Silicon nitride and carbide thin films, primarily in the form of silicon nitride (SiNₓ), silicon carbide (SiCₓ), and silicon carbo-nitride (SiNx:Cₓ), where 0 < x < 1.33 and 0 < y < 1, are experiencing a burgeoning of research interest across multiple application sectors. The appeal of these Si-based coats is attributed to their highly desirable mechanical, tribological, and optoelectronic properties making them prime candidates for applications in the automotive, aerospace, computer chip, solar, light-emitting, and medical industries. In consideration of the intense current interest in SiNₓ and SiNₓ:Cₓ, and the expectation that their applications will continue to witness further expansion and extensive diversification, we present an overview on the latest trends and developments in hydrogenated and non-hydrogenated silicon nitride and silicon carbonitride deposition techniques and associated post-deposition processing technologies. Given the fast-moving nature of SiNₓ and SiNₓ:Cₓ technological advances, the intent is to present an survey of work published within the last five years for silicon nitride and silicon nitride-rich films, i.e., silicon nitride with C inclusion, both in hydrogenated (SiNx:H and SiNx:C:H) and non-hydrogenated (SiNx and SiNx:C) forms. The emphasis is on emerging trends and innovations in these SiNₓ material system technologies, with focus on Si and N source chemistries and thin film growth processes, including their primary effects on resulting film properties. It also illustrates that SiNₓ and its SiNx:Cₓ derivative are the focus of an ever-growing research and manufacturing interest and that their potential usages are expanding into new technological areas.

This article provides an overview of the state-of-the-art chemistry and processing technologies for silicon nitride and silicon nitride-rich films, i.e., silicon nitride with C inclusion, both in hydrogenated (SiNx:H and SiNx:C:H) and non-hydrogenated (SiNx and SiNx:C) forms. The emphasis is on emerging trends and innovations in these SiNₓ material system technologies, with focus on Si and N source chemistries and thin film growth processes, including their primary effects on resulting film properties. It also illustrates that SiNₓ and its SiNx:Cₓ derivative are the focus of an ever-growing research and manufacturing interest and that their potential usages are expanding into new technological areas.

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The application of SiNₓ, SiCy, and SiNₓCy also extends into the green energy field, primarily in solar cell applications. For example, microcrystalline and amorphous SiCy coatings are employed as window layers in thin film solar cells.45 And much like the case of the hard coatings and computer chip industries, SiNₓ and SiCy thin films are applied as passivation layers in silicon solar cells.46–48 Other applications include the use of Si-rich SiNₓ as host matrix for Si nanocrystals and Si nanoscale inclusions (Si-ni) light emitters for solar cell applications.49 In addition, SiNx can be used for certain bio-implants. However, in most cases, the incorporation of other elements, particularly hydrogen, is not accounted for. It is more proper to designate amorphous hydrogenated silicon nitride as a-SiNx:H. Not only does the amount of hydrogen incorporation affect physical, optical, and dielectric properties (in accordance with the Lorentz-Lorenz model), but also its backbone, and are broadly denoted ‘hybrid’ polymers.49

It is also worth noting that the mechanical, optical, and electronic characteristics of SiNx and SiCy can be tightly controlled and systematically customized as a function of carbon (C) and nitrogen (N) concentrations.49–51 This feature makes the SiNxCy phase a prime candidate for applications which require micro-modulation of the SiNxCy characteristics of SiNx and SiCy can be tightly controlled and systematically customized as a function of carbon (C) and nitrogen (N) concentrations.49–51 This feature makes the SiNxCy phase a prime candidate for applications which require micro-modulation of the SiNxCy structure, lattice diffusion and defect chemistry, oxidation, production and general properties were assessed in detail. The work also surveyed the development of microstructure-properties functionality relationships. Also, the review by Hampshire52 presented a survey of silicon nitride ceramics structure, processing, and properties, including microstructural development, sialons, and applications. Newer review articles of silicon nitride thin film deposition techniques are discussed in Overview of silicon nitride formation and deposition techniques section.

Silicon nitride with the nominal stoichiometry Si₃N₄ (c-Si₃N₄) occurs in three crystalline forms: α, β, and γ, while amorphous SiNₓ (a-SiNx) exists in various forms that display a range of physical, chemical, electrical, and mechanical properties. Additionally, the literature generally refers to crystalline and amorphous silicon nitride with different ratios of silicon to nitrogen as silicon nitride (namely, a-SiNx, or c-SiNx with 0 < x < 1.33), although a few reports described significantly higher N/Si ratio.25

Table I presents nominal properties for silicon nitride. The data compilation should be considered as a guide by the reader for bulk or crystalline (c-SiNx), polycrystalline (pc-SiNx), amorphous non-hydrogenated (a-SiNx) and hydrogenated (a-SiNx:H) thin films. The data is intended to represent salient, but not absolute, properties of the various forms of SiNx as determined at temperatures in the range of 20–100°C except for self-evident thermal properties. In this context, the data should provide a baseline in the review and analysis of the properties of SiNx films as reported in the published work.

**Overview of Silicon Nitride Formation and Deposition Techniques**

In general, silicon nitride monolithic (bulk) and film structures can be prepared by: (1) solid phase synthesis (e.g., nitriding of Si, hot isostatic pressing of silicon nitride particles); (2) liquid phase synthesis (porous composite infiltration with thermal conversion or spin-on deposition with thermal conversion from liquid or polymeric precursors); and (3) vapor phase synthesis in primarily thin and ultrathin films.

**Silicon nitride monolithic (bulk) growth methodologies.**—Solid phase synthesis of silicon nitride is usually associated with structural ceramic synthesis and the huge literature in this area is often associated with aerospace and military applications, but recently the technique has been extended to semiconductor substrates.55

Liquid phase synthesis, although it straddles application areas, is the least studied of the processes and less is known about the resulting film or bulk properties. Liquid phase synthesis, including spin-on and sol-gel techniques, is usually associated with linear (thermoplastic) polymers or crosslinked (thermoset) resins with alternating silicon and nitrogen atoms in their backbone, and are broadly denoted polysilazanes and aminolazanes.56–59 Early work in this area was directed toward thermolytic or pyrolytic conversion of polysilazanes directly into shaped or structural silicon nitride ceramics.51 The successful production of structural ceramics from liquid phase synthesis has not been achieved to date due to issues associated with ceramic yield, by-product diffusion, phase composition, density and chemical composition.

In terms of chemical composition one of the two major classes of polysilazanes, organopolysilazanes (structure 1), has organic carbon substitutions on the backbone leading in general to silicon carbonitrudes.62 Inorganic polysilazanes, alternately termed perhydridopolysilazanes (structure 2), lead more directly to silicon nitride structures, but the polymers themselves are apt to have stability issues that lead to variability in performance.
### Table I. Overview of Properties of Bulk and Thin Film SiNx

| Dense Bulk (crystalline/ polycrystalline) c-Si3N4/pc-Si3N4 | Thin Films a-SiNx (H content <5%) | a-SiNx:H (H content >5%) |
|----------------------------------------------------------|---------------------------------|-------------------------|
| PVD/CVD/PECVD                                            | PVD/CVD/PECVD                   | PVD/CVD/PECVD            |

#### Physical Properties

**Structure**
- Trigonal α-phase (Pearson symbol: hP28) or hexagonal β-phase (Pearson symbol: hP14)\(^{5,55}\)
- Increased from 2.3 to 2.8 g/cm\(^3\) with N/Si ratio from 0.0 to 1.1 (Schmidt)\(^{20}\)
  Decreased from 1.97 to 1.82 with decreasing N/Si ratio from 1.42 to 1.15 (Serikawa)\(^{21}\)
- Increased from 2.6–3.0 g/cm\(^3\) (Hickernell)\(^{126}\)
  Increased from 2.6 to 2.90 g/cm\(^3\) with Si/N ratio from 1.04 to 1.53 (Taylor)\(^{127}\)

**Density**
- 3.19–3.20 g/cm\(^3\) (Lube)\(^{5}\)
- Increased from 2.3 to 2.8 g/cm\(^3\) with N/Si ratio from 0.0 to 1.1 (Schmidt)\(^{20}\)
  Decreased from 1.97 to 1.82 with decreasing N/Si ratio from 1.42 to 1.15 (Serikawa)\(^{21}\)
- Decreased from 1.97 to 1.82 with decreasing N/Si ratio from 1.42 to 1.15 (Serikawa)\(^{21}\)

**Mechanical Properties**

**Hardness**
- 9.0 Mohs
- Increased from 15 to 28 GPa with N/Si ratio from 0.0 to 1.1 (Schmidt)\(^{20}\)
  Increased from 9 to 23.4 GPa for as-deposited films with increased N/Ar flow in the sputtering chamber from ~0.4 to no Ar (Vila)\(^{131}\)
  Increased from 16.4 to 18.0 GPa for annealed films with increased annealing temperature from 1200 to 1350 °C @ 100% N flow in the sputtering chamber (Vila)\(^{35}\)

