1989

Radiotracer measurements of sodium ion penetration at low temperature (200°C to 500°C) through thin (approximately one micron) films of chemical vapor deposited silicon oxynitride and phosphosilicate glass

Samuel Vance Dunton
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Radiotracer measurements of sodium ion penetration at low temperature (200°C to 500°C) through thin (approximately one micron) films of chemical vapor-deposited silicon oxynitride and phosphosilicate glass

Dunton, Samuel Vance, M.S.

San Jose State University, 1989

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RADIOTRACER MEASUREMENTS OF SODIUM ION
PENETRATION AT LOW TEMPERATURE (200°C TO 500°C)
THROUGH THIN (APPROXIMATELY ONE MICRON)
FILMS OF CHEMICAL VAPOR DEPOSITED
SILICON OXYNITRIDE AND PHOSPHOSILICATE GLASS

A Thesis

Presented to

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San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

By

Samuel Vance Dunton

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APPROVED FOR THE DEPARTMENT OF CHEMISTRY

Dr. Alan Campbell Ling

Dr. Karen Singmaster

Drs. Wilbert van den Hoek

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[2]	$\text{SiH}_{4(g)} + 2\text{O}_{2(g)} \text{-----> SiO}_{2(s)} + 2\text{H}_2\text{O}_{(g)}$	3
[3]	$3\text{SiH}_{4(g)} + 4\text{NH}_{3(g)} \text{-----> Si}_3\text{N}_{4(s)} + 12\text{H}_{2(g)}$	3
[4]	$3\text{SiCl}_2\text{H}_{2(g)} + 4\text{NH}_{3(g)} \text{-----> Si}_3\text{N}_{4(s)} + 6\text{HCl}_{(g)} + 6\text{H}_{2(g)}$	3
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[20]	$\partial C / \partial t = D (\partial^2 C / \partial X^2)$	24
[21]	$C = [A/(t)^{1/2}] \exp(-X^2/4Dt)$	25
[22]	$M = \int_{X=0}^{\infty} C dX$	25
[23]	$X^2/4Dt = \xi$	25
[24]	$dX = 2(Dt)^{1/2} d\xi$	25

[25]	$M=2A(D)^{1/2} \int_0^t \exp(-\xi^2) d\xi = 2A(\pi D)^{1/2}$	25
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ABSTRACT

RADIOTRACER MEASUREMENTS OF SODIUM ION PENETRATION AT LOW TEMPERATURE (200°C TO 500°C) THROUGH THIN (APPROXIMATELY ONE MICRON) FILMS OF CHEMICAL VAPOR DEPOSITED SILICON OXYNITRIDE AND PHOSPHOSILICATE GLASS

by Samuel Vance Dunton

thesis advisor: Alan Campbell Ling

Radiotracer measurements of Na^+ diffusion in thin films (approximately one micron) of silicon oxynitride (SiON) and phosphosilicate glass (PSG) were evaluated at low temperature (200°C - 500°C) by $^{22}\text{Na}^+$ depth profiling. $^{22}\text{NaCl}$ solutions were deposited on film surfaces and annealed into the films. Subsequent etching of the films in steps of known thickness and counting of radioactive decay from ^{22}Na imbedded in the glass allowed determination of the Na^+ depth profile. $^{22}\text{Na}^+$ depth profiles in SiON were described by a fast long range diffusion and a slower short range diffusion that was related to the density of the glass. $^{22}\text{Na}^+$ depth profiles in PSG revealed that films containing greater amounts of pentavalent phosphorus permitted increased amounts of Na^+ to permeate. However, an activation energy plot revealed that the pentavalent phosphorus moiety immobilizes (getters) migrating sodium ions, increasing the activation energy requirement for diffusion to occur.

Introduction

1. The Problem

The purpose of this study was to evaluate the sodium ion migration at low temperature (200°C - 500°C) in thin (approximately 1-μm) films of phosphosilicate glass and silicon oxynitride. A comparison was made of the diffusivity of Na⁺ through different atomic compositions of silicon oxynitride (SiO_xN_y:H₂) films deposited by plasma-enhanced chemical vapor deposition (PECVD). Measurements of sodium penetration through different compositions of phosphosilicate glass (PSG) films deposited by either PECVD, or atmospheric pressure chemical vapor deposition (APCVD) or low pressure chemical vapor deposition (LPCVD) were made to evaluate the effect of the phosphorus on the ability of phosphosilicate glass to immobilize Na⁺ ions.

1.2 Chemical Vapor Deposition

Chemical vapor deposition (CVD) is a process by which a solid product is deposited onto a substrate by means of a chemical reaction from gas phase reactants. Gaseous products may also be formed in the reaction (Kern and Rosler, 1977).

CVD reactions are used to form glasses used as thin film dielectric layers in integrated circuits. Silane (SiH₄) and oxygen (O₂) are used to form thin films of silicon dioxide; silane or dichlorosilane (SiCl₂H₂) and ammonia (NH₃) are used to form thin films of silicon nitride. Silane and oxygen react spontaneously to form silicon dioxide and water vapor:

This reaction is often employed to deposit thin films of silicon dioxide for fabrication of a dielectric layer in an integrated circuit. The reaction can be performed in an atmospheric pressure chemical vapor deposition (APCVD) reactor, which is an open vessel that introduces SiH_4 and O_2 through separate manifolds, to a heated (usually 400°C) surface, such as a silicon wafer, forming a SiO_2 layer. The reaction takes place under a shroud of inert gas so as to prevent unwanted oxidation of the silane by ambient oxygen. CVD of SiO_2 may also be done in a chamber at reduced pressure (30 - 500 millitorr), thus minimizing incorporation of contamination dust or other unwanted particles into the deposited layer. This reaction is commonly referred to as low pressure chemical vapor deposition (LPCVD).

The deposition of thin films of silicon nitride (Si_3N_4) from silane and ammonia

or dichlorosilane and ammonia,

requires temperatures in excess of 800°C . In the process of making an integrated circuit on a silicon substrate, dielectric films are often deposited on a wafer that has aluminum patterns on it. In order to reduce the substrate temperature so as not to melt the aluminum, the deposition reaction is driven by electronic excitation rather than thermal excitation. This

is accomplished by the application of radiofrequency power to the reactor, with the pressure of the gases adjusted to maintain a plasma. This type of reaction is referred to as plasma-enhanced chemical vapor deposition (PECVD). As illustrated in the expression below, PECVD of silicon nitride does not necessarily result in stoichiometric Si_3N_4 :

The exact stoichiometry of the deposited $\text{Si}_x\text{N}_y\text{H}_z$ film depends on the substrate temperature, the reactant gas flow rate ratios, the rf frequency and power, the reactor pressure and the presence (if any) of diluent gases. Atomic percents of H as high as 30% have been reported (Kanicki and Voke, 1986).

PECVD is used in addition to LPCVD and APCVD for deposition of thin films of SiO_2 . For PECVD SiO_2 films, either nitrous oxide (N_2O) or nitric oxide (NO) is usually substituted for O_2 :

Hydrogen is also present in these films (Adams, Alexander, Capio, and Smith, 1981).

1.2.1 Chemical Vapor Deposited Silicon Oxynitride

Silicon oxynitride films are formed in LPCVD by addition of an oxygen source such as nitrous oxide to the silicon nitride deposition reactions:

PECVD is also used to deposit silicon oxynitride. As in the LPCVD reaction, PECVD silicon oxynitride is formed by addition of an oxygen source such as nitrous oxide to the silicon nitride deposition reaction,

(For brevity, the films in the family $\text{SiO}_x\text{N}_y\text{:H}_z$ will be subsequently referred to as SiON.)

The atom percent Si, O, N, and H in the deposited films depends on the reactant gas flow rate ratios, the pressure of the reactor, substrate temperature and rf frequency (van den Hoek, 1986). Typical reaction conditions are: temperature: 250°C - 400°C; pressure: 0.5 - 3.0 torr; rf frequency: 13.56 MHz or 50 - 450 kHz (Claasen, 1987). Reactant gas flow rate ratios are usually such that the partial pressure of SiH_4 seldom exceeds five to ten percent of the total reactant gas mixture (van den Hoek, 1986; Dennise, Troost, Elferink, Habraken, van der Weg, and Hendricks, 1986).

1.2.2 Phosphosilicate Glass

Phosphosilicate glass, or PSG, is made by the addition of phosphine (PH₃) to the CVD SiO₂ reactant gas mixture:

in the case of APCVD and LPCVD reactions (Kern, Schnable, and Fisher, 1976), and

and

for PECVD (Chiu, Snow, and Dunton, 1985). As in the case of the undoped oxides, the composition of the deposited PSG films does not necessarily reflect the stoichiometric ratio of the partial pressures of the reactant gases; substrate temperature, reactor pressure (for LPCVD and PECVD processes), and rf frequency (PECVD) as well as rf power (PECVD) all affect the composition of the deposited film. The phosphorus may exist in either the trivalent (P₂O₃) or pentavalent (P₂O₅) form, or some combination. Hydrogen has been detected in the CVD PSG films, although it may be mostly from unreacted PH₃ (Xie, Murarka, Guo, and Lanford, 1988).

1.3 Need for the Study

1.3.1 Chemically Vapor Deposited Dielectrics in Integrated Circuits

Insulating films are usually deposited on top of a semiconductor device in order to protect its surface, or to serve as masks through which selective diffusions and implants can be made. They also serve as the base for electrical connections between semiconductor devices in a microcircuit. Often they provide the role of an interlayer dielectric between two levels of metallization. In all these situations, it is desirable that they be free from pinholes and cracks, both when grown, and also if subjected to heat treatments during subsequent processing. Thus their built-in stress, as well as the stress during thermal cycling, must be sufficiently low to maintain their integrity. Deposited films are used to block the movement of light alkali ions such as sodium, or else getter them so as to render them immobile. These requirements become increasingly important in Very Large Scale Integration (VLSI) technology (in which the circuit has over 10,000 gates, or transistors), as the wafer size increases and integrated circuit devices become more densely packed (Pramanik, 1988; Ghandi, 1983, p. 420). Alkali ions are incorporated into the device during or subsequent to its fabrication. Such alkali ion contaminants act as charge carriers in the isolation dielectric layers. Light alkalis, which are mobile in these layers, can be deleterious to the electrical performance of the device. Sodium is of particular concern because of its ubiquity in the fabrication environment.

Most of the deposited dielectrics appear in the device fabrication sequence subsequent to the deposition of at least one metallization layer. The metallization is nearly always aluminum or some alloy of aluminum, neither of which may be exposed to excessive (>500°C) temperature, or else solid state reactions between aluminum and silicon (or SiO₂) begin to exert deleterious effects on devices (Kern, *et al.*, 1976). Even exposure of the

wafers to elevated temperatures below 500°C will increase the tendency of the thin films of aluminum to relieve thermal and thermally-induced mechanical stresses by formation of large vertical features called hillocks (van der Ven, Martin, and Berman, 1987). Ideally, all wafer processing subsequent to the application of a metallization should be performed at room temperature. However, because such critical properties of the CVD dielectric films as density, electrical stability, and chemical stability are improved as the deposition temperature increases, elevated temperatures are required. Typical deposition temperatures range from 250°C to 450°C for PECVD dielectrics (Snow, 1987; Pramanik, 1988) and 400°C to 450°C for LPCVD and APCVD oxides (Pramanik, 1988; Kern, *et al.*, 1976).

