non-uniform film thicknesses ($> 10\%$ standard deviations measured over 225 points). For films deposited under these conditions it is expected that other film properties would also vary substantially across the wafer surface. Therefore the single-point measurements taken at the wafer center (including refractive index and FTIR spectra) are not necessarily representative of the bulk, or large area, film. Average quantities of these same films (such as deposition rate and film stress) should also be treated with caution because they cover a wide range of the film property. A few of the films were too thin for reliable measurement of refractive index by the prism coupler used for this study; films from run conditions #12 and #13 in particular could not be measured at all. This is a result of the fixed deposition time (60 seconds) used for all of the process conditions. The deposition rate turned out to vary by nearly a factor of four between extremes in

Table 3: Summary of film properties (excluding FTIR results)

Run #	As-Deposited Stress (MPa)	Delta Stress Due to Annealing (MPa)	H ₂ Evolution Peak(s) (° C)	Refractive Index	Thickness (Å)	Deposition Rate (Å/min)
0	-190	130	230, 450	2.027	7060	1783
1	-911	77	400	1.941	8005	1334
2	-59	34	250, 430	1.956	5170	862
3	618	-200	150, 460	1.929	9109	1518
4	-79	180	240, 440	2.175	15924	2654
5	-54	160	220, 440	2.181	14728	2455
6	13	100	220, 440	2.203	8872	1479
7	-70	100	240, 440	2.197	10438	1740
8	-798	100	430	2.107	8350	1392
9	-945	40	420	1.945	6640	1107
10	395	-600	130, 400	2.178	16528	2755
11	629	-400	160, 400	1.907	10961	1827
12	86	100	180, 440	*	6231	1039
13	100	100	190, 440	*	4546	758
14	98	50	250, 440	1.956	5006	834
15	-755	130	410	2.100	10856	1809
16	398	-500	160, 420	2.176	16524	2754

*Could not be measured

Table 4: Summary of FTIR data of all the films

Run #	Si-H Peak Wave-number (cm ⁻¹)	Si-H Peak Area	Si-H Bond Concentration (X 10 ⁻²² cm ⁻³)	N-H Peak Wave-number (cm ⁻¹)	N-H Peak Area	N-H Bond Concentration (X 10 ⁻²² cm ⁻³)	Fraction Si-H	Fraction N-H	(Si-H): (N-H) Ratio	Total Bonded H (Si-H + N-H) (X 10 ⁻²² cm ⁻³)	Atomic Conc. H (calculated)
0	2169	7.373	1.27	3343	1.658	0.44	74.27%	25.73%	2.89	1.71	19.00%
1	2217	2.866	0.35	3299	5.182	0.93	27.34%	72.66%	0.38	1.28	14.22%
2	2200	4.068	0.82	3310	2.528	0.81	50.31%	49.69%	1.01	1.63	18.11%
3	2150	9.909	1.46	3338	2.501	0.47	75.65%	24.35%	3.11	1.93	21.44%
4	2160	2.415	1.15	3320	2.415	0.41	73.72%	26.28%	2.80	1.56	17.33%
5	2159	11.639	1.30	3315	1.825	0.36	78.31%	21.69%	3.61	1.66	18.44%
6	2149	7.570	1.42	3334	0.773	0.25	85.03%	14.97%	5.68	1.67	18.56%
7	2144	8.539	1.25	3331	1.301	0.34	78.62%	21.38%	3.68	1.59	17.67%
8	2179	6.720	1.02	3331	1.405	0.35	74.45%	25.55%	2.91	1.37	15.22%
9	2200	1.608	0.36	3301	4.632	0.98	26.87%	73.13%	0.37	1.34	14.89%
10	2144	15.724	1.64	3330	2.781	0.38	81.19%	18.81%	4.32	2.02	22.44%
11	2148	9.346	1.14	3336	4.642	0.65	63.69%	36.31%	1.75	1.79	19.89%
12	2175	3.494	0.89	3326	1.397	0.42	67.94%	32.06%	2.12	1.31	14.56%
13	2170	1.437	0.54	3324	0.525	0.27	66.67%	33.33%	2.00	0.81	9.00%
14	2193	4.207	0.85	3316	3.483	0.79	51.83%	48.17%	1.08	1.64	18.22%
15	2144	15.760	2.17	3374	1.907	0.34	86.45%	13.55%	6.38	2.51	27.89%
16	2149	18.807	1.86	3394	1.417	0.23	89.00%	11.00%	8.09	2.09	23.22%

the process space selected for the experiment (758 - 2755 Å/min).

5.1 DOE Analysis

The process response variables (experimental outputs in terms of film properties) chosen to be analyzed by statistical DOE methods were the chemically bound hydrogen content obtained by FTIR (Si-H, N-H, and the sum of Si-H + N-H), as-deposited stress, and post-anneal stress change. These responses were selected based on their relevance to the objectives of the study. Except for as-deposited film stress, the lack of replication of the chosen measurements made it impossible to validate the assumptions implicit in the ANOVA method.