**Modulus of elasticity (Young’s modulus)**
- 2200 kg/mm\(^2\) (Ferro-Ceramic)\(^{133}\)
- Increased from 100 to 210 GPa As a function of deposition parameters (Vila)\(^{131}\)
  Increased from 150 to 275 GPa with N/Si ratio from 0.0 to 1.1 (Schmidt)\(^{20}\)
  Increased from 118 to 210 GPa for as-deposited films with increased N/Ar flow in the sputtering chamber from ~0.4 to no Ar (Vila)\(^{131}\)
  Increased from 174 to 183 GPa for annealed films with increased annealing temperature from 1200 to 1350 °C @ 100% N flow in the sputtering chamber (Vila)\(^{131}\)

**Tensile Strength**
- 360–434 MPa (Ferro-Ceramic)\(^{133}\)
- Increased from 178 to 221 GPa with Si/N ratio from 1.04 to 1.53 (Taylor)\(^{127}\)

**Flexural Strength**
- 400–500 MPa (Ziegler)\(^{139}\)
- Decreased from 420 GPa to 250 for N/Si ratio from 0.0 to 1.3, remaining constant above that ratio (Hasegawa)\(^{137}\)

**Compressive Strength**
- 689–2760 MPa (Ferro-Ceramic)\(^{133}\)
- Varied from 100 to 242 GPa depending on preferential H bonding to Si or N (King)\(^{128}\)

**Shear Modulus**
- 102–128 GPa (Ferro-Ceramic)\(^{133}\)
- Decreased from 166.5 GPa for Si-rich films, with Si/N ~ 1.1, to ~2.4 g/cm\(^3\) for N-rich films, Si/N ~ 0.5 (King)\(^{129}\)

**Modulus of elasticity (Young’s modulus)**
- 222 ± 3 GPa (Vlassak)\(^{134}\)
- Increased from 320–360 GPa with Si/N ratio from 0.83 to 0.95 (French)\(^{135}\)
  Decreased from 420 GPa to 250 for N/Si ratio from 0.0 to 1.3, remaining constant above that ratio (Hasegawa)\(^{137}\)
  Varied from 100 to 242 GPa depending on preferential H bonding to Si or N (King)\(^{128}\)
  Decreased from 166.5 GPa for Si-rich films, with Si/N ~ 1.1, to ~2.4 g/cm\(^3\) for N-rich films, Si/N ~ 0.5 (King)\(^{129}\)

**Tensile Strength**
- 2.4 GPa (Ziebart)\(^{138}\)
- Increased from 178 to 221 GPa with Si/N ratio from 1.04 to 1.53 (Taylor)\(^{127}\)

**Flexural Strength**
- 400–500 MPa (Ziegler)\(^{139}\)
- Decreased from 420 GPa to 250 for N/Si ratio from 0.0 to 1.3, remaining constant above that ratio (Hasegawa)\(^{137}\)
  Varied from 100 to 242 GPa depending on preferential H bonding to Si or N (King)\(^{128}\)
  Decreased from 166.5 GPa for Si-rich films, with Si/N ~ 1.1, to ~2.4 g/cm\(^3\) for N-rich films, Si/N ~ 0.5 (King)\(^{129}\)
| Property                        | Dense Bulk (crystalline/ polycrystalline) | Thin Films | a-SiNx (H content <5%) | a-SiNx:H (H content >5%) |
|--------------------------------|------------------------------------------|------------|------------------------|-------------------------|
|                               | c-Si3N4/p-c-Si3N4                        | PVD        | CVD                    | PECVD                   | CVD                      | PECVD                   |
| Fracture toughness            | 5.8–8.5 MPa-m⁻²                          |            |                        |                         |                         | Decreased from 3.50 to 1.75 MPa-m⁻² with increasing intrinsic film stress from −1200 MPa to 600 MPa for 2μm-thick films (King)¹²⁸ | Remained constant ~1.25 MPa-m⁻² with increasing intrinsic film stress from −600 MPa to ~50 MPa for 3μm-thick films (King)¹²⁸ |
| Poisson ratio                 | 0.26 (Wang)¹¹⁹                          | 0.28±0.05 (Vlassak)¹³⁴ | 0.253 (Ziebart)¹³⁸     | 0.28 (Carlotti)¹²⁵       |
| Thermal                        |                                          |            |                        |                         |                         |                         |                           |
| Melting point                 | 1900 °C                                  |            |                        |                         |                         |                         |                           |
| Thermal Expansion Coefficient | 2.9 x 10⁻⁶ °C⁻¹                          |            |                        |                         |                         |                         |                           |
| Operating temp-continuous      | 1000 °C (Wang)¹¹⁹                        |            |                        |                         |                         |                         |                           |
| Operating temp-continuous, max.| 1346–1773 °C (Eckel)¹⁴⁰                  |            |                        |                         |                         |                         |                           |
| Operating temp-short-term, max.|                                          |            |                        |                         |                         |                         |                           |
| CoE x 10⁻⁶                    | 2.6–2.9 (Lube, Wang)⁵³³                   |            |                        |                         |                         |                         |                           |
| Heat Capacity, 20°–100°C       | 0.76 Jg⁻¹ K⁻¹                           |            |                        |                         |                         |                         |                           |
| Thermal transition, α-Si3N4 to-Si3N4 | 1400°–1500°C                            |            |                        |                         |                         |                         |                           |
| Thermal Conductivity           | 26 W/mK (Lube)⁵                          | 1.2 W/mK (Govorekov)¹⁴² | 32 W/mK (Mastrangelo)¹⁴¹ | Intrinsic Thermal Conductivity increases from 2.0 W/mK to 2.5 W/mK with temperature increase from 70 to 200°C (Griffin)¹⁴³ | Increased from ~0.25 W/mK to ~0.7 W/mK as temperature increased from 77 to 350K (Lee)¹⁴⁵ | Increased from 0.8 to 1.7 W/mK as film thickness increased from 298nm to 1001nm (Bogner)¹⁴⁶ |
|                              |                                          |            |                        |                         |                         |                         |                           |
| Thermal shock resistance       | 550–650° C/sec (NASA)                    | 750° C/sec (Ferro-Ceramic)¹³³ |                        |                         |                         |                         |                           |
| Electrical                    | 1 x 10⁻¹²–10⁻¹³ ohm-cm                    | 10⁻¹⁵ ohm-cm (Joshi)¹²² | 1 x 10⁻¹² ohm-cm (Piccirillo)¹⁴⁷ | 10⁻¹³ ohm-cm (Joshi)¹²² | <10⁻¹³ ohm-cm (Joshi)¹²² |

Note: All values unless otherwise stated.
### Table I. Continued.