Figure 1 shows a cross sectional diagram of a complementary metal- oxide-semiconductor field effect transistor (MOSFET) architecture (Dell'Oca, 1985). The MOSFET device is fabricated from the bottom, with the passivation dielectric being the final layer added to the structure. The purpose of the passivation dielectric is to provide mechanical and chemical protection at the outer surface. Depending on what material is used, the passivation dielectric either blocks the movement of light alkali ions such as sodium, or else getters them so as to render them immobile. SiO₂ and PSG layers are frequently used as interlayer dielectrics, which serve as a base for electrical connections between semiconductor devices in a microcircuit (Ghandi, 1983, p. 420).

1.3.2 Chemical Vapor Deposited Phosphosilicate Glass in Integrated Circuits

Deposited phosphosilicate is often used as a contact-glass layer material. Depending on the amount of P in the glass, these "doped oxide" materials will flow when exposed to temperatures from 900°C to 1000°C, compared to 1600°C - 1700°C for deposited "undoped" SiO₂ (Schnable, Kern, and Comizzoli, 1975). A reduced flow temperature is a

desirable property for contact glass in integrated circuits, as the contact layer glasses must be flowed so as to form a smooth contour over vertical topographies. Deposited films of PSG also have the desirable property of having lower intrinsic stresses than undoped SiO_2 , and so they are often used as interlayer and protection dielectrics (Schnable, *et. al*, 1975). They have also been shown to getter, or immobilize, sodium ions (Kern and Schnable, 1982; Sato, Abe, and Nishi, 1969).

1.3.3 Plasma-Enhanced Chemical Vapor Deposited Silicon Oxynitride Films in Integrated Circuits

Deposited silicon oxynitride thin glass films are sometimes used as passivation dielectric (van den Hoek, 1986) and intermetal dielectric layers (Ray Marcoux, 1987). As a substitute for PECVD silicon nitride, they offer reduced stress (Claasen, 1987) and greater electrical stability (Takasaki, Koyama, and Takagi, 1980). Depending on the composition, they are transparent to near-ultraviolet (UV) radiation, whereas PECVD Si_3N_4 is opaque. This is an important consideration for UV-erasable, programmable read-only memory (EPROM) devices (van den Hoek, 1986). As a substitute for deposited silicon oxide, they offer greater mechanical and chemical protection (Thanh, Exner, and Balk, 1987).

1.3.4 Sodium Ion Contamination

The presence of charged, mobile ion species in integrated circuit devices can lead to charge instability mechanisms such as ionic drift, polarization and electronic trapping (Kerr, 1970). All of these effects are directly related to the reliability of MOSFET devices. Sodium is particularly important; its small ionic radius leads to ease of migration, and it is ubiquitous in the environment.

Figure 1: Diagram of CMOS integrated circuit architecture . PSG layer is used as electrical isolation between metallization and polysilicon gate (labelled "Si"). Intermetal dielectric provides isolation between metal layers. Passivation dielectric provides underlying circuitry with chemical and mechanical protection. Any of the following (or layered combinations thereof) are commonly used as intermetal dielectric and passivation dielectric materials: PECVD PSG, PECVD SiO₂, PECVD SiON, LPCVD PSG, LPCVD SiO₂, APCVD SiO₂, and APCVD PSG. Also, PECVD Si₃N₄ may be used as a passivation dielectric. (From Dell'Oca, 1985).

Sodium ion diffusivity in thin films of SiO₂ formed by thermal oxidation of silicon substrates has been exhaustively studied by a variety of techniques (Frischat, 1968; Frischat, 1984; Schaeffer, Mecha, and Steinmann, 1979; Buck, Allen, Dalton, and Struthers, 1967). Radiotracer measurement has been used to study Na⁺ penetration in thin films of thermally deposited silicon nitride (Burgess, Baum, Fowkes, Holmstrom, and Shirn, 1969; Dalton and Drobek, 1968; Franz and Langheinrich, 1969).

Evaluation of Na⁺ diffusivity has been made as a function of film composition in thermally deposited (LPCVD) SiON films (Rand and Roberts, 1973), and as a function of the ratios of reactant gas partial pressures used for deposition in PECVD SiON films (Dunton, 1985). However, the problem of Na⁺ diffusivity in PECVD SiON as a function of film structure and composition has not previously been studied. The results of such a

study are timely and pertinent, as PECVD SiON films have recently come into use as protection dielectrics in integrated circuits (van den Hoek ,1986).

Measurements of Na⁺ diffusivity in PSG have been reported (Kern, *et al.*, 1982; Sato, *et al.*, 1969; Smith and Kuper, 1967; Elderidge and Kerr, 1971), however the literature is lacking in a comprehensive study of the effect of phosphorus content in the CVD glasses .

The literature contains hundreds of papers on the subject of field-assisted migration by Na⁺ ions in thin films of SiO₂. This is a critical phenomenon in the reliability of MOSFET devices. Kerr's review paper gives an overview of the issues involved in field-assisted migration. This research will be concerned only with the thermal migration of Na⁺ ions in deposited dielectrics. As the materials studied are not normally used as capacitance dielectrics in MOS devices, field-assisted Na⁺ migration in PECVD SiON and CVD PSG is beyond the scope of this research.

The purpose of this study was to evaluate the sodium ion migration at low temperature (200°C - 500°C) in thin (approximately 1-μm) films of phosphosilicate glass and silicon oxynitride in order to understand the relationships between the composition of PECVD silicon oxynitride and Na⁺ ion diffusion and to evaluate the effect of the phosphorus content on the ability of phosphosilicate glass to immobilize Na⁺ ions. Since most of the applications of the CVD dielectrics involve depositing them on the integrated circuit after metallization, they would not normally be exposed to temperatures exceeding the deposition temperature, which for most of the films was 400°C. This research was limited to a study of Na⁺ diffusivity at temperatures at or below 500°C, with most of the

measurements taken at 400°C. PSG films are often used as contact-glass layers, which are normally flowed at temperatures ranging from 900°C to 1000°C (Schnable, *et al.*, 1975). Taking this fact into consideration, some of the PSG films received a 30-minute densification at 1000°C prior to Na⁺ diffusivity measurements.

1.4 Review of the Literature

1.4.1 Ion Motion in Glass

The theory that both electrostatic forces and physical effects are involved when an ion migrates from one site to another in glass was elucidated by Anderson and Stuart (1954). The model that they presented for ion migration in glass involved an activation energy with two terms: the energy required to move the ion and the strain required to deform the structure enough to allow the ion to pass. The authors referred to these as the electrostatic binding energy, and the elastic strain energy, respectively.

More recently, two comprehensive reviews have appeared on the cation diffusion in glass. Frischat (1975) reviewed in detail experimental techniques used in evaluation of ion diffusion in glass. Hundreds of values were reported for metal ion diffusion coefficients in different glasses. Ingram (1987) discussed recent advances in the understanding of ionic conductivity in glass. According to Ingram, three themes recur during discussion of ionic conduction processes in glass:

1. the above-mentioned Stuart-Anderson approach;
2. a "weak electrolyte theory", in which the $M_2O \rightleftharpoons M^+ + MO^-$ equilibrium exists, (where M⁺ represents a metal ion);

3. a defect hypothesis, in which ions hop directly between sites, displacing a cation from a neighboring site.

1.4.1.i The Anderson-Stuart Approach to Ion Diffusion in Glass

This approach considers the electrostatic energy and strain energy required to move an ion from one site to another. The total activation energy (E_a) for ion transport is described by the equation,

$$E_a = (\beta z z_o e^2) / \gamma (r + r_o) + 4\pi G r_d (r - r_d)^2, \quad [14]$$

where

- β = a "lattice parameter" that depends on the distance between the neighboring sites,
- z = the charge of the migrating cation,
- z_o = the charge of the oxygen ion (2^-),
- e = the electronic charge,
- γ = the covalency parameter, described as the ability of the electron clouds of the oxygen atoms to resist spatial distortion in the presence of positive ions
- r = the ionic radius of the migrating cation,
- r_o = the radius of the oxygen ion,
- G = the elastic modulus of the glass
- r_d = the radius of the normal doorways in the glass

The first term on the right hand side of equation 14 refers to the electrostatic energy and the second term to the strain energy. A pictorial representation of the migration described by Anderson and Stuart is shown in Figure 2.

Figure 2: Anderson-Stuart model for cation migration in glass (Anderson and Stuart, 1954). In the model, diffusing cations (M^+), represented with the shaded circle, are held by electrostatic attraction to electronegative nonbridging oxygens (NBO^-), which are represented by large open circles. The network forming atoms are represented with small, filled circles. In order that the cation M^+ is free to migrate from one site to another, it must have enough energy to overcome the coulombic attraction to the NBO^- . There must also be an open pathway large enough for the cation M^+ to pass through. If the pathway is too small, then extra energy will be required to overcome the lattice strain in the network so that a pathway may be opened. Following passage through the doorway, M^+ will be electrostatically attracted to another NBO^- . (The radii of the open, shaded and closed Figures are approximately to scale for representation of oxygen, silicon, and sodium ions, respectively. Arrows are shown to represent motion.)

1.4.1.ii The Weak Electrolyte Theory of Ion Diffusion

In weak electrolytes (solid or liquid), the number of mobile ions per unit volume is less than the total concentration of ions. The number of cations free to diffuse can be thought of

in terms of an equilibrium between free metal oxide molecules (M_2O), and their ionization products: metal bound to oxygen (MO^-) and the free ion (M^+):

Figure 3: The weak electrolyte theory for cation migration in glass (Ingram, 1987). Small closed circles represent the network silicon atoms and large open circles represent network oxygens. The shaded circles represent metal ions. As in Figure 2, the network formers and migrating cations are represented to scale for silicon, oxygen and sodium, respectively. The M_2O structure is too bulky to migrate through available interstitial pathways. However, the dissociation product $*M^+$ is free to migrate. The asterisk is shown to denote the diffusing species.

This model was specifically discussed for the case of Na^+ ion diffusion in sodium silicate glass (Na_2O-SiO_2), based on the observation that large increases in conductivity were paralleled by large increases in Na_2O activity. The model implies that Na^+ ion mobility is subject to the rate constant of the forward reaction in equation 15.