Run charts of the data for the as-deposited individual hydrogen components (Si-H and N-H) and the total hydrogen (Si-H + N-H), measured by FTIR, are plotted in Figure 1 and indicate no obvious, systematic influence of background variables (sources of error) which would show up as a distinct trend superimposed on the data.

ANOVA indicates that the statistically significant effects for incorporation of bound hydrogen (both Si-H and N-H) are those associated with the factors Silane Flow (A) and LF

Figure 1: Chemically bound hydrogen content of all the films, as measured by FTIR, displayed in experimental run order

Power (D). This finding is consistent with what has been reported in the literature [5]. Normal probability plots of the effects for Si-H, N-and total H incorporation in Figures 2, 3, and 4, respectively, reveal the same graphically; the most important effects are those farthest from the center of the plot and from the interpolated line, which means they are significant with respect to the noise level in the experiment. The plots also illustrate the significance of several interaction effects (the mixed terms). In fact, for N-H incorporation the Silane Flow-LF Power (AD) interaction effect is larger in relative magnitude than the effect of Silane Flow (A) by itself. This means that varying the Silane Flow and LF Power *simultaneously* has more of an impact on the N-H in the film than varying the Silane Flow (A) alone.

The most important effects for as-deposited stress are found to be the factors Pressure (B) and LF Power (D), and their interaction (BD). This is illustrated in the normal probability plot of Figure 5. These results are physically reasonable because pressure affects deposition rate and LF power affects the amount of ion bombardment in the plasma. The deposition rate and ion bombardment, in turn, influence the intrinsic stress of the film [5,63]. A run chart of as-

Figure 2: Normal probability plot of the effects for Si-H
(A=Silane Flow, B=Pressure, C=Total Power, D=LF Power)

Figure 3: Normal probability plot of the effects for N-H

Figure 4: Normal probability plot of the effects for total H

Figure 5: Normal probability plot of the effects for as-deposited film stress

deposited stresses, Figure 6, reveals no significant background influences.

Finally the effects of the factors were analyzed for their impact on stress change (delta stress) due to annealing. Interestingly, the significant factors turned out to be the same ones that influenced as-deposited film stress: Pressure, LF Power, and their interaction. The magnitudes of the effects are similar for both cases, however the signs of the LF Power effect and the Pressure effect are reversed meaning they act in opposite directions. The normal probability plot for effects of stress change is shown in Figure 7.

Figure 6: As-deposited stress of all the films displayed in run order

Figure 7: Normal probability plot of the effects for the change of film stress with annealing (delta stress)

5.2 Characterization of Hydrogen Content

All of the film specimens prepared exhibited the primary characteristic FTIR peaks of Si-H and N-H bond vibrations, at $\sim 2200\text{ cm}^{-1}$ and $\sim 3300\text{ cm}^{-1}$, respectively. Most of the films also exhibited the N-H₂ peak at 1500 cm^{-1} . A few of the films showed the N-H peak at $\sim 1200\text{ cm}^{-1}$. There is no apparent relationship between the appearance of these secondary peaks and any of the other measured film properties. All of the FTIR spectra are shown together in Figure 8, providing a qualitative contrast and comparison of the films.

Total bound hydrogen (as measured from peak areas in FTIR) in the deposited films varied from 0.81 to 2.51×10^{22} (bonds/cm³), a range of about 3X. This was smaller than expected, given the relatively wide range of process conditions investigated. However, these results are consistent with other published experimental data [16,63]. The Si-H/N-H bond concentration ratio varied from 0.37 to 8.09, a broad range of about 22X.

Plots of the individual bond concentrations (Si-H, N-H) and the ratio of the bond concentrations (Si-H/N-H) display interesting trends. In Figure 9, it can be seen that the N-H concentration remains relatively constant ($\sim 0.5 \times 10^{22}$

Figure 8: The FTIR absorbance spectra of all the films produced plotted in run order; the significant peaks are denoted

Figure 9: Plot of the Si-H and N-H bond concentrations versus the total bound hydrogen concentration for all of the films deposited

bonds/cm³) while the Si-H concentration increases nearly monotonically with the total bound H concentration. Figure 10 shows the same upward trend for the Si-H/N-H ratio with increasing total H concentration. These trends are consistent with the process conditions in which the flows of the nitrogen source gases (ammonia and nitrogen) were kept constant while the silane was varied, along with the other factors. The LF power, which was found from the DOE analysis to have the greatest effect on the N-H concentration, also had a strong effect on the Si-H concentration (in the same direction). This implies that the distribution of bound hydrogen in the deposited films was controlled mainly by factors which simply adjusted the amount of Si-H incorporation while the amount of N-H was limited by the flow of reactants or perhaps had already reached a point of saturation in the film.

RBS measurements were done simultaneously with HFS for three selected films, based on FTIR data: the "low" bound hydrogen content specimen (condition #13), the "high" bound hydrogen content specimen (condition #15), and the DOE matrix center point specimen (condition #0). The Si/N ratios obtained from RBS (listed in Table 5) indicate silicon-rich compositions when compared with Si/N = 0.75 for the stoichiometric silicon nitride, Si₃N₄. Silicon-rich

Figure 10: Plot of the Si-H/N-H bond ratios versus the total bound hydrogen concentration of all the films deposited

composition is most common for such PECVD films [64]. The Si-H/N-H bond ratios of these films do not seem to be a good indicator of their Si/N ratios.