| Dense Bulk (crystalline/ polycrystalline) | Thin Films | a-SiNx (H content <5%) | a-SiNx:H (H content >5%) |
|----------------------------------------|------------|------------------------|--------------------------|
| c-Si3N4/pc-Si3N4                       | PVD        | CVD                     | PECVD                    | CVD                       | PECVD                    |
|                                        |            | 10.0 × 10^6 V/cm (Joshi) | Increased from 3.0 to 4.9 × 10^6 V/cm for as deposited samples with increasing RF power density during deposition; Increased from ∼2.5 to ∼4.7 × 10^6 V/cm for annealed samples with increasing RF power density during deposition (Maeda) | 10.0 × 10^6 V/cm (Joshi) | 5.0 × 10^6 V/cm (Joshi) |
|                                        |            | 6.0 (Joshi)             | 7.0 (Piccirillo) 6.31–7.56 (Maeda) | 7.0 (Joshi) | 6.0 to 9.0 depending on H content that ranged from 20 to 30% (Joshi) |
|                                        |            | 2.07 2.01 (Joshi)      | Decreased from 1.97 to 1.87 with decreasing N/Si ratio from 1.42 to 1.15 (Serikawa) | 2.01 (Joshi) | 1.8–2.5 depending on increasing H content from 20 to 30% (Joshi) |
|                                        |            | 2.07 (Joshi)            | Increased from 2.19–2.07 @ 634nm with Si/N ratio from 0.83 to 0.95 (French) | 2.01 (Joshi) | 1.8–2.5 depending on increasing H content from 20 to 30% (Joshi) |
|                                        |            | 6.0 (Joshi)             | Increased from 1.6 to 1.73 with increased N flow ratio from 10 to 100% @ 1800nm (Signore) | 6.0 (Joshi) | 1.8–2.5 depending on increasing H content from 20 to 30% (Joshi) |
|                                        |            |                        | Increased from ∼3.18 to ∼2.01 with increasing N/Si ratio from 0.31 to 1.5 (Davis) | 6.0 (Joshi) | 1.8–2.5 depending on increasing H content from 20 to 30% (Joshi) |
| Optical Refractive Index               | 2.016 @ 589.3 nm 2.073 @ 400 nm | Decreased from 2.4–4.7 | Increased from −0.03 to 0.65 with increased N flow ratio from 10 to 100% @ 200 nm (Signore) | 2.01 (Joshi) | 1.8–2.5 depending on increasing H content from 20 to 30% (Joshi) |
|                                        |            | <6 × 10^{-4}            | Increased from −0.03 to 0.65 with increased N flow ratio from 10 to 100% @ 200 nm (Signore) | 2.01 (Joshi) | 1.8–2.5 depending on increasing H content from 20 to 30% (Joshi) |
| Optical Gap                            |            | 2.4–4.7                 | Decreased from ∼3.18 to ∼2.01 with increasing N/Si ratio from 0.31 to 1.5 (Davis) | 2.01 (Joshi) | 1.8–2.5 depending on increasing H content from 20 to 30% (Joshi) |
| Extinction Coefficient                 |            |                        | Decreased from ∼2.7 to ∼1.6 with increasing N/Si ratio from 0 to 1.2 (Lowe) | 2.01 (Joshi) | 1.8–2.5 depending on increasing H content from 20 to 30% (Joshi) |
| Tribological                           |            |                        | Increased from ∼3.18 to ∼2.01 with increasing N/Si ratio from 0.31 to 1.5 (Davis) | 2.01 (Joshi) | 1.8–2.5 depending on increasing H content from 20 to 30% (Joshi) |
| CoF, SiN mating, low speed             | 0.7 (Dante) |                        | Increased from ∼2.7 to ∼1.6 with increasing N/Si ratio from 0 to 1.2 (Lowe) | 2.01 (Joshi) | 1.8–2.5 depending on increasing H content from 20 to 30% (Joshi) |
| CoF, SiC mating, low speed             | 0.27 (Dante)|                        | Increased from ∼2.7 to ∼1.6 with increasing N/Si ratio from 0 to 1.2 (Lowe) | 2.01 (Joshi) | 1.8–2.5 depending on increasing H content from 20 to 30% (Joshi) |
| CoF, SiN mating, hydrodynamic, high speed | <0.002 (Dante) |                        | Increased from ∼2.7 to ∼1.6 with increasing N/Si ratio from 0 to 1.2 (Lowe) | 2.01 (Joshi) | 1.8–2.5 depending on increasing H content from 20 to 30% (Joshi) |
| Permeation/Absorption                  |            |                        | Increased from ∼2.7 to ∼1.6 with increasing N/Si ratio from 0 to 1.2 (Lowe) | 2.01 (Joshi) | 1.8–2.5 depending on increasing H content from 20 to 30% (Joshi) |
| Water vapor transmission rate, 100 nm film | CVD: 7 × 10^{-3} g m^{-2} day (Majee) | 0.015 × 10^{-2} gm^{-2} day (Wuu) | Increased from ∼2.7 to ∼1.6 with increasing N/Si ratio from 0 to 1.2 (Lowe) | 2.01 (Joshi) | 1.8–2.5 depending on increasing H content from 20 to 30% (Joshi) |

*All values at R.T. unless otherwise indicated.
Limited commercial success of liquid phase synthesis has been the infiltration of porous ceramics followed by pyrolytic conversion to produce densified ceramic-matrix composites (CMCs), as binders in metal-matrix composites (MMCs), and as spin-on film for photolithography with materials supplied initially by Kion Corp and transitioned to Clariant and E Merck Corp. Similarly, commercial acceptance was achieved in fabrication of dielectric layers by spin-on deposition techniques for semiconductor devices in a process in which silicon nitride initially formed from perhydridopolysilazane was ultimately converted to silicon dioxide with materials supplied by Tonen Corp, but this approach has largely been abandoned.

**Silicon nitride thin film vapor processing technologies.**—Silicon nitride thin film vapor processing technologies include physical vapor deposition (PVD), primarily sputtering; chemical vapor deposition (CVD) in its various forms, including thermal, hot wire (HW-CVD), plasma-enhanced (PE-CVD), and remote plasma-enhanced; and atomic layer deposition (ALD), also in thermal, plasma-assisted (PA-ALD), plasma-enhanced (PE-ALD), and remote plasma forms. In this context, Takeyama, King, and Meng present valuable historical reviews of silicon nitride PVD, CVD, and ALD deposition techniques.

PVD, which in principle involves the transport but not the formation of silicon nitride is an area of continued exploration since film composition and properties are influenced by sputtering methods as well as transport, and deposition environments. There is emerging interest and reports of alternatives to ALD for ultra-thin films for both SiN and SiNx by self-limiting processes associated with self-assembled monolayer (SAM) deposition and molecular layer deposition (MLD).

Vapor phase synthesis is associated with the semiconductor, medical, aerospace, energy, and automotive sectors. As such, the present article will predominantly review the latest research work in vapor phase synthesis. In this respect, Tables II and III present details of very recent vapor phase deposition techniques of SiN thin films, along with a synopsis of intended applications. More specifically, Table II summarizes PVD and CVD work, while Table III focuses exclusively on atomic layer deposition ALD.

It is worth noting that, historically, CVD in its various forms, including thermal, HW-CVD, PA-CVD, PE-CVD, and remote plasma-enhanced, had been the method of choice for growing SiN thin films, followed by PVD, mainly magnetron sputtering. More recently, however, ALD (including thermal, PA-ALD, and PE-ALD) appears to be receiving the most attention due to the need for extremely thin SiN films with increasingly tight control of composition and properties.

In what follows, an overview is first presented of silicon nitride source chemistries. In this context, Table IV outlines the Si- and N-based dissociation energies for selected SiN source chemistries, while Table V focuses on relevant properties of many of the recently studied CVD and ALD SiN source precursors. Subsequently, the various CVD, PVD, and ALD processes are summarized, respectively, in Appendices A, B, and C and discussed in more detail in the relevant sections.

**Overview of Silicon Nitride Source Chemistries.**

It should be noted that in the case of CVD and ALD processes, the differences in formation and behavior of SiN thin films can be attributed, in part, to fundamental thermodynamic and chemical properties of precursors. In this context, Table IV lists bond dissociation energies for selected SiN source chemistries, not only those that are most commonly used, specifically, silane (SiH4) and ammonia (NH3). The table is intended to provide the reader with a baseline comparison of bond dissociation energies of selected organic and inorganic Si and N source chemistries with the most commonly used precursors, namely, silane (SiH4) and ammonia (NH3). Table V presents relevant properties of many of the recently studied CVD and ALD SiN source precursors. The precursors are divided into classes: perhydridosilanes, hydridohalosilanes, halosilanes and aminosilanes. Representative structures are depicted below.

The large bond dissociation energy of N2 and relatively high bond dissociation energy of SiH4 are consistent with the fact that energetic environments, typically either thermal or plasma, are necessary for thin film formation. The resulting films tend to be rich in H and the H typically resides on the Si atoms, with post deposition thermal treatment commonly applied to reduce H content. Since the N atom is trivalent and the silicon atom is tetravalent, the H content in the film has minimal effect on the mobility of films: conformity is difficult to achieve and reflow is not observed in post-deposition process windows.

In contrast, the lower dissociation energies associated with NH3 and SiH4 allows deposition at lower temperatures. Additionally, chemical pathways associated with silicon diimide and diiodosilylene formation from SiH4 are enabled for deposition. In this case, H mostly resides on the N atom on films formed from silicon halides and NH3 with the important consequence that the mobility of H substituted N atoms are constrained in two dimensions rather than three. Conformality is therefore expected to be easier to achieve. This advantage is offset by the fact that the chemical deposition pathway leads to gas phase depletion reactions independent of the substrate.

The discussion above is partly simplified, particularly in the case of CVD. Higher energy environments associated with CVD often induce gas phase depletion reactions initiated by unimolecular decomposition of a precursor and/or direct reaction of precursors in the gas phase preceding or concomitant with deposition. ALD more often proceeds by direct reaction with surfaces or by a dissociative adsorption on surfaces (in rate limiting steps) and, as a result, associated reactions, by definition, proceed sequentially.
Table II. Summary of Recent CVD, PECVD, and Sputtering SiNx Work.