1.4.1.iii The Defect Hypothesis for Ion Diffusion in Glass

In this scenario, cations may migrate by a direct interstitial mechanism, either by hopping directly between connected interstitial vacancy sites, or by an interstitialcy mechanism. Preferential migration pathways are suggested to be connected vacancies or surfaces between phase boundaries. Based largely on his own published research, Ingram described the interstitialcy diffusion process as a pair-wise mechanism for exchange of interstitial cations, in which a migrating cation displaces another cation from a neighboring site. This effect is illustrated by the mechanism:

for the case in which sodium is the diffusing species, where the subscripts (1,2, and 3) represent single Na^+ ions in the glass matrix, the (*) symbol represents the interstitialcy, and parenthesis are shown around the Na^+ ions undergoing pair-wise exchange. A common thread in all three (Anderson-Stuart, weak electrolyte and defect) of the themes) is that the cations migrate, or hop, in a step-wise manner.

1.4.2 Strained Mixed Cluster Model for Glasses

In the review paper, Ingram (1987) also discussed Goodman's hypothesis that glasses are comprised of a mixture of bound clusters. According to the hypothesis, as glasses are cooled from a melt, agglomerations of strained mixed clusters are generated and broken up, eventually forming a random strained mixed cluster network with residual liquid distributed within the interstices of the space filling network. On cooling, the residual liquid solidifies into a highly disordered phase (connective tissue), imparting increased ionic mobility to the glass (Goodman, 1985) .

Figure 4: (above) The defect hypothesis for cation migration in glass: interstitialcy mechanism. According to the hypothesis, ion migration, or "hopping" occurs in a pair-wise manner (Ingram, 1987). An interstitialcy may occur at a nonbridging oxygen or a bridging oxygen. Small closed circles represent the network silicon atoms and large open circles represent network oxygens. The shaded circles represent metal ions. As in Figures 2 and 3, the network formers and migrating cations are represented to scale for silicon, oxygen and sodium, respectively. The symbols (M1, M2, and M3) denote cations in the glass matrix, the (*) symbol represents the interstitialcy, and parenthesis are shown around the Na^+ ions undergoing pair-wise exchange.

Figure 5: (above) Pictorial representation of the strained mixed cluster model for glasses (Goodman, 1985). On cooling, the melt gradually condenses into a mixture of clusters and residual liquid. At room temperature (RT), the residual liquid solidifies into a disordered cluster-connecting phase.

1.4.3 Sodium Ion Diffusion in Glass

1.4.3.i Sodium Ion Diffusion in Silicon Dioxide

Frischat (1968) evaluated Na^+ diffusion at 170°C to 1000°C in bulk SiO_2 by $^{22}\text{NaCl}$ radiotracer depth profiling. Below about 600°C, two diffusion processes were observed. It was suggested that the appearance of the second diffusion process was due to changes in the structure of the glass near 250°C and 573°C, the temperatures at which the transitions between different phases of quartz and different phases of crystalline SiO_2 occur, respectively. The activation energies for the two processes were 4.7 kcal/mol at 573°C and 2.5 kcal/mol at 250°C. It was pointed out that this effect must result from the presence of a second phase, or, as he termed it, the influence of a considerable amount of "quartz-like" precrystalline elements in the glass, which were labelled as "melting relics". The argument is similar to the presentation by Goodman (1985) in which the existence of strained mixed clusters is proposed. Frischat's "melting relics" can be thought of as being analogous to Goodman's solidified residual liquid. In a later paper (1984), Frischat argued that electron microscopic evidence for inhomogeneity on a fine scale in silica glasses made from quartz can be taken as a confirmation of the conclusions of the earlier paper, that the appearance of a second phase is responsible for anomalous diffusion of Na^+ in SiO_2 .

Schaeffer, *et al.*, (1979), using $^{22}\text{Na}^+$ as a radiotracer, measured mobilities of sodium ions in various types of SiO_2 glasses at temperatures between 420°C and 770°C. The ^{22}Na concentration profiles revealed two diffusion processes: a short-range profile characterized by the immobilization of large concentrations of Na^+ near the glass surface and a long range profile characterized by permeation of relatively small amounts of Na^+ in the underlying bulk. Tracer experiments with radioactive chlorine (Na^{36}Cl) revealed that the diffusion rate of Cl^- was even slower than the short range diffusivity of Na^+ . It was argued that this

ruled out the possibility that the short range Na^+ profile was due solely to the slower diffusion rate of the charge-balancing Cl^- ions. Reporting an energy of activation for the short range Na^+ diffusion of 8 kcal/mol, the authors suggested that the short range diffusion can be characterized as a reaction between Na_2O and SiO_2 in forming Si-O-Na units. The origin of the Na_2O moiety was not discussed. The long range diffusivity was assumed to be an isotopic exchange reaction with $^{23}\text{Na}^+$ impurity in the glass, as well as with H^+ contributed by Si-OH groups.

Rothman, Marcuso, Nowicki, Baldo, and McCormick (1982) reported long and short range diffusion profiles obtained for K^+ , Rb^+ and Cs^+ diffusion at 300°C to 1000°C in vitreous silica. It was found that the diffusion rate of the alkali metal ions decreased strongly with increasing ionic size. The diffusion coefficient D was found to be largely dependent on the ionic radius of the diffusing species. This dependence was said to be due to changes in the activation enthalpy and to changes in the preexponential term D_0 . The latter term was argued to depend on the number density of connected interstices of minimum size necessary for ion transport.

1.4.3.ii Sodium Ion Diffusion in Silicon Nitride

Burgess, *et al.* (1969) measured Na^+ diffusion at 500°C into structures of 1000 Å of Si_3N_4 deposited over 2000 Å of thermally grown SiO_2 . Si_3N_4 layers deposited by LPCVD at 1000°C and 1100°C were evaluated, as were Si_3N_4 layers deposited by PECVD at 850 °C. The Na^+ was delivered to the film surfaces as aqueous $^{22}\text{NaCl}$ by deposition from a micropipet. It was found that the ^{22}Na concentrations in the Si_3N_4 layers were ten to one hundred times greater than in the underlying SiO_2 layers, indicating Na^+ immobilization in the Si_3N_4 layers. The percent of ^{22}Na immobilized was greater in the Si_3N_4 films deposited at lower temperatures, even though these films had lower densities.

This was attributed to the presence of nitrogen vacancies in the Si_3N_4 network behaving as electron traps. The authors suggested that the nitride layers that were deposited at lower temperature possessed more of these electron traps, enabling immobilization of greater amounts of Na^+ . It was also found that if the diffusion anneals were carried out in wet nitrogen, greater amounts of Na^+ were released from the Si_3N_4 into the underlying SiO_2 layer. The authors postulated that moisture had the effect of neutralizing the electron trapping centers, permitting more sodium to move into the underlying SiO_2 .

Dalton, *et al.* (1968) evaluated $^{22}\text{Na}^+$ diffusion at 600°C into Si_3N_4 films prepared under a variety of conditions. Electron diffraction studies revealed that the silicon nitride films possessed crystallites varying considerably in size and structure, ranging from less than $10 \text{ \AA}$ to approximately $100 \text{ \AA}$. The ability of the Na^+ to penetrate the silicon nitride films was found to be related to the size of the crystallites size. Sodium was found to diffuse more easily into films containing larger crystallites, suggesting that diffusion of Na^+ occurred along continuous paths formed by grain boundaries.

Franz, *et al.* (1969) evaluated Na^+ diffusion at 800°C and 1100°C into pyrolytically deposited Si_3N_4 films by diffusion of $^{24}\text{Na}^+$ directly into the films and by neutron activation of contaminant $^{23}\text{Na}^+$ ions unintentionally incorporated in the film during deposition. The mobility of Na^+ rose suddenly between 900°C and 1000°C . The authors suggested that this may have been due to the formation silicon nitride crystallites. Neutron activation experiments were performed with SiO_2 thermally grown from the Si substrate and structures of Si_3N_4 deposited over the SiO_2 . The $^{24}\text{Na}^+$ depth profiles of the dual layer structure revealed lower Na^+ concentrations than in the single layer SiO_2 film, and a

uniform distribution of Na^+ in the Si_3N_4 . This suggested that the Na^+ was gettered into the Si_3N_4 overlayer. No explanation was offered for this observation.

1.4.3.iii Sodium Ion Diffusion in Silicon Oxynitride

Rand, *et al.* (1973) evaluated Na^+ diffusivity in LPCVD SiON films. $^{22}\text{NaCl}$ was diffused at 600°C into SiON films with different atom compositions. $^{22}\text{NaCl}$ depth profiles were taken to depths of $1000 \text{ \AA}$ into the films. Autoradiographs revealed small "hot spots" surrounded by a depletion zone, and less often, the reverse. The patterns were still present after etching away a third of the film. Electron diffraction showed no ordering over $20 \text{ \AA}$, indicating that the films were amorphous. The authors suggested the hot spots were possibly at areas of inchoate crystallinity in the film.

Dunton (1985) measured Na^+ penetration at 500°C into PECVD SiON as a function of the ratios of the process gases used for film deposition, and into PECVD Si_3N_4 . Long and short range diffusivities, similar to those reported by Schaeffer, *et al.* (1982) and Rothman, *et al.* (1979), were observed in the SiON films. A SiON film with a refractive index of 1.67 was found to be most resistant to long range Na^+ penetration. However, the structure and composition of the films were not reported.

1.4.3.iv Sodium Ion Diffusion in Phosphosilicate Glass

Smith, *et al.* (1967) performed neutron activation depth profiling, C-V measurement $^{22}\text{Na}^+$ radiotracer evaluations of Na^+ migration in PSG ($6-8 \times 10^{21} \text{ P atoms per cm}^3$) films formed over SiO_2 . The PSG films were formed by glassing (diffusing P_2O_5 into the SiO_2). Their examinations revealed that the migrating Na^+ ions preferentially segregated into the PSG phase. They also evaluated the gettering of Na^+ in films with $1350 \text{ \AA}$ of

PSG ($2 - 5 \times 10^{18}$ P atoms/cm³) over 4650 Å of SiO₂, by contamination with NaBr. Higher concentrations of Na⁺ were found throughout the PSG layers in films that were contaminated after glassing with P₂O₅ (8×10^{20} Na⁺/cm³) than in similar films that were contaminated before glassing (2×10^{18} Na⁺/cm³).

Buck, *et al.* (1967) also reported preferential segregation of Na⁺ into PSG from neutron activation and ²²Na radiotracer studies of Na⁺ diffusion at 600°C in a PSG/SiO₂/Si structure. PSG overlayers were formed by exposing thermally grown SiO₂ to P₂O₅ vapor. The influence of an electric field on the tracer sodium in the PSG/SiO₂/Si structure was compared to that of an SiO₂/Si structure. Electrodes consisted of the boron-doped silicon substrate and square gold dots deposited on the surface of the overlayers. Each gold dot was biased at + 4-volts with respect to the Si substrate for 1-minute. Charging currents were detected in the SiO₂/Si structure, and autoradiographs revealed that after application of 4 volts for 1 minute, all the ²²Na had accumulated in areas under the gold dots. However, in the PSG/SiO₂/Si structure, no charging currents were detected, and the area distribution of ²²Na was uniform. Depth profiling and radiochemical counting revealed that more than 99% percent of the ²²Na was retained in the PSG overlayer, leading the authors to the conclusion that the Na⁺ was quickly and uniformly absorbed into the PSG, where it remained immobilized.

