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ENTITLED PROCESS MANUAL FOR PYROLITIC SILICON NITRIDE
DEPOSITIONS

BY WESTINGHOUSE ELECTRIC CORPORATION

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Process Manual
For
Pyrolitic Silicon Nitride Depositions

Contract No. NAS 9-6636
Westinghouse G.O. HS-51431

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Process Manual
For
Pyrolitic Silicon Nitride Deposition

Contract No. NAS 9-6636

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Summary

This manual was prepared for use as a guide in the pyrolytic deposition of silicon nitride (Si_3N_4) films on silicon substrates. The method employed for film formation is the pyrolytic decomposition of silane (SiH_4) in an ammonia (NH_3) atmosphere at temperatures of $775\text{--}975^\circ\text{C}$. The manual contains both general and specific information with regard to materials, equipment, procedures, and process requirements for the above method of Si_3N_4 film deposition. Silicon nitride films prepared by the methods described herein, when deposited onto thin silicon dioxide films, have proven satisfactory for use as the gate dielectric of MOS transistors having a non-volatile memory storage effect. The films are used by others in the industry as diffusion masks and passivating layers for various devices.



1.0 INTRODUCTION

Trapping of carriers within double-layer dielectric films of silicon nitride and silicon dioxide has been reported to controllably change the insulator charge sensitive parameters of metal-insulator semiconductor (MIS) devices.^{1,2,3} The trapping of the charge on relatively deep centers allows highly retentive storage of information within the dielectric film. This is the first such application of insulator defects. Ordinarily, traps are involved in undesirable departures of electrical behavior from that for ideal insulators. It is interesting that in their trap behavior silicon dioxide and silicon nitride are very different.

Intensive studies of thermally grown silicon dioxide over the past few years show little evidence for electron traps in the material as prepared. Hole trapping can be observed, but extraordinary means must be used to introduce holes into the oxide. Schottky-emission from the silicon under large negative metal-silicon bias at very high temperatures ($\geq 300^\circ\text{C}$) has been used.^{4,5} The barrier in this case appears to be about 1 eV in height, associated with the trap potential viewed at the silicon surface, and not the valence band barrier which exceeds 3 eV in height. Hole trapping of carriers produced by ionizing radiation within SiO_2 film has also been observed.^{6,7} Except for these unusual circumstances, silicon dioxide films are remarkably free of carrier trapping effects. Were this not so, the commercial success of silicon dioxide passivated devices probably would not have been achieved.

The other important constituent material for the charge storage structures, silicon nitride, was initially investigated for its high density and expected effectiveness as an ion barrier. Silicon nitride has been clearly demonstrated as



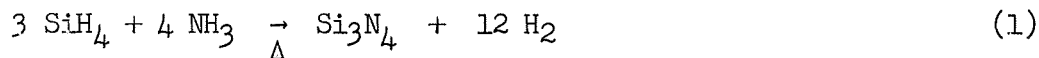
fundamentally useful and commercially feasible for this application. Used directly on silicon, however, the nitride early exhibited charge instability which appeared to be capricious and undesirable.

On close examination, the charge instability of silicon nitride on silicon was found to be a well behaved phenomenon interpretable in terms of tunnel injection exchange between traps in the dielectric near the interface and the silicon surface.³ Introduction of an oxide layer under the nitride reduced the case of charge exchange between nitride traps and the silicon surface.^{2,3} For oxide layers less than several hundred angstroms thick, tunneling from the silicon into the oxide conduction band could still supply electrons for trapping in the nitride at reasonable voltage levels. The charge so trapped is generally stable even at high temperature, indicating its capture in relatively deep centers.

This report describes the materials, equipment, deposition procedures and process requirements for the deposition of silicon nitride films that have been proven useful in metal-nitride-oxide-semiconductor (MNOS) structures with amplifying and memory capability.

2.0 GENERAL DISCUSSION

2.1 Silicon nitride is deposited by the irreversible pyrolytic decomposition of silane (SiH_4) in the presence of ammonia (NH_3). The chemical equation for this reaction is shown as equation 1.