Table 5: Silicon/nitrogen atom ratios determined from RBS measurements and Si-H/N-H bond ratios determined from FTIR

Condition #	Si/N	Si-H/N-H
0	1.05	2.89
13	1.19	2.00
15	1.18	6.38

The refractive index (RI) of PECVD silicon nitride films with the stoichiometric composition ($\text{Si/N} = 0.75$) measured at 633 nm is typically ~ 1.90 [16,64]; in contrast, the RI of stoichiometric LPCVD films is nominally 2.00 [1,16,64]. In general, films with < 1.90 are characterized to be nitrogen-rich and those with $\text{RI} > 1.90$ are silicon-rich. Thus, based solely on the range of refractive indices obtained in this experiment (1.907 - 2.203), all of films produced are considered silicon-rich. The compositions of the samples analyzed by RBS were found to be silicon-rich, in agreement with the RI measurements.

The Si-H/N-H bond concentration ratio determined from the FTIR peak areas should also provide an indirect measure of film composition [7]. A plot of the refractive index, which is largely composition-dependent, versus Si-H/N-H bond ratio indeed produces a reasonable correlation, as shown in Figure 11. The line fitted to the data by regression does not have a very good fit ($R^2 = 0.51$ versus $R^2 = 1$ for the ideal case), possibly due to an insufficient number of data points. However, the analytical expression obtained by linear regression ($RI = 1.95 + 0.037 [Si-H]/[N-H]$) closely matches the empirical formula derived by Knolle [54] ($RI = 1.95 + 0.042 [Si-H]/[N-H]$).

The hydrogen content of the films from conditions #0, 13, and 15 as measured by HFS was 21.7, 20.0, and 17.4 atomic %, respectively. The quantities measured by NRA were remarkably similar for the same specimens: 21.9, 19.2, and 16.8 atomic %. The NRA measurements yielded H/Si ratios so the Si/N ratio obtained from RBS was needed in order to calculate the hydrogen content in atomic percent.

Conversion of the FTIR bond concentrations of the three as-deposited specimens above (#0, #13, #15) to atomic percent yielded a much larger range in comparison with the HFS and NRA analyses. The results are summarized in Table

Figure 11: Plot of the refractive index versus Si-H/N-H bond absorbance of all the films deposited, except two which could not be measured; the interpolated line is obtained from regression analysis of the data

6. The centerpoint specimen (#0) was calculated to contain 19.0 atomic % H, in good agreement with total hydrogen measured by HFS and NRA (within 1 atomic %). The "low" FTIR-hydrogen-content specimen (#13) was calculated to contain 9.0 atomic % H and the "high" FTIR-hydrogen-content (#15) was calculated to have 27.9 atomic % H.

Thus, specimen #13 measured ~10 atomic % lower by FTIR than by HFS and NRA and specimen #15 measured ~10 atomic % higher by FTIR. These discrepancies are outside of the most conservative error margin quoted by the analytical service providers for HFS (10%, absolute, not atomic). The accuracy of the FTIR results thus seems suspect. This is especially troublesome in light of the report by Claassen et al. [16], that of 28 of their various PECVD silicon nitride films (all produced under different conditions) all 28 contained ~20 atomic percent total hydrogen, as measured by IR spectroscopy.

Table 6: Summary of the total hydrogen concentration measurements obtained by three techniques

Specimen # (condition)	FTIR (at.%)		HFS (at.%)		NRA (at.%)	
	as-dep	post-anneal	as-dep	post-anneal	as-dep	post-anneal
0	19.0	20.4	20.0	N/A	19.2	19.8
13	9.0	9.6	21.7	18.5	21.9	20.2
15	27.8	15.7	17.4	16.8	17.1	18.6

The possibility of any free or molecular hydrogen unaccounted for in the IR spectrum, or the omission of the minor bond peaks, might be proposed as explanations for the anomalously "low" bonded H concentration measured in specimen #13 by FTIR in comparison with the NRA and HFS measurements. However, none of these theories explain the anomalously "high" bonded H concentration measured in specimen #15. However, as mentioned previously, thickness effects were not modeled by the FTIR software. A simplistic correction to normalize the peak areas according to film thicknesses would improve the accuracy for both of these particular specimens because the bond concentrations are found to be proportional to the thicknesses.

The problem of accuracy could more fundamentally stem from the FTIR conversion factors being applicable only to a limited range of calibration. Inaccuracies are inherent to the use of the conversion factor (from absorption peak area to atomic percent), which is based on a nominal film composition and assumes a constant film density. The film densities assumed for FTIR and NRA measurements in this study were 2.5 and 2.4 g/cm³, respectively. The actual film density measured from the weight of the center point film (#0) was 2.38 g/cm³, so the assumed densities are reasonably close for this case. However, the true densities of the

films throughout the experimental matrix might have varied more widely [16].