Sato, *et al.* (1969) studied ²²Na⁺ migration into a PSG/ SiO₂ structure formed by chemical vapor deposition (CVD) of PSG over thermally grown SiO₂. The ²²Na⁺ depth profile revealed higher concentrations of Na⁺ in the PSG overlayer, a phenomenon that the authors termed partitioning. Na⁺ segregation coefficients were measured, with the amount of Na⁺ segregated into the PSG overlayer linearly proportional to the phosphorus content of the overlayer. However, when the same ²²Na⁺ contaminated films were

subjected to an electric field of 5×10^5 V/cm at 300°C for 60 minutes, it was found that the $^{22}\text{Na}^+$ in the underlying oxide layer piled up in the vicinity of the SiO_2/PSG interface, with no drift of $^{22}\text{Na}^+$ in the PSG overlayer.

Elderidge, *et al.* (1971) evaluated gettering of Na^+ by PSG as a function of the P content. PSG overlayers with different concentrations of P were formed by glassing of thermally grown SiO_2 with POCl_3 and/or P_2O_5 . Sodium was introduced to the surface of the PSG layer by evaporation of NaCl from a crucible. Field-assisted Na^+ drift was evaluated from 80°C to 350°C by capacitance-voltage (C-V) measurements. The authors presented a model for Na^+ migration in which the energy of activation for Na^+ migration increased with the amount of P_2O_5 in the film, when the sodium level was held constant, and for constant film composition, decreased with the amount of Na^+ contamination. It was found that the amount (N_i) of sodium transported through the PSG to the Si-SiO_2 interface could be represented by a potential energy well scheme in which the energy required for migration between adjacent wells is reduced by the presence of an external field,

$$N_i = N_o K_o \exp[(-E_a + qEW)/2kT] t^{1/2} \quad [17]$$

where N_o is the initial surface concentration of Na^+ , t is the diffusing time, K_o is a constant dependent on the PSG composition, E_a is the energy of activation for Na^+ emission from traps; q the electronic charge, E the strength of the external field and W the average width of a trap well, k the Boltzmann constant and T the temperature in Kelvin units.

Kern, *et al.* (1982) also reported preferential trapping of Na^+ into an APCVD PSG overlayer when a solution of $^{22}\text{NaCl}$ was deposited onto the surface of a PSG/thermal

oxide dual layer and annealed for 16 hours at 430°C. The authors found ^{22}Na preferentially segregated in the PSG overlayer.

1.5 Equations Describing Diffusion

1.5.1 Fick's Laws of Diffusion

Fick's Laws, which describe the movement of one material through another, have been used to describe the movement of cations through glass. Fick's First Law states that

$$J = - D (\partial C / \partial X) \quad [18]$$

where

J = flux of material through a unit area of a surface per unit time,

C = concentration of diffusing material per unit volume,

D = a constant called the Diffusion Coefficient in units of area per unit time,

X = the diffusion direction.

Fick's Second Law applies to situations in which changes in concentration with time have to be considered,

$$\partial C / \partial t = \partial / \partial X (D \partial C / \partial X), \quad [19]$$

or

$$\partial C / \partial t = D (\partial^2 C / \partial X^2) \quad [20]$$

where

t = the diffusing time .

A solution of equation 20 is

$$C = [A/(t)^{1/2}] \exp(-X^2/4Dt) \quad [21]$$

where A is a constant of integration. This is the equation for diffusion in one dimension when D is constant (Crank, 1985, p. 11). The total amount of substance M diffusing in a cylinder of infinite length and unit cross section is given by

$$M = \int_{X=0}^{\infty} C dX. \quad [22]$$

If the concentration distribution is that of equation 21, and the following substitution is made for the term in the exponential,

$$X^2/4Dt = \xi^2, \quad [23]$$

then

$$dX = 2(Dt)^{1/2} d\xi, \quad [24]$$

and

$$M = 2A(D)^{1/2} \int_0^t \exp(-\xi^2) d\xi = 2A(\pi D)^{1/2}. \quad [25]$$

Equation 25 shows that the amount of substance diffusing (M) remains constant and equal to the amount of substance present at $X=0$ at time $t=0$, and is therefore neither a function of X nor a function of t . Thus, on substitution for A from equation 25 to equation 21,

$$C(X,t) = [M/(4\pi Dt)^{1/2}] \exp (-X^2/4Dt), \quad [26]$$

Equation 26 is therefore the solution which describes the spreading by diffusion of an amount (M) of diffusant deposited the plane $X=0$. In equation 18, half the diffusing substance moves in the direction of positive X and the other half along negative X . However, if the diffusant can travel only in the direction of positive X , as is the case for the Na^+ ions deposited onto the surface of the films evaluated in this research, the solution for negative X can be considered to be reflected in the plane $X=0$ and superposed on the original distribution in the region $X < 0$. Since the original solution was symmetrical about $X=0$, the concentration distribution for the semi-inifinite cylinder is given by

$$C = [M/(\pi Dt)^{1/2}] \exp (-X^2/4Dt) \quad [27]$$

(Crank, 1985, p. 13). The equation 27, describing the diffusion controlled migration of a diffusing species through the diffusing medium, is based on Fick's assumption that resistance to diffusion is continuous, *ie*, that D is constant.

1.5.2 Effect of Diffusing Time on Concentration of Diffusing Species

The total amount of material Q having passed through a plane in the diffusion medium at depth X is written as

$$Q(X) = 2 C(X) (Dt/\pi)^{1/2}, \quad [28]$$

where $C(X)$ is the concentration in a slab of infinitesimal thickness δx about the plane of X and t is the time of the diffusion anneal (Crank, 1985, p. 32). The significance of equation 28 is that the total amount of diffusing material penetrating into the diffusing medium is proportional to $t^{1/2}$, the square root of the diffusing time.

1.5.3 The Diffusion Coefficient: Pre-Exponential Term

Normally diffusion is measured as a function of temperature and then analyzed in terms of the equation

$$D = D_0 \exp(-E_a/kT), \quad [29]$$

where k is the Boltzman constant, with D_0 and the energy of activation E_a independent of temperature as long as one mechanism governs the diffusion process (Frischat, 1975).

The pre-exponential term D_0 may be considered as a function of the viscosity of the diffusing medium (Stokes-Einstein relation, Atkins, 1982) or as a function of the entropy (Frischat, 1975). The viscosity relationship is written

$$D_0 = kT/6\pi\eta r \quad [30]$$

where k = is the Boltzman constant,

η = the viscosity of the diffusing medium
and r = the radius of the diffusing species

Frischat (1975) represented the entropy relationship as

$$D_o \propto \exp(\Delta S / R), \quad [31]$$

where ΔS represents the entropy change and R the ideal gas constant. Increases in local density during interstitial diffusion can result in a decrease in entropy ($\Delta S / R < 0$) (Frischat, 1975, p. 109).

The Einstein-Smoluchowski relation is used to describe the diffusion in terms of a one-dimensional random-walk mechanism, in which the diffusing species is considered to jump between discrete points separated by a distance d in a time t (Atkins, 1982, p. 909):

$$D = (1/2) d^2/t. \quad [32]$$

The relationship in equation 32 expresses the connection between the microscopic properties of the size (d) and rate ($1/t$) of a molecular jump and the macroscopic property of the diffusion constant (D).

1.5.4 Equations Describing Diffusion in the Presence of a Chemical Reaction

Crank (1985, p. 338) described diffusion accompanied by a chemical reaction in which C is the total concentration of the material of interest and S is the concentration of the material that has been immobilized (or decomposed) by the chemical reaction:

$$\partial C/\partial t = D (\partial^2 C/\partial X^2) - \partial S/\partial t \quad [33]$$

S depends on k and μ , the respective rate constants for the forward (immobilizing) and backward (liberating) reactions :

$$\partial S/\partial t = k C - \mu S, \quad [34]$$

So, in the presence of an immobilizing chemical reaction, Fick's Second Law (equation 20) can be modified so that it represents the sum of simple diffusion, sources, and sinks:

$$\partial C/\partial t = \text{simple diffusion} - \text{sinks} + \text{sources}, \quad [35]$$

or, using symbols,

$$\partial C/\partial t = D (\partial^2 C/\partial X^2) - k C + \mu S. \quad [36]$$

Equation 34 describes a phenomenon similar to that of the weak electrolyte theory for ion diffusion in glass (equation 15), in which the forward reaction is analogous the dissociation of the metal oxide to the free cation and metal-oxide pair, and the backward reaction is analogous to recombination to the metal oxide. Equation 36 describes the diffusion of free metal cations in such a system. If the forward rate constant k is much larger than the backward rate constant μ , then the term μS can be ignored, and equation 36 may be approximated

$$\partial C/\partial t = D (\partial^2 C/\partial X^2) - k C. \quad [37]$$

Experimental

2.1 Thin Dielectric Films: Deposition and Composition

2.1.1 Deposition of Thin Dielectric Films

Thin (approx. 1- μm) dielectric films (A, appendix) deposited on 100-mm silicon wafers (B, appendix) were obtained from Philips Research Laboratories Sunnyvale (PRLS). PSG films were deposited by APCVD, LPCVD, and PECVD. SiON films were deposited by PECVD. The deposition conditions are listed in Table 1.

2.1.2 Thin Film Composition Analyses

The following composition analyses were performed at PRLS: The SiON films were analyzed by ellipsometry for refractive index measurements; Rutherford backscattering (RBS) measurement was done for determination of percent Si, O, and N composition and nuclear reaction analysis for determination of percent H composition; Fourier transform infrared spectroscopy was done for chemical bonding information (C,D,E,F respectively, appendix). The PSG films were analyzed by x-ray fluorescence (XRF) and energy dispersive x-ray (EDX) analysis for phosphorus content and ion chromatography (IC) for measurement of mole percent P_2O_5 and P_2O_3 (appendix: G, H, and I, respectively).

In ion chromatography measurements, the PSG films were removed from the silicon wafer substrates by dissolving in a buffered hydrofluoric acid solution. The etching fractions were eluted and the concentrations of P_2O_3 and P_2O_5 were calculated by comparison to standard solutions of H_3PO_3 and H_3PO_4 . The results of the analyses of the SiON and PSG films are presented in Table 1.