Variations in deposition parameters result if 100% silane is used because of the difficulty of metering very small quantities of silane reproducibly. As a result, 3.5% silane with nitrogen as the carrier gas is recommended. Since the carrier

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gas does not enter into the chemical reaction it is not shown in equation 1.

The pyrolytic decomposition is accomplished in an rf induction heated reactor. A block diagram of the reactor is shown in figure 1. The wafer carrier is a silicon carbide coated graphite susceptor with nominal dimensions of 8" x 1.5" x 0.5". It is placed on a quartz frame to give it maximum inclination within the quartz tube. The quartz reactor tube used for this work was 60 mm I.D. x 80 cm long. All reactor tubing is Grade 316 Stainless Steel. Schutte & Koerting flow meters are used. The silane is a 3.5% mixture with nitrogen as the carrier gas. The nitrogen is obtained from a liquid source. The ammonia is obtained from a liquid source. Silane, nitrogen and ammonia are all obtained as semiconductor grade 99.999% purity with a chemical analysis accompanying the gas.

The gases are metered individually into the stainless steel tubing where they mix. Upon entering the quartz reactor they come in contact with the heated susceptor containing the substrates to be deposited upon. The silane pyrolytically decomposes in an irreversible manner and reacts with the nitrogen formed by the dissociated ammonia. Silicon nitride then deposits on the wafers and the susceptor. The reactor is flushed with 100% nitrogen in the pre-heat and cool-down cycles.

2.2 Materials

2.2.1 Susceptor

The susceptor is silicon carbide coated graphite. It is manufactured by the materials division of T.I. under the trade-name of Ti-Kote. The boat is 8" x 1.5" x 0.5". Prior to use, the susceptor is fired up in a hydrogen and hydrogen chloride for approximately one hour. The details of the process are:

Temperature	≈ 1200°C
Time	≈ 60 min.
H ₂	≈ 20 l/min
HCl	≈ 1 l/min

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2.2.2 Quartz

The quartz tube has an ID of 60 mm and a length of 80 cm. The quartz frame that the susceptor rests on is made of approximately $\frac{1}{4}$ " diameter rod. The glassware is cleaned in the standard HNO_3 -HF mixtures for quartz.

2.2.3 RF Generator

The generator and rf coil must be such that a $\pm 5^\circ\text{C}$ spread in temperature can be achieved along the length of the susceptor. The present system utilizes a 15 KW generator to give a 6" flat zone.

2.2.4 Flow Meters

The meters used are supplied by Schutte & Koerting although other meters could certainly be substituted. The ammonia flow rates are 10-20 liters/min. The nitrogen flow rates are 0-10 liters/min. The silane flow rates are 0-150 milliliters/min. Since the silane is a 3.5% mixture in a nitrogen carrier, the flow used are for nitrogen. The meter serial numbers used are:

Ammonia	$\frac{1}{4}$ -20-G5
Nitrogen	$\frac{1}{4}$ -15-G5
Silane/Nitrogen	3/32-06-P5

2.2.5 Gases

Silane - The silane is supplied by the Matheson Company to a semiconductor 99.999% purity level. The early experiments used a 100% silane supply, but difficulties were encountered in attempting to reproducibly meter small quantities into the system. As a result, a 3.5% mixture of silane in nitrogen as a carrier gas is used. Two flow rates used were 37 ml/min and 90 ml/min. No other flow rates were experimented with. Changes in the deposition rate with silane flow are shown in figure 2.

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Ammonia - The ammonia was supplied by Air Products Company to both a 99.99% and 99.999% purity level. The four nines purity level was used for determination of the physical properties of the film. When the five nines purity grade was available, it was used for growing the films that were evaluated as MNOS devices. The two flow rates of ammonia that were investigated are: 12.4 l/min and 20.4 l/min. Changes in the ammonia flow rate within the above range, did not effect the deposition rate of the silicon nitride.

Nitrogen - The nitrogen used is obtained from a liquid source that is 99.999% pure. The nitrogen is supplied by Air Products Company. Experiments were performed with no nitrogen flowing (other than the nitrogen present in the silane tank) and with 8.0 l/min flowing. No effect on the deposition rate, within this range, was observed.