Another possible explanation for the apparent inaccuracies is a non-linearity in the actual relationship between atomic concentration and absorption peak areas. This could lead to small total peak areas underestimating the actual hydrogen concentration and large total peak areas overestimating the concentration.

In summary, the most likely cause of the measurement discrepancies is an erroneous conversion factor from absorption units to atomic concentration (i.e., a constant and/or formula not equally applicable to all the films) in combination with the impreciseness of quantifying peak areas with respect to a baseline. Data about the absolute hydrogen content of the other specimens would be required to make a more definitive determination of differences between measurement results and, if necessary, to develop a more comprehensive model.

5.3 Changes in Hydrogen Content and Distribution

Quantification of the hydrogen lost from the films during annealing was done by: (1) comparison of the FTIR spectra, pre- and post-annealing; (2) weight loss measurement of the film (centerpoint specimen, #0, only); (3) outgassing measurement (also centerpoint specimen only); (4) comparison of HFS and NRA measurements, pre- and post-annealing (Table 3). Qualitative assessments were made by TDA and FTIR. Plots of the FTIR spectra before and after annealing, TDA spectra, and stress-temperature hysteresis curves for all of the films are shown in the Appendix.

HFS and NRA indicate about 1 ~ 3 atomic % change in the amount of total hydrogen after annealing. These values are at the noise level of the measurements and therefore indicate very little or no change in the hydrogen concentration of the films. FTIR is consistent with specimens #0 and #13 indicating essentially no change, but again is questionable with specimen #15 showing a significant change. The average change in bonded hydrogen content of all the films is about one atomic percent. This amount is negligible given the large errors in quantitative measurement by FTIR.

Visual inspection of the peaks in the IR spectra reveals no noticeable change in either the area or position of prominent peaks. However, it was observed that all of the films displayed a visible rise (approximately the same magnitude) in the Si-H peak height at $\sim 630\text{ cm}^{-1}$ after heat treatment. A clear example of this phenomenon is shown in Figure 12. Noskov [65] refers to "homogenization" of the hydrogen distribution throughout the film upon annealing due to passivation of dangling bonds by migrating hydrogen. The growth of the bond wagging peak at 630 cm^{-1} might provide an indication that some capture of hydrogen is taking place during annealing.

Due to the nature of the specific vibrational mode associated with the 630 cm^{-1} peak, it is possible that the above phenomenon could be limited to interfaces of the film, such as the top surface, the substrate-film interface, and voids or pores within the film. Such interfaces are not distinguished from the bulk of the film by FTIR but have higher local concentrations of dangling silicon bonds than the bulk. Interfaces serve to capture hydrogen, and provide an additional degree of freedom for bond vibration. The two films depth-profiled by HFS (specimens #13 and #15, shown in Appendix 3), albeit a limited set of data, do not support the premise of interfacial segregation of hydrogen, however.

Figure 12: Plot of the IR spectra of the film from Run #3, before and after annealing, illustrating the typical appearance of an Si-H absorbance peak at $\sim 630 \text{ cm}^{-1}$

The source of the hydrogen supplying the new Si-H bonds is unknown but might be the so-called "loosely" bound species, such as the molecular form. Monitoring the growth of the 630 cm^{-1} peak during annealing would perhaps provide more insight into its origin.

There has been mention in the literature [23] of the absorption peak position shift indicating a change in the microscopic stress state of the film, which in turn could correspond to hydrogen loss. Although most of the films became more tensile upon annealing there is no consistent trend among the peak shifts, for either Si-H or N-H bonds, as shown in Figure 13. Most of the peak shifts are at, or near, the 4 cm^{-1} resolution limit of the instrument.

Figure 13: Plot of the changes in Si-H and N-H peak positions as a function of the change in stress after annealing (failed films are those which exhibited cracking and peeling after annealing)

5.4 Thermal Desorption Analysis

The TDA spectra collected from all of the films were truncated to the temperature range of room temperature to 500°C to allow direct comparison with results from the stress-temperature cycles. Measurements revealed that most of the film specimens produced two distinct hydrogen outgassing peaks, exemplified in Figure 14; a complete compilation of all the films is provided in the Appendix. At least two previous papers have also reported the appearance of such peaks [66,67] from SiN films, although at higher temperatures than was observed in this study.

The first outgassing peak is observed in the range of 130 ~ 250°C and the second in the range of 400 ~ 460°C. The first peak is perhaps due to the desorption of hydrogen at or near the top surface of the films. The first, lower temperature, peak was suppressed in the four most compressive films (ranging in as-deposited stress from about -750 to less than -900 Mpa). The reason for this behavior is unclear but might be related to higher film density in these specimens, as explained later. The second peak occurs at, or just above, the deposition temperature. This might be due to the liberation of the "loosely" bound hydrogen from the bulk of the film. Originally trapped

Figure 14: Plot of the TDA spectrum of the film from Run #10, illustrating the two distinct outgassing peaks observed in most of the films (the labels on each trace refer to atomic mass units: "1" = H, "2" = H₂, "18" = H₂O)

during condensation of the films, this hydrogen might outgas as the film expands upon heating.