Table 1: Chemical Composition of Silicon Oxynitride and Phosphosilicate Glass Films**Silicon Oxynitride**

film type	refractive index	at % Si	at% O	at% N	at % H
89	1.80	33	20	34	14
93	1.73	31	22	32	15
95	1.70	33	26	31	9
109	1.63	30	30	26	13
111	1.77	32	18	35	15
standard SiON	1.75	32	20	33	15
silicon nitride	1.99	34	1	47	13
60 (silicon dioxide)	1.48	31	57	8	4

Phosphosilicate Glass

sample deposition technique	(Temp)	treatment	Atom Percent Phosphorus			
			EDX +/-0.02	XRF +/-0.1	IC: as P ₂ O ₅ +/-0.02	as P ₂ O ₃ +/-0.01
44 AP	(400°C)	as dep.	2.83	2.00	2.33	0
45 PE (13.56 MHz)	(400°C)	as dep.	2.24	1.55	1.29	0.12
46 PE (380 kHz)	(300°C)	as dep.	2.53	2.03	0.04	0.59
47 PE (380 kHz)	(300°C)	as dep.	1.94	1.16	0.12	0.29
50 AP	(400°C)	dens.	2.83	NM	2.13	0
51 PE (13.56 MHz)	(400°C)	dens.	2.24	NM	1.36	0
52 PE (380 kHz)	(300°C)	dens.	2.53	NM	0.45	0
53 PE (380 kHz)	(300°C)	dens.	1.94	NM	0.08	0
59 AP	(400°C)	as dep.	NM	3.4	NM	NM
83 LP	(400°C)	as dep.	NM	2.9	NM	NM

Undoped Silicon Dioxide Films

60 PE (450 kHz) (380°C)	as dep.
63 PE (380 kHz) (330°C)	as dep.

Table 1: Deposition conditions and chemical composition of SiON and PSG films. SiON films were deposited by PECVD at 380 °C and 450 kHz. The relative error in the RBS measurements is +/- 5%, in the NRA measurements it is +/- 15%. The errors in the PSG analyses are absolute error in at % P. dens.: densified (30-min., flowing N₂), as dep.: as deposited. EDAX: energy dispersive electron microprobe xray analysis. XRF: xray fluorescence (energy dispersive). IC: ion chromatography. AP, LP, PE: atmospheric pressure, low pressure and plasma enhanced CVD, respectively. NM: not measured.

2.2. Sodium-22 Diffusion Experiments

2.2.1 Initial Contamination of Thin Films with Sodium-22

Prior to sodium diffusion experiments, the film surfaces of each wafer were cleaned by dipping for 30-sec. in 50:1 buffered oxide etch (BOE: 1.2 % HF, 39.2 % NH_4F , J, appendix) then rinsed in distilled water. Surface profilometry with a Tencor Alpha-Step (K, appendix) did not reveal any surface features (pits, spikes, granules or otherwise) with vertical dimensions (*ie*, normal to the plane of the wafer) larger than 50 Å, and nearly all the surface roughness measured was less than 10 Å, considered the sensitivity limit for the instrument in this application. A 25-μL aliquot of carrier free solution of $^{22}\text{NaCl}$ (L, appendix) in isopropanol was deposited onto the surfaces of the films from a micropipet (M, appendix) (Figure 6). The samples were dried under an infrared heating lamp for 30-minutes (N, appendix). Autoradiographs were taken to insure uniform dispersion of ^{22}Na , corresponding to a surface concentration of about 10^{12} $^{22}\text{NaCl}/\text{cm}^2$.

In order to better estimate the $^{22}\text{Na}^+$ dispersion areas, aliquots of 25-μL of $^{23}\text{NaCl}$ in IPA solution were deposited onto the surfaces of ten samples of $n=1.75$ SiON film. The solutions were dried on the wafer surfaces by heating under the infrared lamp. After drying, the diameters of the remaining residues were measured with a ruler. The results of these measurements appear in Table 2. By this (albeit crude) set of measurements, the approximate dispersion area of ^{22}Na over the SiON films was $5.6 \pm 0.2 \text{ cm}^2$.

A few solutions were prepared to deliver 10 % $^{22}\text{NaCl}$ in IPA solutions of $^{23}\text{NaCl}$, $^{23}\text{NaBr}$, and ^{23}NaI . These solutions were used to evaluate any effects of the size of the negative counterion on the ability of Na^+ to penetrate the glass.

Figure 6 (right): Application of $^{22}\text{NaCl}$ solution to a wafer with a micropipet.

Figure 7 (below): Muffle furnace used for annealing ^{22}Na into thin films.

After drying the dispersed solutions of $^{22}\text{NaCl}$, the contaminated films were next placed in a temperature controlled furnace (P, appendix) (Figure 7), where they were annealed at temperatures from 200°C to 500°C . Most of the diffusion anneals were done under flowing nitrogen (Q, R, appendix), and some of them were done in air.

2.2.2 Radioactive Decay of Sodium-22

Sodium-22 undergoes radioactive decay to Neon-22 by emission of a positron, which is abbreviated with the symbol ${}^0_1\beta^+$. The positron is a particle that has the same mass as an electron but has a charge exactly opposite to the charge of the electron. When positrons are ejected by Na-22 atoms during radioactive decay

they encounter electrons in the surrounding media and eventually undergo an electron-positron annihilation reaction

A sodium iodide - multichannel analyzer (MCA) assemblage (S-V, appendix) was used to count the 0.511 MeV photons from the ^{22}Na positron annihilation (Figures 8,9). The MCA was set up to count 1024 channels. The 0.511 MeV photopeak was counted by integrating the counts in a window 65 channels wide, corresponding to a window of 0.01 MeV. The efficiency of the counting system was checked with a 70-nCurie ^{22}Na standard (W, appendix) several times over the duration of experiment, and averaged about 10%,

Figure 8: Block diagram of the NaI-MCA detection system

Figure 9a (above):
NaI-multichannel
analyzer detection system.

Figure 9b (below):
Multichannel analyzer
with typical output on
screen from ^{22}Na source.

were not attenuated by the thin (approx. 1- μ) SiON and PSG films from which they were emitted.

Table 2

Dispersion area calculations for ten 25- μ L aliquots of isopropanol solutions of $^{23}\text{NaCl}$ on n=1.75 SiON coated wafers

sample no.	diameter-x	diameter-y	approx. surface area
1	25 mm	24.5 mm	4.8 cm ²
2	27 mm	26 mm	5.5 cm ²
3	26.5 mm	26.5 mm	5.5 cm ²
4	29 mm	26.5 mm	6.1 cm ²
5	24 mm	28 mm	5.3 cm ²
6	25 mm	26 mm	5.1 cm ²
7	27 mm	27 mm	5.7 cm ²
8	30 mm	26 mm	6.2 cm ²
9	29 mm	27 mm	6.2 cm ²
10	27 mm	26 mm	5.5 cm ²

2.2.3. Sodium-22 Depth Profiling

Following the anneal, each wafer portion was rinsed for 1-min. with distilled water then rinsed with methanol and blown dry with compressed air. ^{22}Na radioactivity was then recounted to measure the total amount of ^{22}Na actually retained in the film. Sodium depth measurements were made by progressively etching at the surface layers in 50:1 BOE and counting the amount of ^{22}Na remaining in the underlying unetched film. A shallow phototray filled to about 0.75-cm with BOE was used for the etch bath. All etching was performed at room temperature. The bath was stirred with a 1-inch x 0.25-inch diameter cylindrical teflon-coated magnetic stir bar. The tray sat atop a magnetic stirrer adjusted to stir the bath as rapidly as possible without splattering (X, appendix) (Figure 10).

Figure 10: Buffered oxide etch bath
used for etching steps

A record of the thicknesses of film removed in each etch step was retained by application of Apiezon® black wax to an uncontaminated portion of the film before each etch step. When the sequence of etching and radiochemical counting was completed, the wax was removed, revealing vertical steps that were measured with a Tencor Alpha Step profilometer. The etching times chosen depended on the etch rate of the film and the distribution of the $^{22}\text{Na}^+$ in the film. The duration of each etch step was chosen so as to attempt to remove approximately 10 - 20 % of the total retained $^{22}\text{Na}^+$ per etch step. The etch rates varied from approximately 6 Å/min. for Si_3N_4 to nearly 500 Å/min. for the 3.4 at % P phosphosilicate. For each count of ^{22}Na 0.511 MeV photons, either the number of seconds required for the MCA to accumulate 10,000 counts or the total number of counts accumulated in 600 seconds, whichever came first, was measured. The Alpha-Step surface profiles revealed no topographical features much larger than about 10 Å, (within the accuracy limit of the instrument for this experiment), while the typical etch step heights varied from 100 Å to 1500 Å. After each etch step the wafers were rinsed with distilled water, then methanol, then blown dry with compressed air. The sequence of masking, etching, rinsing, drying, and counting was repeated until either the count rate reached background or until all the film was etched away from the wafer surface. For most of the samples about 10 steps were required. When etching and counting were completed, the wax masks were removed with trichlorethylene, then rinsed with acetone, isopropyl alcohol, and distilled water, then blown dry with compressed air.

Results and Discussion

3.1 Influence of Annealing Atmosphere on Sodium Absorption in Silicon Oxynitride

The percentage of initially deposited ^{22}Na that was retained in the SiON glass after rinsing with distilled water was greater for the air-annealed films than for those annealed under N_2 . This effect is illustrated in Figure 11, which compares the Na^+ depth profile in an $n=1.75$ SiON annealed in air to that in an $n=1.75$ film annealed under a nitrogen purge. It is suspected that a thin layer of the films became thermally oxidized during the 72-hour diffusion anneal in air, creating a surface region with reduced resistance to sodium ion absorption. There may also have been (and probably was) some oxidation to the surface of the oxynitride films during the N_2 -diffusion anneal, as the temperature of the furnace was elevated during loading and unloading of wafers, allowing exchange of the purging N_2 with air from outside the furnace. Oxidation may also have occurred during the N_2 -diffusion anneal from possible moisture contamination in the bottled nitrogen used for purging (Q, appendix). However, the thickness of any oxidation that may have occurred to the surface of the oxynitride films during the N_2 -diffusion anneal is probably lower than on the films that were annealed in air. The shapes of the ^{22}Na concentration profiles in Figure 11 are similar, suggesting that there is no difference in the resistance to Na^+ permeation in the underlying unoxidized bulk region of the films.

Figure 11: A comparison of the $^{22}\text{Na}^+$ depth profile in an $n=1.75$ SiON annealed in air to that in an $n=1.75$ film annealed under a nitrogen purge. The shapes of the curves are similar, suggesting that the $^{22}\text{Na}^+$ resistance in the underlying unoxidized bulk region of the air annealed film is no different than that of the nitrogen-annealed sample. (The sizes of the data points reflect the absolute uncertainty in the $^{22}\text{Na}^+$ content in each measurement).

3.2. Effect of Diffusing Time (Silicon Oxynitride)

In order to check that whether the migration of Na^+ into the SiON thin films obeys the Fickian diffusion kinetics described in equation 28, equivalent amounts of $^{22}\text{Na}^+$ were annealed into SiON films with a refractive index (n) of 1.75 at 400°C for 24, 48, 72 and 144 hours. The percentage of deposited Na^+ ions that penetrated through 500 Å and 5,000 Å of the films are plotted against the square root of the anneal time (Figure 12). The straight slopes indicate that the diffusion can be described by Fick's Laws.