3.0 DEPOSITION PROCEDURE

The procedure for the deposition of silicon nitride films is:

1. Clean and load wafers.
2. Pre-heat wafers and check temperature.
3. Silicon nitride deposition.
4. Flush, cool down and unload wafers.
5. Evaluation of silicon nitride films.

The glassware must be cleaned periodically using the standard HNO_3 -HF acid solutions. The susceptor must be cleaned and fired prior to the first use.

3.1 Clean and Load Wafers

If the silicon nitride is deposited as part of the MNOS process, then the wafers are not cleaned prior to loading in the reactor. Rather, they come directly from the oxide furnace and are loaded into the reactor. Alternately, the thermal oxide ($100\text{--}500\text{ \AA}$) can be grown in the reactor prior to the silicon nitride

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deposition. If this is the case, the oxide should be evaluated using C-V monitoring to determine the level of ionic contamination (N_a^+ ions) present in the reactor system.

If the silicon nitride is deposited as a diffusion mask or a passivating layer, than a standard pre-diffusion clean involving HNO_3 and H_2SO_4 with deionized water rinses would be used.

3.2 Pre-Heat Wafers

The wafers are pre-heated in a nitrogen atmosphere to the desired temperature (See Fig. 1), and using an optical pyrometer, the flat zone is checked. The temperature is to be controlled to $\pm 5^\circ C$ over the required flat zone. The time required for the pre-heat depends on the r-f generator and coils. This will insure a film thickness variation of $\pm 150 \text{ \AA}$ across a 1.3" wafer. If the thermal oxide is grown in the reactor to give the MNOS structure, then the oxidation is done after the pre-heat. The oxidation would be accomplished with 100% dry O_2 . The reactor would then be flushed with nitrogen prior to introducing the silane-ammonia mixture.

3.3 Silicon Nitride Deposition

The deposition rates are given in figure 2. It was found that if the total flow rate through the reactor is in the 20-30 l/min range, then film thickness variations across the wafer and along the susceptor will be minimum. The curves indicate for two flow rates of SiH_4 the deposition rate of Si_3N_4 versus temperature. The actual values used should be chosen so that the length of the deposition is at least ten minutes. This insures a minimum variation in film thickness due to timing errors. The higher silane flow rate indicates that the deposition rate becomes less sensitive to temperature as the temperature is increased. Unfortunately,

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the deposition rates here are too high for MNOS applications since the deposition time would be 3-4 minutes to give 750-1000 Å of silicon nitride.

3.4 Flush, Cool Down and Unload Wafers

The flush, with power-on, is for one minute with 100% N₂ flowing. Then the power is turned off and the wafers are allowed to cool in a 100% N₂ atmosphere for five minutes.

In the MNOS process, the silicon nitride must be covered with a metal or a deposited oxide for use as an etchant mask. This will be discussed in more detail in Section 4.0. If a silane or carbon dioxide process is used for depositing the SiO₂ film, then it would be accomplished after the flush (the flush would have to be 5 minutes) and followed by the cool-down. The deposition temperatures are consistent for the silicon nitride and the silica processes.

3.5 Evaluation of the Silicon Nitride Film

The film thicknesses are evaluated by Talysurf measurement or by the Tolansky technique. A color chart is included as Table 1. This can be used when a standard thickness is grown repeatedly and thickness is not important. For MNOS processing the Talysurf technique is recommended. If the silicon nitride is covered over with a silica film before removing from the reactor, then the film can be etched away prior to measurement of the silicon nitride film thickness.

If the silicon nitride film is used for a MNOS device, then periodic C-V monitoring of the process is essential. This insures that ionic contamination remains within acceptable limits.

4.0 SELECTIVE ETCHING OF SILICON NITRIDE

Silicon nitride cannot be etched using the standard buffered HF etchants. It

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etches slowly in full strength HF, but photoresist does not hold up. It etches well in hot phosphoric acid, but photoresist does not hold up. As a result, some mask other than photoresist must be used to allow selective etching of Si_3N_4 with phosphoric acid. Two techniques have been successful; i.e., gold or silica films. The silicon nitride is over-coated with gold or a silica film, and using photoresist the desired pattern is etched. The photoresist is then removed and the silicon nitride is etched in hot orthophosphoric acid ($T = 180^\circ\text{C}$). The etch rate is $125 \text{ \AA}/\text{min}$. The etch rate is dependent on the percentage of water present in the orthophosphoric acid. Since the water is slowly evaporated from the solution at 180°C , the etchant must be replaced frequently or some means of restoring the water to the solution should be provided. Placement of a watch glass over the beaker is the simplest technique. Use of a quartz beaker is recommended to minimize beaker breakage at temperatures of 180°C .