| Deposition Technique | Potential Application | Brief Description | Reference |
|----------------------|-----------------------|------------------|-----------|
| PE-CVD followed by patterning | Si solar cells | Passivation and dielectric layer | 37 |
| RF Magnetron Sputtering | Microelectromechanical systems (MEMS) | Barrier and passivation layers and etch stop. | 74,116 |
| DC Magnetron Sputtering | Non-volatile memory (NVM) devices | Dielectric layer in stacked high-dielectric constant (κ) structures | 75 |
| PE-CVD and RF magnetron sputtering | Optimal, electrical, and chemical devices | Overlays on cylindrical fused silica optical fibers | 76 |
| RF PE-CVD (see also Reference 19) | Organic electronic devices on polymer flexible substrates | Multilayers as permeation barriers | 21 |
| Hot Wire CVD | | | |
| Surface-wave-plasma low temperature CVD | OLEDs | Highly water-impermeable transparent barrier and protective layer | 22,23 |
| Hot Wire CVD (HW-CVD) with post deposition Ar treatment | OLEDs and organic solar cells on polymer flexible substrates | Encapsulation and passivation layer | 20 |
| Remote-controlled Plasma-Enhanced CVD (PE-CVD) | Photoluminescent and optoelectronic devices, solar cells | Host for Si nanocrystals as active light emitters | 32 |
| Low-Pressure CVD with post-deposition thermal annealing | Non-volatile memory devices | Layer in metal–oxide–nitride–silicon semiconductor memory architectures | 77 |
| PE-CVD | Solar cells on graphite substrates | Passivation layer as part of a SiN/a-Si:H stack | 78 |
| RF Magnetron Sputtering and PE-CVD | Solar cells, through-Si vias for 3D devices, electroluminescent and display devices | Passivation and optical layer | 25 |
| Remote microwave PE-CVD | OLEDs | Anti-moisture permeation transparent barrier and protective layer | 79 |
| PECVD/RF-PE-CVD | Organic Thin Film Transistors (TFTs) | Gate insulator | 33 |
| Low-Temperature Pulsed-RF PE-CVD | TFTs on fragile substrates, such as plastic or paper | Gate and passivation dielectric, anti-reflective coating | 34 |
| PE-CVD with post-deposition rapid thermal annealing (RTA) | Photoluminescent and optoelectronic devices, solar cells | Host for Si nanocrystals as active light emitters | 38 |
| PE-CVD | Solar cells | Passivation layer | 36 |
| Radio-frequency (RF) PE-CVD (see also Reference 47) | Optical devices operating in the infrared spectral range (optical sensors, filters and resonators) | Optical layer in the infrared spectral range | 24 |
| Magnetron co-sputtering | Photoluminescent and optoelectronic devices | Si nanocrystals embedded in ultrathin SiNx barrier layers | 31 |
| PE-CVD | Gallium Arsenide (GaAs) heterojunction bipolar transistors (HBTs) | Metal-insulator-metal (MIM) capacitor dielectric film | 16 |

Chemical Vapor Deposition (CVD)

Appendix A presents a synopsis of SiNx thermal, plasma-enhanced, hot-wire, and remote plasma-enhanced CVD parameters and post processing treatments (where applicable). Table II and Appendix A show the following common trends in recent CVD work:

CVD SiNx films are employed as barrier/protective layer, etch stop, and higher dielectric constant (κ) dielectric in IC microprocessor and memory (primarily metal-insulator-metal capacitor structures) devices; transparent and, moisture permeation barriers, and dielectric layer in solar cells; and organic light-emitting devices (OLEDs). More unique applications include SiNx overlays on cylindrical fused silica optical fibers and host material for Si nanocrystals as active light emitters both for use in photoluminescence (PL) and optoelectronics devices. One common attribute in all these applications is the inherent ability of CVD to provide conformal SiNx coatings in complex topographical structures, such as high aspect ratio channels, vias, and trenches in IC applications.

Silane (SiH₄) and ammonia (NH₃) are the predominant source chemistries for, respectively, silicon and nitrogen. Under PE-CVD conditions, high quality SiNx films with minimal hydrogen content can be obtained in the temperature range of 300–400°C. This temperature range is also needed to yield higher density films with low porosity and surface roughness, since it allows longer surface diffusion length of adsorbed radicals in comparison to when lower substrate temperatures are applied. Significantly lower substrate temperature (<100°C) was used in the case of polymer flexible and polyethyleneterephthalate substrates to minimize thermal budget induced damage to the fragile plastics, resulting in a-SiNx:H films with significant hydrogen content (>5%). The inclusion of increasingly higher hydrogen content (up to 30%) with gradual decrease in processing temperatures was supported by other work.

CVD SiNx thin film formation appears to involve the typical CVD reaction pathways (108,109) (1) transport of gaseous SiH₄ and NH₃ precursor species to the substrate surface, in the case of thermal CVD, or the occurrence of gas phase reactions, in the case of PE-CVD or PA-CVD, followed by transport of the resulting gaseous reactants (e.g., SiH₄ where x < 4 and NH₃ where y < 3) to the surface; (2) adsorption of the Si-bearing and N-bearing species to substrate surface; (3) surface diffusion with potential desorption of some reactant groups; (4) surface reaction with film nucleation in island growth or step growth mode; and (5) emission of resulting volatile reaction products. As mentioned above, higher substrate temperature allows longer surface diffusion lengths, leading to extended surface reaction times, and resulting in improved step coverage and reduced hydrogen incorporation. Alternatively, the pre-adsorption reactions in the case of PA-CVD or PE-CVD could produce more active reactant species, leading to higher surface reaction rates at shorter surface diffusion lengths, potentially producing less contaminated SiNx films but with poorer step coverage and lower etch resistance.

Although a significant body of research in thermal CVD SiNx can be found in the literature prior to 2010, there are very few recent reports (within the last five years) on the topic, due most likely to the high thermal budget required for dissociation and reaction of the Si and N chemistries, except for...
Table III. Summary of Recent ALD SiNx Work.

| Deposition Technique | Potential Application | Brief Description | Reference |
|----------------------|-----------------------|------------------|-----------|
| Thermal ALD          | Integrated Circuitry (IC) devices | Thin films in transistors, memory cells, logic devices, memory arrays | 100       |
| Plasma-Enhanced ALD (PE-ALD) | IC devices | Hydrofluoric acid (HF) etch stop layer and electrically insulating spacer | 80       |
| PE-ALD               | IC, MEMS, and biomedical devices | HF etch stop layer and electrically insulating spacer | 81 |
| PE-ALD               | MOSFET devices | Diffusion barrier | 82 |
| PE-ALD               | IC devices | Gate spacer of dynamic random access memory and logic devices, and charge trap layer of 3D vertical NAND flash devices | 83 |
| PE-ALD               | IC devices | Functional material for logic and memory devices | 84 |
| PE-ALD               | IC logic and memory devices | Oxidation mask, diffusion barrier, gate dielectric, liner, and spacer | 85 |
| Thermal and Plasma-Assisted ALD (PA-ALD) | IC logic and memory devices | Nitride spacer, floating gate | 86 |
| Thermal ALD          | Non-volatile memory (NVM) devices | Dielectric layer in stacked high-κ structures | 87 |
| PA-ALD               | IC devices, photovoltaic devices | Dielectric layer, sidewall spacer, hard etch mask, passivation layer, antireflection coating | 88 |
| PE-ALD               | IC memory devices | Gate spacers for high κ transistors | 92 |
| PE-ALD               | MOSFET devices | Spacer material | 90 |
| PE-ALD               | Organic light-emitting diodes | Encapsulation layer against moisture and O₂ permeation | 91 |
| PE-ALD               | IC devices | Barrier film and masking material | 89 |
| PE-ALD               | IC logic and memory devices | High κ material, spacer material | 93 |
| PE-ALD               | IC devices, photovoltaic devices | Anti-reflective coating, passivation and encapsulation layer, diffusion barriers, gate dielectric, stress liner | 94 |
| Thermal ALD          | IC devices | Dielectric layer, barrier for alkali or moisture | 95 |
| Thermal or PE-ALD    | IC devices | Liner and spacer material | 96 |
| Thermal ALD          | IC devices | Spacer, mask | 101 |
| PE-ALD               | IC devices | Spacer, etch stop material | 11 |
| PE-ALD               | IC devices | Host matrix for Ru nanocrystals as seed/barrier layer for Cu metallization | 97,98 |
| Thermal ALD          | IC devices | Dielectric material | 117 |

A noteworthy research on the thermal CVD reaction of dichlorosilane (SiH₂Cl₂) and nitrogen (N₂). This reaction required a substrate temperature of 700°C, which is prohibitively high for most electronic and solar applications. 77

A significant report34 included the use of pulsed RF generated by modulating a continuous 200Hz low-frequency wave signal generator with a 50% duty cycle in the PE-CVD reaction of SiH₄ and NH₃ at 150°C. The process yielded film densification (over 20% increase in film density) and smoothing (a decrease in average surface grain size standard deviation from 0.2nm² to 0.04nm²), with the SiNx films exhibiting smoother surface morphology and lower void density.