Figure 12: Plot of total amount of ^{22}Na penetrated from surface through 500 and 5,000 Å of SiON ($n=1.75$) (400° C diffusion anneal). The sizes of the data points reflect the absolute uncertainty in each measurement of ^{22}Na .

3.3. Effect of Film Type

Figure 13 shows the Na^+ concentration profiles, plotted as the percent of initially deposited Na^+ penetrating versus the penetration depth in $\text{Si}_3\text{N}_{3.9}\text{O}_{0.01}\text{H}_2$ (the nominal Si_3N_4 composition), SiON ($n=1.75$), SiO_2 , and PSG (3.4 atom percent P). The diffusion anneals were carried out at 400°C for 24-hrs in the PSG and SiO_2 , and 72 hours in the other materials. Clearly, there are significant differences between the Na^+ penetration curves for the four different glasses. The diffusivity of Na^+ in each material is discussed in further detail below. In order to facilitate a direct comparison between sodium penetration in Si_3N_4 and SiON with those of PSG and SiO_2 , values for percent Na^+ penetration in Si_3N_4 and SiON in Figure 13 are calculated for a 24-hr diffusion anneal using the $t^{1/2}$ dependence (equation 28).

Figure 13: ^{22}Na depth profiles in (●)APCVD PSG (3.4 at % P), (○) PECVD SiO_2 , (▲) PECVD SiON ($n=1.75$), and (■) PECVD Si_3N_4 . Diffusion anneals were carried out at 400 °C under flowing nitrogen for 24-hrs for PSG and SiO_2 , and 72-hrs for SiON and Si_3N_4 . For direct comparison of depth between profiles for the different annealing time, values for PECVD SiON ($n=1.75$) and PECVD Si_3N_4 were recalculated for a 24-hr diffusion anneal from the 72-hr data using the relationship in equation 28 ($Q \propto t^{1/2}$). (The sizes of the data points reflect the absolute uncertainty in each measurement of ^{22}Na).

3.4 Silicon Oxynitride

3.4.1 Silicon Oxynitride: Two Diffusion Coefficients

Two sodium diffusion processes were observed in all but the n=1.48 SiON films:

1. a faster, long range diffusion process, by which small percentage of absorbed Na⁺ ions migrated through the bulk of the film; and, 2. a slower, or short range process, by which Na⁺ ions migrated only through the upper layers of the film. The diffusion coefficient (D) is extracted from the slope of the plot of the log of the Na⁺ concentration (Na⁺ ions per unit depth) vs. the square of the depth of penetration.

This can be done using equation 26,

$$C \{X,t\} = [M/(\pi Dt)^{1/2}] \exp (-X^2/4Dt)$$

where C is the concentration of a diffusing substance in a section the center of which is a distance X from the surface, M is the amount of diffusing substance deposited per unit area on the surface, and t is the diffusing time. When obtaining depth profiles by etching and counting, the diffusion anneal time t was constant for all depths X, and M the amount of ²²Na deposited on the SiON film surfaces was also constant, making the pre-exponential term a constant. The equation can be rewritten as

$$C \{X,t\} = \mathcal{K} \exp [(-X^2) / (4Dt)]. \quad [40]$$

where all factors in the pre-exponential are grouped into $\mathcal{K}$. Taking logarithms gives

$$\log C \{X,t\} = \log \mathcal{K} - [1/2.303] \times [1/(4Dt)][X^2] \quad [41]$$

or

$$\log C \{X,t\} = \log C_0 - [1 / (9.212 D t)] [X^2] \quad [42]$$

which is the slope-intercept form of an equation for a straight line with

$$\text{slope} = -1 / (9.212 D t). \quad [43]$$

D is obtained from

$$D = -1 / [9.212 t (\text{slope})] . \quad [44]$$

The $\log C\{X,t\}$ plot is shown in Figure 14 for the $n=1.75$ SiON film. Diffusion coefficients were obtained from similar plots of Na^+ penetration in each SiON film, and in SiO_2 and Si_3N_4 as well. The short range and long range diffusion coefficients for these films are plotted in Figure 15 against refractive index, which is a convenient parameter for comparing film compositions. A single diffusion process was observed in the nominal SiO_2 ($n=1.48$) film. It is impossible to tell whether or not the long range diffusion occurred in this film. If so, it was swamped out by the extent of the "short-range" process. Long range Na^+ migration can be understood as migration by Na^+ , *ie*, ion hopping, between adjacent sites along such intrinsic film defects as grain boundaries (Frischat, 1968 and 1984) formed by the presence of particles imbedded in the glass (Dalton, *et al.*, 1968; Franz, *et al.*, 1969). Short range Na^+ migration can be understood as an interstitial process (Ingram, 1987), with ion hopping between adjacent holding sites (Anderson, *et al.*, 1954) through newly opened pathways (Rothman, *et al.*, 1982).

Figure 14: Plot of the log of the concentration of $^{22}\text{Na}^+$ (per unit film depth) vs. the square of the depth of penetration in SiON ($n=1.75$) (72-hr 400°C diffusion anneal). Diffusion coefficients are extracted from the slopes.

Figure 15: Short and long range diffusion coefficients of SiON films (and SiO₂, Si₃N₄) plotted against refractive index. (The refractive index is a convenient parameter to use for comparing the composition of the films.) A single diffusion process was observed in the SiO₂ film.

3.4.2 Silicon Oxynitride (n=1.75): Activation Energy

The activation energies (E_a) for the long and short range diffusion processes are calculated from the slopes of the Arrhenius plots of $\log D$ vs. $1/T$ for the $n=1.75$ films over the annealing temperature range 200°C to 450°C. E_a is extracted from the slope of each plot of $\log D$ vs. $1/T$ by the relationship

$$E_a = 2.303 \text{ slope } k \quad [45]$$

where D is the diffusion coefficient, T is the absolute temperature, and k is the Boltzman constant. No long range diffusion was observed in films annealed at 200° or 250 °C, so the Arrhenius plot for long range diffusivity was made over the temperature range 300°C to 450°C. Activation energies of 13.6 +/- 1.6 kcal/mol and 0.76 +/- 0.12 kcal/mol (0.59 +/- 0.07 eV and 0.033 +/- 0.005 eV, respectively) were obtained for the short and long range diffusion processes, respectively (Figures 16 and 17).

3.4.3 SiON: Effect of Atom Density

The atomic densities of the films were measured by RBS at PRLS and are compared to the short range diffusion coefficients in Figure 18. From Figures 14 and 15, it is apparent that most of the Na^+ ions are mechanically trapped in the glass layers near the film surface, with increased amounts of Na^+ being trapped nearer to the surface of the denser films. This density effect is illustrated in Figure 18, in which the Na^+ diffusivity is plotted against the density of the glass network-forming Si, O, and N atoms (per cm^3) in the films.

Figure 16: Activation energy plot for short range Na^+ diffusion in SiON ($n=1.75$, 72-hr diffusion anneal).

Figure 17: Activation energy plot for long range Na^+ diffusion in SiON ($n=1.75$, 72-hr diffusion anneal).

Figure 18: The atomic densities of the films as measured by Rutherford Backscattering (RBS) (see D, appendix) and are compared to the short range diffusion coefficients. ▲: Density (+/- 5%) of bridging atoms only: Si, O, N (H is not a bridging atom in these glasses). Δ: Log of the short range diffusion coefficient. Diffusion coefficient: +/- 7%.

The densities were measured by RBS for Si, N, and O. According to Loehman (1987), the SiON network can be thought of as silica, with network substitution of trivalent nitrogen for bivalent oxygen. According to this model each trivalent nitrogen ion is linked to three silicons, thereby partly crosslinking the anion subnetwork of the glass. This conceptual model has been validated in thin PECVD SiON films by Fourier transform infrared spectroscopy (FTIR) measurement (van den Hoek, 1986). The infrared spectra of these silicon oxynitride films showed a broad absorption band between 1300 and 800 cm^{-1} (Figure 19). This continuum lies mostly between the Si-N stretch centered near 850 cm^{-1} (Nguyen, Burton, and P. Pan, 1984) and the Si-O stretch that is centered near 1050 cm^{-1} (Fortunato and Della Sala, 1987), suggesting that the microscopic structure of the films is characterized by a random distribution of atomic components, giving rise to O-Si-N vibration modes. Assuming no hydrogen, no Si-Si bonds and no dangling Si bonds, six different local configurations around Si can be constructed (SiO_2N_2 , SiO_3N , SiO_4 , SiON_3 , SiN_4). All the oxynitride compositions studied in this research contained some H bonded to Si (van den Hoek, 1986). In high-resolution FTIR of PECVD SiON films with similar atom compositions prepared under similar conditions, Rostaing, Cros, Gujrathi, and Poulain (1987) assigned subpeaks within the broad O-Si-N peak to 31 possible O-Si-N configurations of $\text{SiO}_x\text{N}_y\text{H}_z$ where $x+y+z=4$. In all the films prepared for the present work, the 850 cm^{-1} Si-N stretch was identified under the broad peak. In SiON films with refractive indices higher than 1.82 this Si-N peak was the strongest peak with the SiON peak showing as a weak shoulder (van den Hoek, 1986). The presence of the Si-N peak could be due to presence of microscopic Si_3N_4 domains or clusters in the SiON network. This " Si_3N_4 shoulder" near 850 cm^{-1} has also been identified in PECVD SiON films prepared by Lucovsky and Tsu (1987).

Figure 19: The position of the absorption maximum of the broad "O-Si-N" absorption band plotted against the refractive index of PECVD SiON films (from van den Hoek, 1986). Δ: SiON films, ▲: PECVD Si₃N₄ and SiO₂ films.

3.4.4. Silicon Oxynitride: No Effect of Counterion on Short Range Diffusivity

The results presented above suggest that the short-range diffusivity of Na^+ in SiON by interstitial migration is related to the density of intersitices of sufficient size for ion passage to occur. To test whether the short-range diffusion process was limited by the diffusivity of the negative counter ion (Cl^- in $^{22}\text{NaCl}$ solutions), experiments were done with the $^{23}\text{NaBr}$ and ^{23}NaI solutions. The results are shown in Table 3. Assuming that the negative counter ions must migrate into the glass along with Na^+ ions in order to maintain charge balance, the ^{22}Na depth profile will depend on the radius of the larger ion and the density of pathways of sufficient size for passage of the larger ion. From Table 3 (a listing of the ^{22}Na depth profiles of $^{22}\text{NaCl}$ - $^{23}\text{NaCl}$, $^{22}\text{NaCl}$ - $^{23}\text{NaBr}$, and $^{22}\text{NaCl}$ - ^{23}NaI mixtures), equivalent penetration by Na^+ was observed to be independent of the counterion.