5.0 PROPERTIES OF SILICON NITRIDE DEPOSITED FILMS

Dielectric Strength ⁸	$9.3 \cdot 10^6 \text{ V/cm}$
Dielectric Constant	6.5
Index of Refraction	1.97
Absorption Band	10-14 microns

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"COLOR" THICKNESS

SiO₂ COLOR GAUGE

Si₃N₄ COLOR GAUGE

<u>Thickness Å</u>	<u>Color</u>	<u>Thickness Å</u>	<u>Color</u>
475	light brown	100	very light brown
685	darker brown	170	medium brown
840	brown purple	250	brown
895	light purple	340	brown-pink
1024	dark purple	350	pink-purple
		430	intensive purple
		525	intensive dark blue
1105	purple-dark blue		
1230	dark blue	600	darker blue
1470	light blue	690	medium blue
1500	very light blue	950	light blue
1770	very light yellow		
1950	light yellow	1050	very light blue
1951	light medium yellow	1150	light blue-brownish
		1250	light brown yellow
2100	yellow	1350	very light yellow
2155	dark yellow	1450	light yellow
2359	yellow pink	1550	light to medium yellow
2563	petal pink	1650	medium yellow
2766	magenta	1750	intensive yellow
2969	purple	1850	intensive yellow pink
3078	purple blue		
3173	blue purple		
3488	hunter green		
3693	yellow green		

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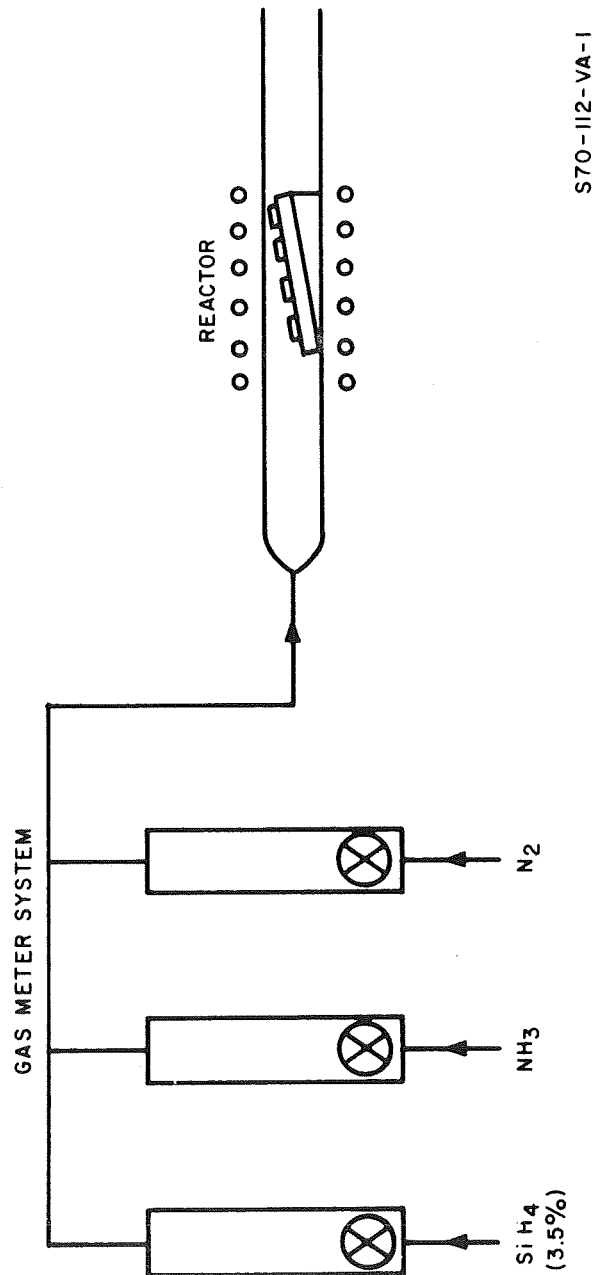