It might be expected that the two characteristic outgassing peaks might somehow be related to the dissociation of Si-H and N-H bonds in the film. The bond energies associated with isolated Si-H and N-H bonds are 3.5 and 4.1 eV, respectively [31] (Russian references cite values of 2.9 and 3.1 eV, respectively [65]). These values are all too high to be significantly affected thermally at temperatures below 500°C. In fact, temperatures over 600°C are required for their dissociation [31] in PECVD silicon nitride.

The other point to be considered is that the energy required to break bonds in the material will probably depend on the atomistic surroundings in the amorphous silicon nitride film. Therefore, the bond dissociation energy of a hydride specie in the film is likely to be different from the same bond in ideal isolation [36]. Two separate studies of the annealing of plasma-deposited silicon nitride films found the activation energies for bond dissociation to be 0.93 and 1.42 - 1.91 eV [31], and 0.47 and 1.08 eV [23], for N-H and Si-H, respectively. Thus, these studies not only found the activation energies to be lower than what might be

inferred from simply the bond energies themselves, but they were also reversed in relative magnitude, i.e., $E_a(\text{N-H}) < E_a(\text{Si-H})$. This means the N-H bond is actually the weaker one in these films, contrary to the assumptions of several authors, e.g., [22].

Measurements of the mass of the outgassed hydrogen during TDA and measurements of the film weight change after annealing both indicated that the total amount of hydrogen lost during annealing is very small, only in the ppm range of atomic fraction. This exceedingly small quantity of hydrogen released from the film is inconsistent with the rupture of the major hydride bonds in the film. Despite the fact that much less than one atomic percent of hydrogen is released from the films, the dramatic gas evolution curves from the TDA serve to demonstrate the sensitivity of quadrupole mass spectrometry.

5.5 Film Stress Relations

Examination of the as-deposited film stresses as a function of both the absolute hydrogen content and the hydrogen distribution indicates little or no correlation between these parameters; the lack of clear relationships is depicted in Figures 15 and 16. There have been suggestions in the literature that hydrogen incorporation affects the stress state of the film in a systematic way [21], but empirical results have been inconsistent. Both positive and negative trends in stress have been shown. In general, the effect of hydrogen incorporation on film stress is probably less than the physical influence of ion bombardment on development of the film's structure during deposition.

Similarly there appears to be no obvious relationship between either bonded hydrogen content or hydrogen bond distribution and the *change* in film stress upon annealing, illustrated in Figures 17 and 18. This finding seems to be a counterpoint to the hypothesis of this project. However, closer examination of delta stress as a function of Si-H bond concentration reveals an interesting division, as shown in Figure 19. For Si-H concentration less than 55% of the total bound hydrogen concentration, delta stress is less than 100 MPa. Films with Si-H concentration greater than

Figure 15: Plot of the as-deposited film stresses versus total bound hydrogen concentration

Figure 16: Plot of the as-deposited film stresses versus hydrogen bond ratios

Figure 17: Plot of the change in film stresses upon annealing versus hydrogen bond concentrations for all of the films

Figure 18: Plot of the change in film stresses upon annealing versus hydrogen bond ratios for all of the films

Figure 19: Plot of the change in film stresses upon annealing versus Si-H bond concentrations (Note: failed films are not shown here because they are off the vertical scale)

55% exhibit a much broader range of stress change; this range includes the films which failed (as defined previously, failure of the films was manifested by cracking and peeling from the substrate after annealing). The wider variability of stress shifts above a certain composition level seems consistent with a structural effect.

Higher Si-H fraction has been shown to correspond to higher Si/N ratio [5]. Higher Si/N ratio lowers the film density [6,16]. Thus higher Si-H fraction results in lower film density. This is because the hydrogen is substitutional (it replaces Si and N atoms in the structure) and it has a lower mass. Additional information relevant to the effect of film density on performance can be inferred from two separate studies, one relating the film density of PECVD silicon nitride to the diluent gas used in the deposition process, and the other relating the thermal stability of hydrogen in the film to the diluent gas. Claasen et al. [16] found that among hydrogen, nitrogen, and argon the use of argon as the diluent gas produced the highest density films across the broad range of Si/N ratios investigated. Allaert et al. [68] compared helium and argon as the diluent gases and also found argon to produce a higher density film. In addition, they found that Ar-

diluent films always had much less hydrogen loss than the He-diluent films after 300°C annealing treatments of varying durations. The results of these two studies in combination are interpreted to indicate that higher density films allow less movement or permeation of hydrogen through them.

Returning to the data plotted in Figure 19, the following explanation is presented: the films with lower Si-H concentration have lower Si/N ratios and hence higher atomic density; this higher density then limits movement of bound hydrogen in the structure. Conversely, the films with higher Si-H concentration have higher Si/N ratios and hence lower density; the density might also be reduced by microvoids or pores in the film. In the case of the higher Si/N ratio films, there probably exists a high concentration of dangling bond defects caused by the excess silicon content. All of these defects provide abundant trapping sites and allow hydrogen, both bound and unbound forms, more degrees of freedom to move in the structure. The mobility of hydrogen within the film then controls the stress stability. The migration of hydrogen upon heating could be limited to local rearrangement among similar traps, or, in other words, homogenization. Movement of hydrogen need not entail diffusion. Instead, the bonded hydrogen atoms could undergo displacive transformations, or

conformations in the polymer sense, which relax some of the strain in the as-deposited film structure and reduce the free volume of the film. Altering the free volume would result in macroscopically detectable changes in the stress state because the film is constrained to the substrate (except when failure occurs). The theory outlined here remains to be tested by precisely measuring changes in film thickness after annealing; a similar concept was described in [26] and [65].