A common rule of thumb32,38,75 in the PE-CVD and PA-CVD work appears to be that lower R = NH₃/SiH₄ flow ratios (R < 1) lead to Si-rich films (Si/N ratio > 1.1), while higher R (R > 1) produces N-rich films (N/Si ratio < 1.4), with inclusions of Si nanostructures or nanoscale intrusions at even higher R values. Also, lower substrate temperatures tend to yield a-SiNx:H films, with thermal annealing required to reduce H content and lead to film crystallization, while higher processing temperatures produce c-SiNx films with reduced hydrogen content. Comparable results were obtained in the case of PE-CVD SiNx from a N₂+SiH₄ mixture, with Si-rich films being formed at higher N₂ flows. 75

A study of post-deposition thermal annealing effects were also reported under different annealing modes, gases, and durations, with 36 or without vacuum break between the deposition and annealing steps. 38,41,42

In the case of in situ annealing, 21 SiNx multilayered permeation barrier stacks deposited on PET substrates < 100°C were transported to a PE-CVD chamber between every two successive 50-nm thick SiNx layers and exposed to a 13.56 MHz RF Ar plasma at varying power density, working pressure, and treatment duration. The work led to the identification of an optimized Ar plasma treatment

Table IV. Si- and N- Bond Dissociation Energies for Selected SiNx Source Chemistries*.

| Source Precursor | Bond Dissociation Energy (kJ/mole) |
|-----------------|-----------------------------------|
| Nitrogen N₂ (N-N) | 946 |
| NH₃ (N-H) | 435 |
| H₂NNH₂ (N –N) | 272 |
| Silicon SiCl₄ (Si-Cl) | 460 |
| H₂SiCl₂ (Si-Cl) | 456 |
| H₂SiCl₃ (Si-H) | 394 |
| SiH₄ (Si-H) | 384 |
| SiBr₄ (Si-Br) | 377 |
| Si₂H₆ (Si-H) | 374 |
| Si₂H₆ (Si-Si) | 321 |
| Si₂ (Si-I) | 284 |

*The table is intended to provide baseline comparisons of bond dissociation energies of selected organic and inorganic Si and N source chemistries with the most commonly used precursors.102,103
Table V. Relevant Properties of Recently Studied CVD and ALD SiNx Source Precursors.

| Class            | Name                        | Acronym | Formula          | Molecular Weight | % Si  | form       | Boiling Point | Melting Point | Vapor Pressure | Density g/cm³ |
|------------------|-----------------------------|---------|------------------|------------------|-------|------------|---------------|---------------|----------------|---------------|
| Perhydridosilanes| silane                      | SiH₄    | 32.12            | 87.4             | gas   | −112°C     | −185°C        | −110°C        | 0.775          | 0.680         |
|                  | disilane                    | Si₂H₆   | 62.22            | 90.3             | gas   | −145°C     | −132°C        | 21.1°C        | 2586           | 0.686         |
|                  | trisilane                   | Si₃H₈   | 92.32            | 91.2             | liquid| 52.9°C     | −117°C        | 0°C           | 95.5           | 0.743         |
|                  | n-tetrasilane               | Si₄H₁₀  | 122.42           | 91.7             | liquid| 106°C     | −85 to −95°C  | 20°C          | 22             | 0.825         |
|                  | isotertrasilane             | Si₅H₁₀  | 122.42           | 91.7             | liquid| 101°C     | −99°C         | 20°C          | 25             | 0.793         |
|                  | neopentasilane              | NPS     | 152.52           | 92.1             | liquid| 132–134°C | <−40°C        | 25–15         | 0.805          |               |
| Hydridohalosilanes| monochlorosilane            | MCS     | SiH₃Cl           | 66.56            | 42.2  | gas        | −30.4°C       | 118°C         | 25°C          | 1.145         |
|                  | dichlorosilane              | DCS     | SiH₃Cl₂          | 101.01           | 27.8  | gas        | 8.3°C         | −122°C        | −34°C          | 100           |
|                  | diiodosilane                | DIS     | SiH₃I₂           | 283.91           | 9.9   | liquid     | 149–150°C      | −1°C          | 55–25         | 2.834         |
|                  | diiodotrisilane             | DIT     | 409.81           | 31.0             | liquid| 220°C     | 8°C           | 95             | 12             | 3.314         |
| Halosilanes      | tetrachlorosilane           | SC1₄    | 169.90           | 16.5             | liquid| 57.6°C    | −70°C         | 20°C          | 194°C          | 1.481         |
|                  | hexachlorodisilane          | HCDS    | Si₃Cl₆           | 268.89           | 20.9  | liquid     | 144–16°C       | −1°C          | 85–109        | 1.562         |
|                  | octachlorotrisilane         | OCTS    | Si₃Cl₈           | 367.88           | 22.9  | liquid     | 213–5°C        | −67°C         | 90–10         | 1.61          |
|                  | tetrabromosilane            | SB₄₅    | 347.70           | 8.1              | liquid| 154°C     | 5°C           | 0.18          | 2.772          |               |
|                  | triiodotrisilane            | STI₄    | 535.70           | 5.2              | solid | 287–8°C   | 120–1–125°C   | 25–10         | 4.198          |               |
| Aminosilanes     | trisilylamine               | TSA     | Si₃H₆N          | 107.33           | 78.5  | liquid     | −106°C        | 0°C           | 110–109       | 0.895         |
|                  | bis(dimethylaminosilane)    | BDEAS   | SiH₂₂C₆N₂       | 174.36           | 16.1  | liquid     | 188–189°C      | 0°C           | 70–30         | 0.804         |
|                  | bis-(butylamino) silane     | BTBAS   | SiH₂₂C₆N₂       | 174.36           | 16.1  | liquid     | 167°C         | <−50°C        | 25–15         | 1.15          |
|                  | tris(dimethylamino) silane  | 3DMAS   | SiCH₂Cl₂C₆N₃   | 161.32           | 17.4  | liquid     | 145–8°C        | 90°C          | 4°C           | 1.68          |
|                  | tris(isopropylamino) silane | TIPAS   | SiH₂₂C₆N₃       | 203.40           | 13.8  | liquid     | 165–166°C      | 25°C          | 1             |               |
|                  | tris(ethylamino) silane     | TEAS    | SiH₂₂C₆N₄       | 204.39           | 13.7  | liquid     | >90–90°C       | <0°C          | 25°C          | 1.3           |
|                  | tris(dimethylamino) silane  | 4DMAS   | SiH₂₂C₆N₄       | 204.39           | 13.7  | liquid     | 180°C         | <2°C          | 75°C          | 0.19          |
|                  | bis(dimethylaminomethylsilyl)|           | DTDNS-2H₂    | 263.60           | 32.0  | liquid     | 237°C         | 60°C          | 1.0           |               |
|                  | (trimethyl) silane          | TICTZ   | Si₃C₆H₉N₃      | 261.59           | 32.2  | liquid     | 220–224°C      | −69°C         | 67±1.8        | 0.919         |
|                  | tetramethylsilazane         | TMDZ    | SiC₆H₁₃N       | 133.34           | 42.1  | liquid     | 99–100°C       | <−60°C        | 25–55         | 0.766         |
|                  | diisopropylamino silane     | DPAS    | SiC₆H₁₇N       | 131.30           | 21.4  | liquid     | 117°C         | <−20°C        | 55±10.6       | 0.76         |

Data in this table from sources cited in text or experimentally determined by the authors.

In the case of annealing in a conventional oven with vacuum break, one study performed annealing of Si-rich SiNx films in a conventional oven in N₂ flow, with thermal treatment at 1100°C leading to the formation of Si nanocrystals (Si-NCs) within the SiNx host matrix. The Si-NCs acted to significantly enhance the SiNx films photoluminescence properties due to quantum confinement effects. In another study, SiNx samples were annealed in a conventional oven at 830°C to improve hydrogen passivation and ensure reduced leakage current in the resulting metal-insulator-semiconductor (MIS) structures. Alternatively, another approach implemented rapid thermal annealing (RTA) in vacuum break in pure Ar, Ar with 20% O₂, and Ar with 50% O₂ of Si nanoscale intrusions (Si-ni) embedded in Si-rich SiNx films. It was found that only at temperatures above 950°C did the thermal treatment have any effect on the optical properties of the Si nanoscale intrusions, although the effect was less significant than the NH₃ to SiH₄ ratio during the deposition step.

Physical Vapor Deposition (PVD)

Appendix B presents a synopsis of SiNx sputtering parameters and post processing treatments (where applicable). A review of Table II and Appendix B shows the following common trends in recent sputtering work:

Most common applications for sputtered SiNx films consist primarily of a barrier/passivation coating and etch stop in microelectromechanical systems (MEMS), high reflective index material for solar cells, through-Si vias for three-dimensional (3D) semiconductor devices, electroluminescent devices, and display devices. High k dielectric layer in stacked high-dielectric constant (k) structures for non-volatile memory (NVM) devices. A unique application is as a host material for Si nanocrystals as active light emitters for uses in PL and optoelectronic devices. Given that sputtering tends to be a line of sight technique, the application of sputtering techniques is primarily limited to topographies that are less aggressive with more relaxed design rules and smaller aspect ratios than their CVD and ALD counterparts.

DC or RF magnetron sputtering were the deposition techniques of choice for PVD, although the deposition rates for RF magnetron sputtered SiNx were significantly lower than their DC counterparts. Furthermore, the DC magnetron sputtered SiNx films exhibited superior chemical and physical properties than their RF magnetron sputtered analogs, while displaying equivalent electrical characteristics in MEMS devices.
These findings support the conclusion that DC magnetron sputtered films are more suitable than their RF equivalents for most SiN films applications, except in cases where substrates are mechanically or chemically fragile, thus requiring reduced impact energy to minimize ion and radical Induced damage.