Figure 1. Block Diagram of Silicon Nitride Deposition System

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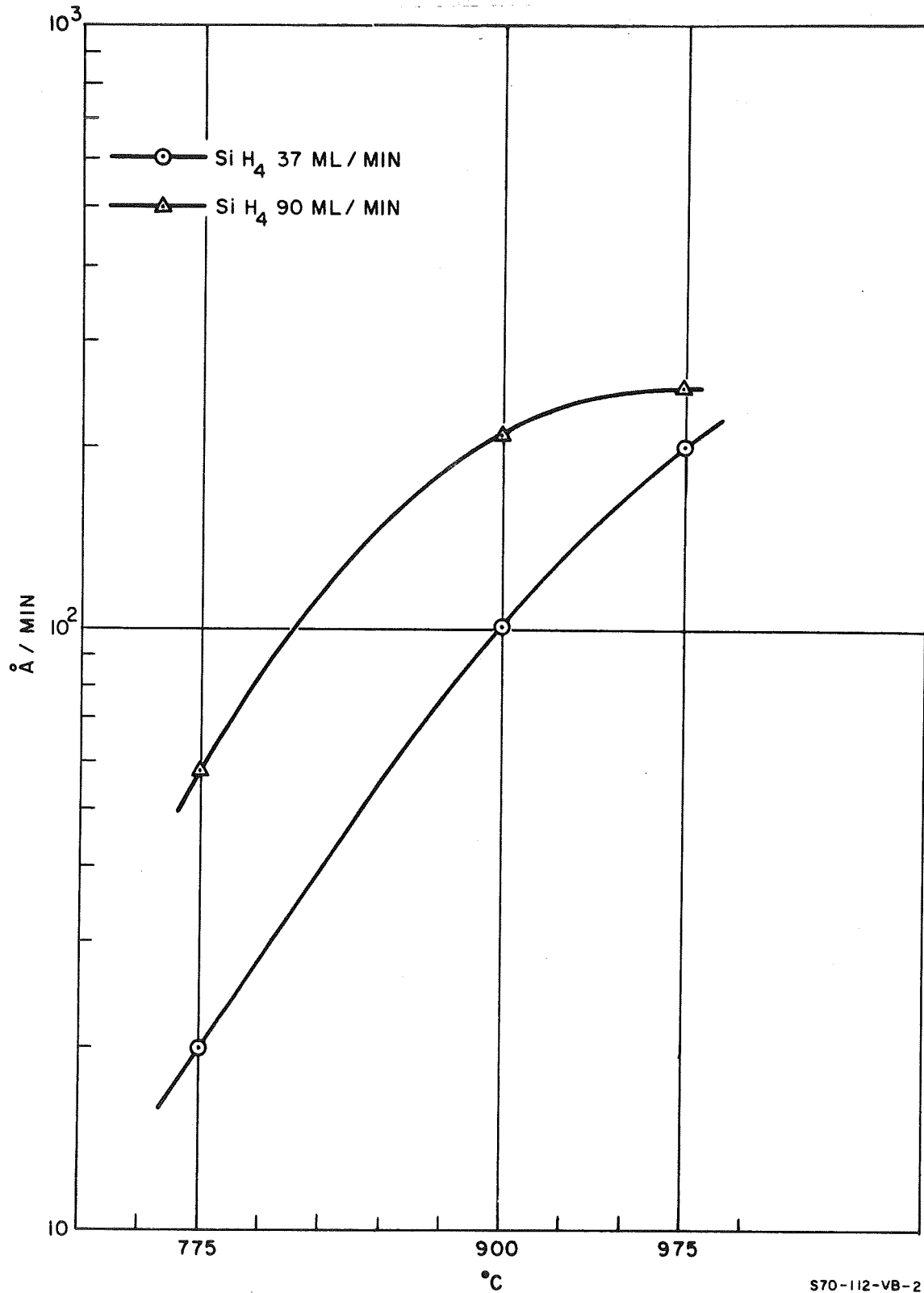


Figure 2. Silicon Nitride Deposition Rate vs. Temperature.

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