The scenario of displacive movement is most applicable to the N-H and (original) Si-H bonds in the film. These same hydrogen bonds would remain unbroken throughout the entire temperature cycle of the annealing process and appear unchanged by FTIR. Trapping and local rearrangement would apply to the hydrogen which produces the 630 cm^{-1} absorption peak seen by FTIR after annealing.

The stress changes of the films after annealing through the temperature cycle appear to have an interesting relationship to their refractive indices. A plot of these properties is shown in Figure 20. As mentioned previously, the RI is a function of the composition and density of the films. RI is modulated primarily by the Si/N ratio (bonded hydrogen is believed to have a negligible contribution at

visible and shorter wavelengths [69]). Higher Si/N ratio has been directly correlated with higher RI [16,21]. On this basis, Figure 11, showing the relationship between RI and the bond ratio (Si-H/N-H), provides a link between RI and the Si-H concentration. In turn, the arguments above can be applied to establish a connection between the RI and the stress change. The larger stress changes on the graph all occur at RI > 2.00, a composition presumed to correspond to Si-H concentration $\approx$ 55%. Figure 20 thereby provides other evidence for the structural dependence of stress change by way of film composition and density.

Figure 21 shows change in film stress plotted against as-deposited film stress. The failed films can be seen to have a delta stress value exactly the same magnitude and opposite sign of their as-deposited stress indicating that film cracking and delamination occurred to such a great extent as to allow the substrate to relax back to its original curvature (prior to film deposition). Films with high compressive stress (less than -750 MPa) have an apparent linear correlation between as-deposited film stress and stress delta (at least for these few data points). This behavior is possibly due to the higher density generally associated with compressive versus tensile films of the same

Figure 20: Plot of the change in film stress versus the refractive index; the solid curve is a manual interpolation of the data points

Figure 21: Plot of the change in film stress upon annealing versus as-deposited film stress for all of the films

type. Higher density means smaller free volume in these films, therefore leading to the behavior described above. There are not enough data points of as-deposited film stresses between the extremes to formulate a comprehensive explanation of the responsible mechanism.

There are no events observed in the stress versus temperature plots consistent with the lower hydrogen outgassing temperatures (first TDA peak). A typical plot of stress-temperature hysteresis along with the TDA spectrum of the same specimen is shown in Figure 22. All of the films do display a characteristic upward change in slope of the stress-temperature hysteresis curve coincident with the second outgassing peak at $\sim 400^{\circ}\text{C}$. This might correspond to migration of loosely bound hydrogen from the bulk of the film. However, there is no additional evidence to support a phenomenological connection between these two events.

Figure 22(a,b): Plots of the typical change in film stress versus annealing temperature (top) and the TDA spectrum over the same temperature range (bottom) for the same film, produced in Run #12

5.6 High Temperature Effects

The visual appearance of films ramp-annealed to 1000°C in the TDA instrument varied markedly. (Recall that all specimens underwent this treatment but only the temperature range of room temperature to 500°C was considered for outgassing, to match the stress-hysteresis cycle.) The films exhibited three characteristic behaviors as observed optically without magnification: (1) no visible change; (2) formation of bubbles or blisters; (3) crystallization.

It is noteworthy that the set of blistered films were all of the high compressive stress specimens (less than about -750 MPa: films from Runs #1,8,9,15), and the set of crystallized films were all of the high tensile stress specimens (greater than about 400 MPa: films from Runs #3,10,11,16). Because the time at temperature was identical for all eight of these specimens, and there were no compositional characteristics unique to either group, the mechanism responsible for the transformation behavior seems to have been driven only by the state of film stress, compressive or tensile, and probably its relatively large magnitude. The highly compressive films are apparently dense enough to limit the out-diffusion of hydrogen from the film, but cause it to accumulate in pockets at the film-substrate interface. Sufficient pressure builds up to

locally delaminate the film and form the observed blisters: an example of the representative morphology is shown in Figure 23. On the other hand, the highly tensile films are surmised to have very open structures which allow hydrogen to pass through easily; the macroscopic cracks observed occurring at lower temperatures no doubt also help release hydrogen from the film. Microscopic defects, particularly silicon dangling bonds, are thereby relieved of hydrogen. Silicon atoms in the film could then form sufficient Si-Si bonds in certain areas to not only allow but favor epitaxial growth from the substrate. A representative example of the crystalline morphology is shown in Figure 24. More detailed examination of the resulting film microstructures and investigation of the transformation mechanisms involved are deferred for future study.