In DC magnetron sputter work,\textsuperscript{113} it was shown that the N\textsubscript{2} plasma back pressure played a key role in modulating the N/Si ratio in the resulting SiN\textsubscript{2} films, with higher back pressures leading to increased N content in the films. Alternatively, in another report, the N/Si ratio in SiN\textsubscript{2} films was controlled by employing RF Magnetron sputtering to produce Si-rich films, and PE-CVD to yield N-rich films.\textsuperscript{28}

A pertinent report\textsuperscript{28} compared the properties of SiN\textsubscript{2} films grown by RF magnetron sputtering and PE-CVD at low temperature. The resulting findings indicated that sputtering was more appropriate than PE-CVD in yielding higher quality SiN\textsubscript{2} films with enhanced density, with the lower density in the PE-CVD coatings being attributed to the inclusion of hydrogen (due to the lower processing temperature employed).\textsuperscript{25}

Another report of note\textsuperscript{31} focused on the formation of Si nanocrystals (Si-NC) in multilayered structures consisting of alternating Si-rich SiN\textsubscript{2} (SRN) and Si\textsubscript{N3} ultrathin films. In this case, the N/Si ratio in the SRN layers was regulated by co-sputtering from Si (DC magnetron sputtering) and Si\textsubscript{N3} (RF magnetron sputtering) targets. The Si content in the resulting SRN films was modulated by adjusting the deposition rates from the targets through control of the power applied to the targets, with the application of higher DC power to the Si target leading to an increase in Si concentration. Alternately, stoichiometric Si\textsubscript{1}N\textsubscript{2} ultrathin films were achieved by RF magnetron sputtering from the stoichiometric target. After the formation of 25 alternating layers consisting of 5 nm thick SRN and 1 nm thick Si\textsubscript{1}N\textsubscript{2}, the structures were capped with a 10 nm-thick Si\textsubscript{N3} protective coating and annealed above 900 °C in N\textsubscript{2} environment to form Si-NCs in the Si-rich layers. The annealing step led to improved PL performance, which was attributed to improved crystallization and enhanced nitride passivation in the Si-rich layers.

**Atomic Layer Deposition (ALD)**

Appendix C presents a synopsis of SiN films, thermal, plasma-assisted, and plasma-enhanced ALD parameters and post processing treatments (where applicable). A simple first-order observation is that under similar conditions, regardless of technique, growth per cycle (GPC) is significantly greater with precursors containing multiple silicon atoms. For example, neopentasilane has a higher growth rate than silane. Similarly, hexachlorodisilane has a higher growth rate than dichlorosilane.\textsuperscript{113} Table III and Appendix C reveal the following additional trends in recent ALD work:

The most common applications for ALD SiN films are barrier/protective layer, etch stop, passivation layer, spacer material, and high dielectric constant (κ) dielectric in emerging nanoscale IC microprocessor and memory devices,\textsuperscript{100} and, to a lesser extent, transparent barrier, anti-reflective coating, anti-moisture permeation layer, and dielectric layer in solar cell and OLED systems.\textsuperscript{89} Other applications include host matrix for ruthenium nanocrystals as seed/barrier layer for copper metallization in IC structures,\textsuperscript{97,98} and hydrofluoric acid etch stop layer and electrically insulating spacer in MEMS and medical devices.\textsuperscript{80,83} One common attribute in all these applications is the inherent ability of ALD to produce stringent atomic level control and excellent conformality\textsuperscript{25} for SiN films in challenging geometries where CVD begins to show its deficiencies and shortcomings. These geometries include highly complex topographical structures, such as extremely high aspect ratio or exceedingly narrow channels, vias, and trenches in IC applications.

In contrast to recent CVD work, very few ALD reports used SiH\textsubscript{4} and other perhydrosilanes, such as neopentasilane (SiH\textsubscript{5}H\textsubscript{4}), as Si source chemistry.\textsuperscript{113} Instead, the Si sources employed in the most recent ALD investigations could be organized into two categories: (a) inorganic Si sources, including hydridosilanes, such as monochlorosilane (SiH\textsubscript{3}Cl),\textsuperscript{93} dichlorosilane (SiH\textsubscript{2}Cl\textsubscript{2}),\textsuperscript{90} and disiloxane (SiH\textsubscript{2}O\textsubscript{2}),\textsuperscript{103} and halosilanes, such as hexachlorodisilane (Si\textsubscript{2}Cl\textsubscript{6}),\textsuperscript{86,97} octachlorotrisilane (Si\textsubscript{3}Cl\textsubscript{6}),\textsuperscript{87} and tetraiododisilane (Si\textsubscript{2}I\textsubscript{4});\textsuperscript{101} and (b) organic Si sources, primarily amidosilanes, such as BT-BAS (Si\textsubscript{2}N\textsubscript{2}C\textsubscript{4}H\textsubscript{12}),\textsuperscript{92} For nitrogen, the majority of the work described the use of NH\textsubscript{3} or N\textsubscript{2}. One report suggested the additional use of hydrazine (N\textsubscript{2}H\textsubscript{4}),\textsuperscript{101} which is quite undesirable given its elevated toxicity and high instability, while another proposed the utilization of t-butylhydrazine (C\textsubscript{4}H\textsubscript{9}N\textsubscript{2}H\textsubscript{4})\textsuperscript{102} Although no dissociation energy is available in the literature for t-butylhydrazine, it is estimated to be significantly lower than N\textsubscript{2} based on reports in the literature on the dissociation energy of N\textsubscript{2}H\textsubscript{4},\textsuperscript{103} thus making t-butylhydrazine more conductive for ALD growth of SiN films at lower temperatures than N\textsubscript{2}.

ALD SiN work\textsuperscript{86,87,100,117} was carried out in three different modes: thermal (no plasma), PA-ALD (where the plasma was generated in the reactor directly above the substrate), and PE-ALD (where the plasma was generated remotely and transported into the reactor).

For thermal ALD, the majority of the work focused on the reaction of halosilanes and N-bearing reactants, including: (a) SiH\textsubscript{4} and NH\textsubscript{3} or C\textsubscript{4}H\textsubscript{9}N\textsubscript{2} in the temperature range of 175–250 °C;\textsuperscript{100} (b) Si halides containing Br and/or I (e.g., Si\textsubscript{2}Br\textsubscript{2}, Si\textsubscript{2}Br\textsubscript{4}I\textsubscript{2}, and X is one or more Br or I) and a N-containing reactant, such as NH\textsubscript{3}, in the temperature range of 350–600 °C;\textsuperscript{86} (c) Si\textsubscript{2}Cl\textsubscript{6} and NH\textsubscript{3} in the temperature range of 310–500 °C;\textsuperscript{87} (d) Si\textsubscript{2}Cl\textsubscript{6} and NH\textsubscript{3} in the temperature range of 515–573 °C.\textsuperscript{117} Only two of the reports\textsuperscript{86,117} presented compositional analysis results for the SiN films. The findings indicated that lower deposition temperatures generated stoichiometric films that oxidized upon exposure to air. Higher processing temperatures generated films that were closer to a N/Si ratio of ~1.3, and led to a reduction but not complete elimination of oxidation upon removal from the ALD reactor. These results suggest that thermal ALD might require prohibitively higher deposition temperatures (well above 573 °C) to yield stoichiometric films with effective resistance to oxidation.

PA-ALD SiN is the subject of relatively few reports,\textsuperscript{86,88} and the work focused on the reaction of halosilanes and N-bearing reactants, primarily: (a) Si halides containing Br and/or I (See section Overview of silicon nitride source chemistries) and a N-containing reactant, such as NH\textsubscript{3}, in the temperature range of 350–600 °C;\textsuperscript{86} and (b) Si\textsubscript{2}Cl\textsubscript{6} and NH\textsubscript{3} in the temperature range 350–450 °C.\textsuperscript{88} The apparent lack of interest in PA-ALD SiN could be attributed, at least in part, to concerns about the potential adverse effects of plasma generation directly above the substrate, including the potential inclusion of contaminants in the films. Furthermore, compositional analysis\textsuperscript{88} showed that the PA-ALD films were N-rich (N/Si ratio ~1.71) with significant H incorporation (e.g., as high as 23% at 400 °C). Infrared studies\textsuperscript{88} supported the preferential reaction of Si\textsubscript{2}Cl\textsubscript{6} with surface NH\textsubscript{2} clusters, instead of NH groups, with the latter being incorporated in the SiN films due to their reduced reactivity with Si\textsubscript{2}Cl\textsubscript{6}. Interestingly, the infrared analysis demonstrated that the inclusion of H in the films was primarily in the form of NH species. This is consistent with earlier reports of Atmospheric Pressure CVD (APCVD) silicon nitride generated from solid 