Table 3:
Percent of ^{22}Na penetrated through 90 Å and 180 Å of SiON ($n=1.75$).

carrier solution	anion radius%	^{22}Na through 90 Å	% ^{22}Na through 180 Å
90 % $^{23}\text{NaCl}$	1.81 Å	47.2 %	24.3 %
90 % $^{23}\text{NaBr}$	1.95 Å	47.7 %	23.7 %
90 % ^{23}NaI	2.16 Å	47.7 %	25.2 %

Table 3: Results of counterion effect on Na^+ penetration. Solutions consisted of 10 % $^{22}\text{NaCl}$ and 90 % carrier. As the amount of radioactive ^{22}Na initially deposited to the films surfaces was so small, reliable counts of ^{22}Na radioactive decay could not be obtained below 180 Å (2 minutes of etching in BOE). The anion radii are crystal radii. The crystal radius for Na^+ is 0.95 Å (Pauling, 1960, page 514).

These results demonstrate that the average size of the interstitial regions is either large enough to permit passage of I^- (2.16 Å radius) or too small even for passage of Cl^- (1.81 Å radius). If the former is true, then codiffusion of Na^+ and its charge balancing counterion may occur. However, as discussed above, the short range Na^+ diffusion process is strongly related to the atom density of the glass. Apparently any charge-balance requirements are met by isotope exchange with intrinsic $^{23}Na^+$ ions (or ion exchange with some other positively charged species) already present in the glass.

3.5 Silicon Nitride: Estimate of Activation Energy

Activation energy was estimated from a plot of (with only three data points) $\log D$ vs. $1/T$ (Figure 20). The value 13.1 kcal/mol (0.57 eV) was obtained. This energy value is typical for interstitial diffusion processes (Ghandi, 1983, p. 115). Due to the small (3) number of points measured, this activation energy for nitride is reported only as an estimate to be used for comparison to the other CVD films studied in this thesis. Although the E_a is very close to that of the $n=1.75$ SiON film, much less Na^+ penetrated into the nitride (Figure 13). Apparently the high density of the silicon nitride network permits little opportunity for interstitial Na^+ ion hopping at 400°C. Even though the activation energy requirement suggests that diffusion occurs mainly by a process similar to the short range interstitial process in the $n=1.75$ SiON film, the superior diffusion resistance D for short-range Na^+ migration in the Si_3N_4 films, coupled with the observation of a very fast, low-activation energy long range diffusion process in SiON suggests that the SiON films are not nearly as effective as the Si_3N_4 at stopping Na^+ ions. Apparently a thickness of the nominal Si_3N_4 film much less than the 1- μm customarily used in the passivation dielectric layer of integrated circuits (*ie*, 1,000 Å or less) is adequate to act as a near absolute barrier

to low temperature (300°C - 400°C) interstitial diffusion by Na⁺ ions deposited from the isopropanol (IPA) solution (Figure 13).

Figure 20: Arrhenius plot of Na⁺ diffusion in Si₃N₄ (72-hr diffusion anneal).

3.6 Phosphosilicate Glass

3.6.1 Sodium Ion Gettering

Sodium ion migration in the gettering PSG films can be thought of as analogous to diffusion in the presence of an immobilizing chemical reaction, as described in equation 37:

$$\partial C/\partial t = D (\partial^2 C/\partial X^2) - k C.$$

The immobilization reaction for Na⁺ PSG is thought to be:

where Na⁺_f represents a sodium ion that is free to diffuse, (∂⁻) and (∂⁺) represent partial negative and positive charges, respectively, and O=P represents the nonbridging pendant oxygen bonded to phosphorus characteristic of P₂O₅ (Elderidge, *et al.* 1971). Elderidge, *et al.* (1971) described the immobilization reaction with the equation 15:

$$N_i = N_o K_o \exp[(-E_a + qEW)/2kT] t^{1/2}$$

where N_i is the amount of Na⁺ transported (per unit area) through a given thickness of PSG and N_o is the initial surface concentration of Na⁺ ions (per unit area).

3.6.2 Phosphosilicate Glass: Effect of Densification on Film Thickness and Composition

Figure 21 shows the effect of the densification step (1000°C, flowing N₂, 30 minutes) on the thickness of the PSG films. Densification of PSG results in conversion to films that are less porous, with reduced internal volume (Kern, *et al.*, 1976; Wu and Saxena, 1985). The PECVD PSG films deposited at 300°C showed a significant (approximately 20%) decrease in thickness on densification. Ion chromatography (IC) of the etching fractions of each PSG film revealed varying amounts of phosphorus pentoxide (P₂O₅) and phosphorus trioxide (P₂O₃), neither of which was consistent with the total phosphorus content as measured by x-ray fluorescence (XRF) and energy dispersive x-ray analysis (EDX) (Table 1).

Figure 21: Thickness of PSG films change on densification (1000°C, 30-minutes). The sample number (corresponding to Table 1) is shown under each column.

The XRF system was calibrated with PSG films of known P₂O₅ content, whereas the EDX system was calibrated with thermally grown SiO₂ for Si and an NBS P₂O₅ standard for P. It can be seen that the apparent P content as measured by XRF is 30 % lower than by EDX, indicating a calibration problem with the EDX system. The large differences between total phosphorus as measured by EDX and XRF and oxidized phosphorus

detected by IC in the PECVD films deposited at 300° C are perhaps due to detection of P as trapped phosphine (PH₃) gas.

3.6.3 Phosphosilicate Glass: Effect of Phosphorus Content on Depth Profiles

The migration of ²²Na⁺ (400°C, 24 hrs) into as-deposited and densified films as a function of percent P₂O₅ is shown in Figures 23 and 24. The trends in Figures 23 and 24 suggest that the ²²Na⁺ migrated faster in films with greater amounts of P₂O₅. According to the model, other forms of P that may be present in the glass but are lacking the pendant oxygen moiety, such as trivalent P (P₂O₃), will not immobilize Na⁺. This effect is illustrated in Figure 22. The trends in Figures 23 and 24 suggest the opposite: PSG films with greater mole percents of P₂O₅ permitted more Na⁺ ions to migrate deeper through the films than PSG films with less P₂O₅.

Figure 22: Model for Na⁺ gettering by PSG: the nonbridging pendant oxygen of pentavalent phosphorus (P₂O₅) is believed to be the gettering site for Na⁺ ions. According to the model, trivalent phosphorus (P₂O₃), lacking a pendant oxygen, will not getter Na⁺.

Figure 23: Na⁺ penetration (400°C, flowing N₂, 24-hrs) through as-deposited APCVD (○:44; ■:59, Table 1), LPCVD (□:83, Table 1), PECVD (●:45; ▲:46; △:47; Table 1) PSG, and PECVD SiO₂ ([-+]:60; and [····]:63, Table 1).

Figure 24: Na^+ penetration (400°C, flowing N_2 , 24-hrs) through densified APCVD (○:50, Table 1), and PECVD (●:51; △:52; ▲:53, Table 1) PSG.

3.6.4 Phosphosilicate Glass: Effect of Thermal Drive-In Temperature

$^{22}\text{Na}^+$ depth profiles were taken at 200°C, 300°C, 400°C, and 500°C in both as-deposited and densified APCVD PSG films (Figure 25). The data for the 200°C diffusion anneals are omitted from Figure 25 as they gave profiles that were nearly vertical. Figure

Figure 25: Na^+ penetration in APCVD PSG ($\square$: as deposited, 300°C $^{22}\text{Na}^+$ anneal; $\blacksquare$: densified, 300°C $^{22}\text{Na}^+$ anneal; $\circ$: as deposited, 400°C $^{22}\text{Na}^+$ anneal; $\bullet$: densified, 400°C $^{22}\text{Na}^+$ anneal; $\triangle$: as deposited, 500°C $^{22}\text{Na}^+$ anneal; $\blacktriangle$: densified, 500°C $^{22}\text{Na}^+$ anneal). Open symbols represent as deposited films (sample 44, Table 1), closed symbols represent densified films (sample 50, Table 1).

Figure 26: Na^+ penetration (400°C, flowing N_2 , 24-hrs) in PECVD PSG films that were deposited at 300 °C: (○): sample 46, Table 1; (△): sample 47, Table 1; (▲): sample 52, Table 1; (●): sample 53, Table 1.

26 shows the $^{22}\text{Na}^+$ depth profiles, taken at 400°C in both as-deposited and densified PECVD PSG films, with varying amounts of P. In both cases, greater penetration by Na^+ is observed in the densified films than in the as-deposited films. Apparently the gettering, or retarding of Na^+ ions by PSG is influenced by the thermal history of the glass.

3.6.5 Phosphosilicate Glass: Discussion

Apparently the gettering, or retarding of Na^+ ions by PSG is influenced by the thermal history of the glass. Apparently the gettering, or retarding of Na^+ ions by PSG is influenced by the thermal history of the glass. The equation

$$N_i = N_o K_o \exp[(-E_a + qEW)/2kT] t^{1/2}$$

was derived by Elderidge, *et al.* (1971) to describe the immobilization of Na^+ contamination by PSG at temperatures from 80°C to 350°C . Dividing the above expression by N_o and taking logs yields

$$\log (N_i/N_o) = [K_o t^{(1/2)}] - [(E_a)/4.606kT]. \quad [47]$$

In order to facilitate comparison with activation energies (E_a) obtained by Elderidge, *et al.* (1971) for Na^+ transport in PSG, equation 15 was used for E_a calculations. For a constant diffusing time t , E_a is extracted from the slope of an Arrhenius plot. N_i was arbitrarily set to be the Na^+ concentration (Na^+ ions/ cm^2) after removal by etching of the top 1,000 Å of PSG. The ratio (N_i/N_o) represents the ratio of the amount Na^+ initially deposited to the film surface to the amount of Na^+ that penetrated through 1,000 Å. The activation energy

plot of $\log N_i/N_o$ vs $1/T$ reveals approximately the same E_a (18.3 kcal/mol, 0.80 eV) in as deposited and densified APCVD PSG films, and a lower E_a (12.63 kcal/mol, 0.55 eV) for Na^+ migration in the PECVD nominal SiO_2 (Figure 27). The values are close to those obtained by Elderidge, *et al.* (1971) for field-assisted Na^+ migration in PSG films formed by glassing, suggesting that the gettering processes in those films are similar to the gettering processes in CVD films studied in this paper.

The trends in Figures 23 and 24 indicate that PSG films with more phosphorus offer reduced resistance to migration by Na^+ . However, the Arrhenius plot in Figure 27 suggests otherwise. These seemingly contradictory observations may be better understood in terms of the phase diagram for PSG presented by Tien and Hummel (1962), and later modified by Elderidge and Balk (1968). The original phase diagram represents PSG with less than about 10 mole percent P_2O_5 as a phosphosilicate liquid that is saturated with SiO_2 . Elderidge, *et al.* (1968) extended the phase diagram to lower temperatures (800°C), finding the eutectic point of the PSG liquidus line near 850°C (Figure 28). They showed that below these temperatures PSG consists of two phases: a SiO_2 phase and a phosphosilicate phase with the stoichiometry $2\text{SiO}_2 \cdot \text{P}_2\text{O}_5$. According to the phase diagram, the PSG compositions studied in this work should have formed a phosphosilicate liquid on densification. The deeper penetration by Na^+ ions in densified PSG may be a manifestation of Goodman's proposal, that after glasses are cooled from a melt they form a random strained mixed cluster network with a highly disordered connective tissue phase (Goodman, 1985). According to the theory, this disordered connective tissue phase, formed by solidification of residual liquid distributed within the interstices of the space filling network, acts as a network of channels that impart increased ionic mobility to the glass (Goodman, 1975).