50 μ m

Figure 23: Optical micrograph of typical blistered film (200 X)

20 mm

Figure 24: Optical micrograph of typical "crystallized" film (~2 X)

6. Conclusions

The most important factors influencing hydrogen partitioning into the PECVD silicon nitride films produced in this study were found to be silane flow and low frequency RF power. The most important process factors affecting as-deposited stress were found to be the total pressure and low frequency RF power.

FTIR analysis of the as-deposited films indicated a range in hydrogen content of about 10 - 30 atomic percent across the experimental matrix. The Si-H/N-H bond concentration ratio varied from 0.37 to 8.09, a factor of approximately 22X. Based on the known problematic and error-prone nature of quantitative analysis by FTIR, in conjunction with the HFS and NRA data, the true hydrogen concentration of all the specimens is taken to be approximately 20 atomic percent. This value is the midpoint of the measured range, it is the concentration of the centerpoint specimen measured by FTIR, and it is consistent with the other hydrogen measurement techniques, HFS and NRA. A review of the literature also supports the value of 20 atomic percent.

There was no experimentally significant change measured in either the FTIR absorption peak area or the peak position of any of the bound hydrogen species (Si-H and N-H) after the ramp annealing cycle. Interestingly, all of the film specimens displayed a noticeable rise of the Si-H bond wagging absorption peak at $\sim 630\text{ cm}^{-1}$ after annealing. The new peak might arise due to the presence of "loosely bound," possibly molecular, hydrogen (undetectable by FTIR) in the as-deposited material and later captured at defect sites in the films during the process of thermal diffusion.

There was no clear relationship found between the as-deposited stress and the chemical partitioning of hydrogen in any of the films. However, the stress change was found to be related to the as-deposited fraction of silicon hydride (% Si-H measured by FTIR) in the material. Films with Si-H concentration $< 55\%$ had $\Delta\text{ stress} \leq 100\text{ MPa}$ whereas those films with Si-H concentration $> 55\%$ had a broad range of $\Delta\text{ stress}$ values $> 100\text{ MPa}$ (including the films which failed by cracking and delamination after

annealing). Higher Si-H concentration corresponds to a higher Si/N ratio. The wider variation of stress shifts above a certain composition is consistent with a structural effect which allows more degrees of freedom for redistribution of strain-relieving hydrogen. Hydrogen rearrangement could allow reduction of free volume and an associated stress change. Thus, the hypothesis of thermally-driven stress changes based on hydrogen partitioning is upheld.

Most of the film specimens exhibited two distinct hydrogen outgassing peaks as measured by quadrupole mass spectrometry during TDA. The first peak occurred at 130 ~ 250°C and the second occurred at 400 ~ 460°C (at or above the deposition temperature). The four most compressive films (ranging in stress from 700 to over 900 MPa) did not exhibit the first peak, perhaps due to high film density which prevented outgassing, or the absence of a certain form of the "loosely bound" hydrogen. There is no connection between the stress-hysteresis curves and the TDA peaks except a sudden rise in the stress curve at 400°C (the

deposition temperature) which approximately coincides with the second TDA peak. The lack of change in the existing IR absorption peaks of the films and the growth of a new absorption peak suggests that the source of both hydrogen evolution peaks is a form, or forms, of the loosely bound hydrogen. The TDA peaks are very pronounced by virtue of the detection sensitivity of the quadrupole mass analyzer. This is somewhat misleading because mass measurements of the actual quantity of outgassed hydrogen indicate that it is extremely small (on the order of ppm atomic fraction of the film composition).

The practice in most of the previous literature of implicitly neglecting unbound or molecular hydrogen in silicon nitride films is validated by the results of this study, based upon the fact that the chemically bound hydrogen content determined by FTIR is essentially equivalent to the total hydrogen content. However, using FTIR for measurements of total hydrogen content should be done with the caveat that the absolute accuracy is quite poor.

Lastly, the specimens processed by vacuum annealing (in the TDA instrument) to 1000°C were found to have three characteristic morphologies: no apparent physical change, bubbles or blisters, and planar poly-crystals. The transformations appear to be driven by the stress states of the films. All of the highly compressive specimens (less than about -750 MPa) blistered, and all of the highly tensile specimens (greater than about 400 MPa) crystallized. The precise mechanism responsible for this behavior will be a topic for future investigation, as will a method to ascertain the presence of molecular hydrogen.

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Appendix

Figure A.1(a): Stress versus temperature curve for the film from Run #0
(Note that the units on the ordinate are stress change)

Hydrogen Evolution Analyzer : Graphing Screen

Figure A.1(b): Gas evolution curves for the film from Run #0 showing the species detected by the mass spectrometer ("1" = H, "2" = H₂, "18" = H₂O); maximum temperature on the abscissa is 500°C

Figure A.1(c): Top plot is the FTIR spectrum of the film from Run #0 taken as-deposited, bottom plot is the FTIR spectrum taken after ramp annealing to 500°C

Figure A.2(a): Stress versus temperature curve for the film from Run #1

Figure A.2(b): Gas evolution curves for the film from Run #1 showing the species detected by the mass spectrometer

Figure A.2(c): Top plot is the FTIR spectrum of the film from Run #1 taken as-deposited, bottom plot is the FTIR spectrum taken after ramp annealing