Most recent ALD work consisted of plasma assisted processing, wherein the plasma was generated remotely and transported into the reactor.\textsuperscript{117,79,85,89,94–96,98,100,101} The benefits of remote plasma include lower deposition temperatures while ensuring minimal plasma-induced damage, exclusion of...
A number of reports examined the role of substrate temperature in PE-ALD SiNx, with a primary focus on the effects of low thermal budget on PE-ALD process characteristics and resulting film composition and chemical and electrical properties. One such report investigated low temperature PE-ALD growth from bis(tert-butyloxy)silane (BTBAS) and a N2/Ar plasma at 150 °C.96 Subsequent structural and chemical characterization of the SiNx layers indicated the absence of open pores larger than 0.3nm in diameter, with films as thin as 10 nm displaying good barrier properties. A second investigation examined low temperature PE-ALD (<300 °C) of SiNx films from neopentasilane (NPS) as source chemistry using trisilylamine (TSA) as comparative baseline. The study determined that both precursors exhibited similar N2 plasma saturation behavior, with NPS displaying higher growth rates. The films were Si rich (Si/N ratio ∼1.13) with minimal O and C contaminants. A third study94 analyzed the thermal dependence of PE-ALD SiNx films grown from trisilylamine (TSA) and NH3 in the temperature range 250–350 °C. All the films were nearly stoichiometric (N/Si ratio increased from 1.32 at 250 °C to 1.35 at 350 °C). Alternatively, hydrogen content decreased from ∼13% to ∼8% with the rise in thermal budget. In terms of higher temperature growth, processing temperatures of 400 °C and 500 °C were used in the PE-ALD of SiNₓ from NH3 and, respectively, monochlorosilane (MCS) and dichlorosilane (DCS).95 The work demonstrated that the resulting SiNₓ spacer (grown at 400 °C) and gate encapsulation (deposited at 500 °C) were crucial components in successful high-k metal gate applications. Similar findings were presented100 for PE-ALD SiNx from Si precursors containing an iodine ligand (such as HSiI3, H2SiI2, or H3SiI) and a N-containing plasma. The resulting N/Si ratio ranged from 0.5 to 2.0. The findings are consistent with prior work that employed tetraodasilane and titanium tetraiodide to generate Ti-Si-N diffusion barriers for copper metallization at low temperatures.73

In terms of the PE-ALD adsorption and decomposition mechanisms for inorganic sources, one recent report65 analyzed the reactivity of β-Si3N4 surface sites with Si2Cl6 (using SiH4 as comparative baseline) during the PE-ALD Si2Cl6 substrate exposure step by combining ab initio density functional theory calculations with actual PE-ALD SiNx film deposition. The analysis examined three types of substrate surface sites: (a) hydrogen passivated N and Si sites (NH/SiH); (b) NH and SiH2 sites formed during the NH3 exposure step (NH/SiH2); and (c) under-coordinated bare Si=N sites. It was determined that the bare Si=N sites were more energetically favorable than their NH/SiH and NH/SiH2 counterparts to react with the Si or Cl atoms from the source precursors. It was also concluded that the reaction energy was lower for Si2Cl6 than SiH2. These findings led to the identification of a 3 step PE-ALD process to attain the most energetically favorable surface sites during the Si source PE-ALD substrate exposure step. Another investigation11 analyzed the role of a N2 plasma pre-treatment prior to the SiH4 exposure step on Si substrates and found that atomic N and N+ are the central reactant species that adsorb to the Si surface to form Si-N. The latter then act as reactive adsorption spots for SiH4 at N dangling bond sites, generating adsorbed SiH2 and NH species. Further adsorption is excluded until the formation of Si–N bonds, leading to a repetition of the previous N species adsorption cycle. Reiterating the alternating N2 plasma/SiH4 exposure steps results in the growth of a complete Si-N layer followed by the formation of a continuous SiNx film. This alternating exposure process was applied to produce SiNx:H films with enhanced conformality and improved moisture barrier behavior.

In terms of the PE-ALD adsorption and decomposition mechanisms for organic sources, a similar theoretical and experimental study62 of the energies of adsorption and decomposition of bis(dimethylaminomethyl)silyltrimethylsilylamide (DTDN2-H2, C₈H₅N₃SiH₂) during DTDN2-H2 exposure step on the growing PE-ALD SiNx film surface. The bare Si=N sites (as formed by the N2 plasma) were found to be the most energetically favorable for the adsorption and reaction of DTDN2-H2. The study also showed that the N/Si ratio in the films increased from 0.98 to 0.99 as the substrate temperature was raised from 300 °C to 400 °C, with oxygen content ∼7.5% due to oxidation upon exposure to air. Further increase in substrate temperature to 500 °C caused higher C incorporation, as well as a significant increase in O content. Alternatively, another study50 combined first-principles density functional theory with experimentation to examine the effects of N-bearing plasmas (N2, H2, N2-H2, NH3) on the mechanisms of adsorption of bis(t-butyloxy)silane (BTBAS, SiNₓCₓH₁ₓ₊₂) on β-Si₃N₄ (0001) surfaces with various surface terminations. The study concluded that the use of H2, N2-H2, and NH3 plasmas caused termination of reactive β-Si₃N₄ (0001) surface sites with H and NH3 species, thus inhibiting precursor adsorption and film formation. The study also determined that the application of a N2 plasma did regenerate reactive surface sites terminated with H and NH3 groups. Interestingly, a complementary investigation118 for PE-ALD SiNx from BTBAS pointed to the existence of so-called “re-deposition effects” resulting from the dissociation of aminoalkylsilanes in the plasma and the re-adsorption of fragments of such species on the surface of the growing SiNx film. It was found that this effect is driven primarily by the plasma gas residence time, with a shorter residence time leading to a reduction in re-deposition effects and yielding films of higher purity and improved quality.

A report of note66 incorporated ab initio techniques into theoretical models to examine the effects of PE-ALD reaction mechanisms on precursor adsorption and decomposition pathways for a variety of inorganic and organic Si precursors, including SiH4, SiH2Cl2, SiH2(CH3)2, Si3N4(NH3)12, and SiN2C8H22. The techniques employed realistic cluster models of amine-covered surfaces to derive the configurations and energies of chemisorption and reaction of these Si sources via functional group removal. These calculations were combined with density functional theory derivations that determined that the initial precursor physisorption phase was essential toward SiNx film formation, which led to accurate predictions regarding the reactivity of a collection of amino-silane precursors. The theoretical derivations also provided critical corrections on H retention in the PE-ALD SiNx films. A recent report used density functional theory to model the dissociative chemisorption of silicon nitride precursors (mono(alkylamino)silanes) on silicon dioxide to determine the effect of different aminoalkyl ligands.118 Adsorption energies, driven primarily by hydrogen bonding did not vary significantly with size of aminoalkyl ligands, however, a large variation in the reaction energy barriers was observed with ligand size due to transition state interactions and steric effects. The ALD window for suitable thin film growth was found to be widest for diisopropylaminosilane (DIPAS) and dipropylaminosilane (DAPAS) precursors (∼100 °C–500 °C). Another report67 of note developed a PE-ALD SiNx process as part of forming RuSiNx films as diffusion barriers for copper (Cu) interconnects for IC applications. The process employed tris(alkylamino)silane (TAPAS) and N2H4 for SiNx support films with varying Ru/SiNx ratios were formed by controlling the number of PE-ALD SiNx formation cycles while maintaining that for PE-ALD Ru constant. The resulting RuSiNx ternary phase consisted of an amorphous SiNx host matrix containing
taining Ru nanoclusters of ∼3 nm in diameter, and exhibited stable diffusion barrier performance against Cu diffusion up to 650 °C.

Studies of pre-, during, and post-deposition plasma treatment effects were also reported under different treatment modes, gases, and durations, with and without vacuum break between the deposition and treatment steps. Some of the key findings are reported below:

In the case of pre-deposition plasma treatment, substrate exposure to Ar plasma prior to SiΝ3 thermal ALD was shown to yield significantly lower SiΝ3 wet etch rates (WERs) compared to the case of no plasma treatment. Alternatively, the opposite effect was observed in the case of a post-deposition H2 plasma treatment which was attributed to the role of H2 plasma in removing contaminants from the film or causing its densification.

A similar finding was reported in the post-deposition treatment in a H2 plasma for 3 hours at 350 °C, which was ascribed to the efficacy of the H2 plasma at residual C removal from the films.

Ar plasma was also observed to improve surface adsorption and activation pathways for PE-ALD SiΝ3 films from DIPAS and NH3. In this work, successful SiΝ3 low temperature chemisorption (325 °C) was achieved through the application of an additional Ar plasma treatment step after the Si precursor purge step, but prior to the NH3 exposure cycle. However, when the intermediate number of Ar plasma treatments was increased from 1 to 3, the resulting films exhibited a rise in C and O contamination from, respectively, 0 to 10% and 15 to 30%. The films were Si rich with Si/N ratio over 2.