The presence of such a solidified interstitial liquid in the densified PSG samples, acting as the so-called "connective tissue", may account for their greater Na^+ mobilities as compared to as-deposited PSG films. While incorporation of pentavalent phosphorus provides gettering sites for migrating Na^+ as described above, the presence of two phases (SiO_2 and $2\text{SiO}_2 \cdot \text{P}_2\text{O}_5$) in the films may allow increased opportunity for Na^+ migration along boundaries. This may explain why PSG films with higher amounts of P_2O_5 tended to show greater permeation by Na^+ , even though the Na^+ diffusion process in PSG required a greater energy of activation than in undoped SiO_2 .

Figure 27: Arrhenius plot of Na⁺ penetration through PECVD and APCVD PSG films. Vertical axis represents the percentage of initially deposited ²²Na that penetrated through 1,000 Å of the glass. (○): Undoped PECVD SiO₂, (■): densified APCVD PSG, (□): as deposited APCVD PSG.

Figure 28: Phase diagram for the system $\text{SiO}_2\text{-P}_2\text{O}_5$.

Conclusions

The activation energy values obtained for Na⁺ penetration in CVD PSG, PECVD SiO₂, PECVD Si₃N₄, and short range Na⁺ penetration in PECVD SiON (18.3, 12.63, 13.1 and 13.6 kcal/mol, respectively) suggest that over the range of temperature (200°C - 500°C) studied in this report, these Na⁺ diffusion processes occur via interstitial mechanisms. The similar activation energies for Na⁺ diffusion in SiO₂ and Si₃N₄, and short range Na⁺ diffusion in the n=1.75 SiON suggest an equivalent transport mechanism in these films. (The activation energy values were 12.63, 13.1 and 13.6 kcal/mol, respectively, all of which are equivalent within the measurement error). The PSG films required a higher activation energy (18.3 kcal) for Na⁺ transport. This is attributed to a coulombic attraction between the positive Na⁺ ions and nonbridging pendant oxygens in the PSG network.

The ability of the PSG films to retard Na⁺ penetration decreased if the PSG films were densified at 1000°C. This may be explained by the formation of disordered interstitial phase on the cooling of phosphosilicate liquid that is formed during the densification. The amount of Na⁺ ions that penetrated the PSG films increased with increasing phosphorus content. This observation was also surprising in view of the fact that PSG was observed to be more effective at immobilizing Na⁺ ions than undoped SiO₂. This may be explained by the possible presence of diffusion pathways along the boundaries of microscopic SiO₂ and 2SiO₂•P₂O₅ phases, increasing with the appearance of the 2SiO₂•P₂O₅ phase.

A fast, long range diffusion process was observed in the SiON glass, by which a very small fraction of Na⁺ permeated through the films. In spite of the very low (0.76 kcal/mol) activation energy that was measured for long range diffusion in a SiON film, less than 1 %

of the Na^+ ions were able to diffuse through the bulk of the glass via this process. Apparently the long range migration in the SiON glasses occurs along such intrinsic film defects as voids or grain boundaries. In view of the presence of the 850 cm^{-1} Si-N peak in the FTIR spectra of all the SiON films studied, the possibility of fast diffusion along boundaries between microscopic Si_3N_4 and SiON domains cannot be dismissed.

The resistance of Si_3N_4 to Na^+ diffusion is much greater than that of the other CVD films. In fact, such small quantities of Na^+ penetrated into this material that to the experimental sensitivity limit in this work, (approximately 10^8 $^{22}\text{Na}^+$ ions), no Na^+ penetration below $100\text{ \AA}$ was observed following a 72-hour diffusion drive-in at 400°C . The implications of this result may be especially significant to manufacturers of integrated circuits, in view of the undesirable properties of PECVD Si_3N_4 , as on the order of $1\text{-}\mu\text{m}$ of Si_3N_4 is deposited when this material is used as the passivation dielectric in integrated circuits. A dual-layered passivation dielectric structure consisting of approximately $1\text{-}\mu\text{m}$ of PECVD SiO_2 (or PECVD SiON or PSG) topped by significantly less Si_3N_4 ($100\text{-}1000\text{ \AA}$?) than is customarily used ($\sim 1\text{-}\mu\text{m}$) may permit integrated circuits manufacturers to eliminate or reduce the undesirable aspects of Si_3N_4 while retaining their ability to prevent deleterious intrusion of Na^+ ions.

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APPENDIX

A. Oxynitride- and PSG- films:

APCVD Reactor: Tempress Pyrox® reactor. Tempress, Inc. The films were deposited at Signetics Co., Sunnyvale, CA.

LPCVD Reactor: Thermco MLX-9000 reactor. Thermco Systems, Orange, CA. The films were deposited at Signetics Co., Albuquerque, NM.

PECVD Reactors:

SiON films and SiO₂ film #60: ASM PLX-2000 PECVD reactor. ASM America, Phoenix, AZ. The films were deposited at Signetics Co., Sunnyvale, CA.

PECVD films 46,51: Novellus Concept One® PECVD reactor. Novellus Systems, San Jose CA. The films were deposited at Novellus Systems, San Jose, CA.

PECVD films 47,48,52,53: ElectroTech ND 6200 PECVD reactor. E.T. Systems, Santa Clara, CA. The films were deposited at ElectroTech, Bristol, England.

B. Silicon wafers: <100> single-crystal silicon. B-doped 17-33 Ω -cm.

C. Ellipsometer: Rudolph auto EL III automatic ellipsometer equipped with a HeNe laser (632.8 nm). Rudolph Research Corp., Flanders, NJ. The ellipsometry analyses were performed at Signetics Co., Sunnyvale, CA.

D. Rutherford Backscattering instrument: Rutherford backscattering analyses of Si, O and N content were performed with 2.0-MeV He⁺ particles produced by a 2.5-MV Van der Graaf accelerator. The He⁺ particles were separated from other ions by means of a 90-degree magnet with a radius of 1.5 m. The backscattered He⁺ particles were measured with an ORTEC surface barrier detector at a distance of about 15 cm from the target. The detector was 25-mm² and the measured energy resolution of the detector 12 keV FWHM. Pulse height analysis was done with a computerized measuring system. The pressure in the target chamber and beam lines was between 10⁻⁷ and 10⁻⁶ Torr. The spot size under the normal incidence beam

was 1 x 1 mm². The measurements were performed at Philips Research Laboratories, Eindhoven, The Netherlands.

- E. Nuclear reaction analysis: Hydrogen content was determined by counting the intensity of the 4.43 MeV gamma radiation produced in the reaction $^{15}_7\text{N}^{++} + ^1_1\text{H} \rightarrow ^{12}_6\text{C} + ^4_2\alpha + \gamma_{4.43 \text{ MeV}}$. A 6.380 MeV beam of N⁺⁺ ions was produced in a 7 MV van der Graaf accelerator. The beam encountered the samples at an incidence angle of 45°. The beam current was 80 nA and the spot size was 0.1 cm². Pressure was maintained below 10⁻⁸ Torr with an ion pump and Ti-sublimation pump. The 4.43 MeV radiation was detected with a 5-inch diameter NaI scintillator mounted 2-cm from the sample. The measurements were performed at the Technical Physics Department, Utrecht State University, Utrecht, The Netherlands.
- F. FTIR instrument: Digilab FTS 80, Bio-Rad Semiconductor Measuring Systems, Cambridge, MA. The measurements were done at Signetics Co., Sunnyvale, CA.
- G. XRF measurements: Kevex model 5000 energy dispersive xray fluorescence spectrometer, molybdenum source and thin-window (1.5-μm beryllium-coated) lithium-drifted silicon surface barrier detector (Kevex Corp., Foster City, CA). Atom percent P was calculated by comparison the ratio of the 1.74 keV Si and 2.01 keV P fluorescence peaks to a calibration curve of photopeak intensity ratios for PSG films of known composition. The measurements were done at Signetics Co., Sunnyvale, CA.
- H. The EDX measurements: EDAX model 9100 energy dispersive xray microanalysis spectrometer. (Edax International, Paire View, IL) 10 kV beam, 10 x 10 μm sampling area. The measurements were done at Signetics Co., Sunnyvale, CA.
- I. The ion chromatography measurements: Dionex model 16 ion chromatograph (Dionex Corp., Sunnyvale, CA) with a Hewlett Packard (Hewlett Packard Co., Palo Alto, CA) 3393 integrator. PSG films were removed from the silicon wafer substrates by dissolving in hydrofluoric acid. Etching fractions were eluted in solution

of 0.0030 M NaHCO_2 /0.0024 M Na_2CO_2 at a flow rate of 2.5 mL/min. Concentrations of P_2O_3 and P_2O_5 were calculated by comparison to standard solutions of H_3PO_3 and H_3PO_4 . The measurements were done at Signetics Co., Sunnyvale, CA.

- J. 50:1 BOE without surfactant (1.2 % HF, 39.2% NH_4F , balance H_2O): KTI Chemicals, Sunnyvale, CA.
- K. Alpha-Step "depth profiler" model 10-00020 step-height gauge and model 10-00030 strip-chart recorder, Tencor Instruments, Mtn. View, CA.
- L. $^{22}\text{NaCl}$: New England Nuclear, Boston, MA.
- M. Micropipet: Eppendorff 25 microliter pipet model 3130: Eppendorff Geratebau, Hamburg, FGR.
- N. 250-watt General Electric Infrared Heatlamp, General Electric Nela Park, Cleveland, OH.
- P. Blue-M "Lab Heat" muffle furnace model E-555C-1, Blue M Co., Blue Island, IL.
- Q. Bottled N_2 (99.7 - 99.97 %, maximum moisture content 32 ppm): A.G. Pond Co., San Jose, CA.
- R. Gas Flow Meter: AirCo model 752, AirCo Inc., Murray Hill, NJ.
- S. NaI scintillator: Bicron model 3M3/3, Bicron Corp., Newbury, OH.
- T. Photomultiplier tube: Ortec model 266 p.m. tube, Ortec Co., Oak Ridge, TN.

- U. Amplifier + High Voltage power supply: Ortec model 4890 preamp-amplifier:
Ortec model 4890 preamp-amplifier, Ortec model 456 high voltage power supply.
- V. Multichannel analyzer: Ino-tech model 5200, Ino-Tech Inc., Madison, WI.
- W. Sodium-22 standard: (1.00 microCuries on 10-1-76): Isotope Products Laboratories, Burbank, CA.
- X. Magnetic Stirrer: Thomas "Magne-matic" stirrer, model 14, Arthur Thomas Co., Philadelphia, PA.