Figure A.3(a): Stress versus temperature curve for the film from Run #2

Figure A.3(b): Gas evolution curves for the film from Run #2 showing the species detected by the mass spectrometer

Figure A.3(c): Top plot is the FTIR spectrum of the film from Run #2 taken as-deposited, bottom plot is the FTIR spectrum taken after ramp annealing

Figure A.4(a): Stress versus temperature curve for the film from Run #3

Figure A.4(b): Gas evolution curves for the film from Run #3 showing the species detected by the mass spectrometer

Figure A.4(c): Top plot is the FTIR spectrum of the film from Run #3 taken as-deposited, bottom plot is the FTIR spectrum taken after ramp annealing

Figure A.5(a): Stress versus temperature curve for the film from Run #4

Figure A.5(b): Gas evolution curves for the film from Run #4 showing the species detected by the mass spectrometer

Figure A.5(c): Top plot is the FTIR spectrum of the film from Run #4 taken as-deposited, bottom plot is the FTIR spectrum taken after ramp annealing

Figure A.6(a): Stress versus temperature curve for the film from Run #5

Figure A.6(b): Gas evolution curves for the film from Run #5 showing the species detected by the mass spectrometer

Figure A.6(c): Top plot is the FTIR spectrum of the film from Run #5 taken as-deposited, bottom plot is the FTIR spectrum taken after ramp annealing

Figure A.7(a): Stress versus temperature curve for the film from Run #6

Figure A.7(b): Gas evolution curves for the film from Run #6 showing the species detected by the mass spectrometer

Figure A.7(c): Top plot is the FTIR spectrum of the film from Run #6 taken as-deposited, bottom plot is the FTIR spectrum taken after ramp annealing

Figure A.8(a): Stress versus temperature curve for the film from Run #7

Figure A.8(b): Gas evolution curves for the film from Run #7 showing the species detected by the mass spectrometer

Figure A.8(c): Top plot is the FTIR spectrum of the film from Run #7 taken as-deposited, bottom plot is the FTIR spectrum taken after ramp annealing

Figure A.9(a): Stress versus temperature curve for the film from Run #8

Figure A.9(b): Gas evolution curves for the film from Run #8 showing the species detected by the mass spectrometer

Figure A.9(c): Top plot is the FTIR spectrum of the film from Run #8 taken as-deposited, bottom plot is the FTIR spectrum taken after ramp annealing

Figure A.10(a): Stress versus temperature curve for the film from Run #9

Figure A.10(b): Gas evolution curves for the film from Run #9 showing the species detected by the mass spectrometer

Figure A.10(c): Top plot is the FTIR spectrum of the film from Run #9 taken as-deposited, bottom plot is the FTIR spectrum taken after ramp annealing

Figure A.11(a): Stress versus temperature curve for the film from Run #10

Figure A.11(b): Gas evolution curves for the film from Run #11 showing the species detected by the mass spectrometer

Figure A.11(c): Top plot is the FTIR spectrum of the film from Run #10 taken as-deposited, bottom plot is the FTIR spectrum taken after ramp annealing

Figure A.12(a): Stress versus temperature curve for the film from Run #11

Figure A.12(b): Gas evolution curves for the film from Run #11 showing the species detected by the mass spectrometer

Figure A.12(c): Top plot is the FTIR spectrum of the film from Run #11 taken as-deposited, bottom plot is the FTIR spectrum taken after ramp annealing

Figure A.13(a): Stress versus temperature curve for the film from Run #12

Figure A.13(b): Gas evolution curves for the film from Run #12 showing the species detected by the mass spectrometer

Figure A.13(c): Top plot is the FTIR spectrum of the film from Run #12 taken as-deposited, bottom plot is the FTIR spectrum taken after ramp annealing

Figure A.14(a): Stress versus temperature curve for the film from Run #13

Figure A.14(b): Gas evolution curves for the film from Run #13 showing the species detected by the mass spectrometer

Figure A.14(c): Top plot is the FTIR spectrum of the film from Run #13 taken as-deposited, bottom plot is the FTIR spectrum taken after ramp annealing

Figure A.15(a): Stress versus temperature curve for the film from Run #14

Figure A.15(b): Gas evolution curves for the film from Run #14 showing the species detected by the mass spectrometer

Figure A.15(c): Top plot is the FTIR spectrum of the film from Run #14 taken as-deposited, bottom plot is the FTIR spectrum taken after ramp annealing

Figure A.16(a): Stress versus temperature curve for the film from Run #15

Figure A.16(b): Gas evolution curves for the film from Run #15 showing the species detected by the mass spectrometer

Figure A.16(c): Top plot is the FTIR spectrum of the film from Run #15 taken as-deposited, bottom plot is the FTIR spectrum taken after ramp annealing

Figure A.17(a): Stress versus temperature curve for the film from Run #16

Figure A.17(b): Gas evolution curves for the film from Run #16 showing the species detected by the mass spectrometer

Figure A.17(c): Top plot is the FTIR spectrum of the film from Run #16 taken as-deposited, bottom plot is the FTIR spectrum taken after ramp annealing