Alternatively, in PE-ALD of SiΝ3 from BTBAS and N2, it was shown that a constant increase in N2 plasma exposure time led to a continuous decrease in C content at lower deposition temperatures (<500 °C). For example, for films grown at 200 °C, C content decreased from ∼15% at 1s N2 plasma exposure time to ∼8% at 15s N2 plasma exposure time. Films formed at N2 plasma exposure times below 15s showed high affinity to O, while those deposited at 15s exhibited good resistance to oxidation. However, the composition of SiΝ3 films grown at 300 °C was nearly stoichiometric (Si3N4), with minimal O and C contents, irrespective of N2 plasma exposure time.

Summary and Commentary

The authors have presented an overview of the most recent published work (last five years or so) for SiΝ3 and SiΝ3-rich films, primarily SiΝ3 with C inclusion, SiΝ3(C). This survey highlights major emerging developments in the SiΝ3 material system technologies, with focus on Si and N source chemistries and thin film deposition processes and their effects on resulting properties. It also demonstrates that SiΝ3 is the subject of an ever-growing interest and that its use is expanding into new technological areas.

From a chemistry perspective, and while generalizations are difficult when such a wide range of SiΝ3 applications is considered, certain trends are observed. Traditionally, SiΝ3 deposition, particularly in IC devices, utilized Si- and N-rich precursors such as SiH4 and N2 in relatively high-energy environments (>700 °C or the use of plasma activation to achieve deposition at lower substrate temperatures). More recently, there has been a continual push toward lower energy deposition processes (reduced processing temperature) driven by the need to minimize thermal budget induced damage to thermally fragile substrates, such as low dielectric constant (κ) materials in IC devices and polymer materials in OLED applications. This trend has engendered the utilization of precursors that possess “pre-assembled” Si-N bonds as exemplified by “single-source” precursors such as trisilylamine and, in order to achieve deposition in even lower energy environments, precursors that contain C, such as bis(t-butyldimethylamino)silane. Concomitant with this trend, there was recognition that desirable dielectric or passivation properties could be achieved despite the adventitious incorporation of C into films. Functional or performance properties, independent of a simple compositional definition of SiΝ3, expanded interest in reproducible film formation with controlled and reproducible C inclusion. Silicon carbosilicides films became widely accepted and deposition techniques and conditions were explored. As dimension constraints became tighter and ALD techniques became generally accepted, the differences in gas-phase and substrate reactivity with Si-N, Si-C, C-N and Si-halide bonds have been exploited and furthered the evolution and introduction of new precursors.

Another independent trend that is readily recognized is the acceptance of silicon halides as precursors. Historically, while silicon halides react with ammonia and other amines at low temperature, thus making them attractive for lower energy deposition processes, the low gravimetric percentage of silicon in precursors and the troublesome ammonium salt byproducts would have eliminated them from consideration. The acceptance of hexachlorodisilane as a SiΝ3 precursor in full-scale manufacturing is leading to consideration of other silicon halides such as tetraiodosilane in near-term full-scale manufacturing. Inherent in the development of SiΝ3 films is the evolution of SiΝ3 as an encompassing descriptor of the technology to Si-N rich films, such as SiΝ3 with C inclusion, SiΝ3(C), as well as the precursors and the deposition techniques used to achieve these films.

From a processing perspective, CVD in its various forms, including thermal, hot wire (HW-CVD), plasma-enhanced (PE-CVD), and remote plasma-enhanced CVD, had been historically the method of choice for growing SiΝ3 thin films, followed by physical vapor deposition (PVD), primarily magnetron sputtering. More recently, however, ALD has been receiving the most attention due to the need for extremely thin SiΝ3 films with tight control in composition and properties. This trend is attributed to the inherent ability of ALD to provide strict atomic level control and excellent conformality for SiΝ3 thin films in aggressive geometries where CVD begins to suffer from poor step coverage. These geometries include highly complex topographical structures, such as extremely high aspect ratio or exceedingly narrow channels, vias, and trenches in IC applications.

Another trend that has contributed to the growth of interest in Si-N rich films is the area of heterodevices. Until now, the primary driver for thin film materials has been the manufacture of IC devices. Despite the enormous scholarly literature in virtually every area of thin film technology for microelectronics, there has been little opportunity for new techniques to achieve adoption in full-scale IC manufacturing. Heterodevices, particularly those associated with life sciences, have different sets of material requirements and can be successful at lower manufacturing scale. Heterodevices open a wide range of new commercialization opportunities for silicon nitrogen-rich materials. The field of Si-N rich films will continue to evolve with new film requirements, new techniques such as Molecular Layer Deposition (MLD) and Self-Assembled Monolayers (SAMs) and associated new Si- and N- precursors.

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Appendix A. Summary of SiNx Thermal, Plasma-Enhanced, Hot-Wire, and Remote Plasma-Enhanced Chemical Vapor Phase Deposition Parameters and Post Processing Treatments.

| Reactor Type                          | Subs. Type                                                                 | Subs. T (°C) | NH3 Flow Rate (sccm) | SiH4 Flow Rate (sccm) | H2 Flow Rate (sccm) | Duration of Deposit (sec) | Working Pressure (torr) | RF Power (W) or Power Density (W/cm²) | Film Thick. (nm) | Post Deposition Treatment | Pertinent Details                                                                 | Reference |
|---------------------------------------|-----------------------------------------------------------------------------|--------------|----------------------|-----------------------|---------------------|--------------------------|--------------------------|----------------------------------------|----------------|--------------------------|-------------------------------------------------------------------------------------|-----------|
| Standard PE-CVD chamber               | (100) p-type boron-doped monocrystal. Si substrates (ρ = 1–3 Ωcm)          | 350          | N/A                  | R = SiH4/NH3 flow ratio = 1 | None                | N/A                      | 3.5                      | 0.75                                   | 80             | None reported             | The intent of the work is to demonstrate a strategy for the indirect removal of SiNx by patterning an a-Si:H etch mask with an 800 nm 140 fs laser | 37        |
| Standard PE-CVD chamber               | 4.5 nm to 7 nm-thick HfO2 films                                              | 350          | N/A                  | N/A                   | N/A                 | N/A                      | 1000 W                   | 12                                     | None Reported | Investigation of the influence of optical fibers’ suspension height and diameter on SiNx deposition rate and resulting properties | 75        |
| Standard PE-CVD chamber               | (100) p-type Si subs (ρ = 1–10 Ωcm) Cylindrical fused silica optical fibers (length from 2.5–8mm and diameters of 125 μm and 400 μm) | 200          | 50                   | 150                   | None                | 900                      | ~0.9                     | 50 W                                   | 80             | None reported             |                                                                                                                                   | 76        |
| HW-CVD reactor with single coil shaped hot Ta filament as catalyst to decompose reactants (SiH4 and NH3 diluted in H2) Filmament placed at 7.5 cm to minimize its effect on substrate temperature | 175 μm-thick plastic substrates (heat stabilized PET with a stiffness of 3 × 10⁻³ N/m planarized on one side) | <100         | N/A                  | N/A                   | N/A                 | N/A                      | N/A                      | N/A                                    | 45–50 per SiNx layer | Samples transported without vacuum break to a PE-CVD chamber for Ar plasma treatment @13.56 MHz and 350 mW/cm² in-between deposition steps | Permeation barriers for organic electronic devices on polymer flexible substrates were realized by combining stacked silicon nitride (SiNx) single layers (50 nm thick) deposited by HWCVD with Ar plasma treatment between successive layers | 20        |
### Appendix A. Continued.

| Reactor Type | Subs. Type | Subs. T (°C) | NH<sub>3</sub> Flow Rate (sccm) | SiH<sub>4</sub> Flow Rate (sccm) | H<sub>2</sub> Flow Rate (sccm) | Duration of Deposit (sec) | Working Pressure (torr) | RF Power (W) or Power Density (W/cm<sup>2</sup>) | Film Thick. (nm) | Post Deposition Treatment | Pertinent Details | Reference |
|--------------|------------|--------------|-------------------------------|-------------------------------|-----------------------------|--------------------------|------------------------|---------------------------------|----------------|---------------------------|----------------|----------|
| CVD reactor with Ar wave plasma generated near the surface of a dielectric alumina window with a microwave frequency of 2.45 GHz Distance between alumina window and substrate stage set at 200 mm | 25 μ-thick polyimide base substrates | 90 | 500 (mixed with 350 sccm Ar) | 70 | None | 360 | 75 × 10<sup>-3</sup> | 1.57 W/cm<sup>2</sup> | 50 | None reported | Prior to deposition, polyimide base film was baked at 100°C for 30 min in a glove box with moisture and oxygen maintained at less than 0.1 ppm, then directly transferred from the glove box to the SWP-CVD system without exposure to the air. For multilayered SiN<sub>x</sub> depositions, samples transferred back and forth between HWCVD to PECVD chamber without breaking vacuum between deposition steps. For Ar treatment, samples were clamped to top electrode and heated to 100°C and bottom electrode was RF-powered. Optimal SiN<sub>x</sub> growth conditions achieved by varying 3 parameters: Hydrogen dilution, ratio of NH<sub>3</sub> to SiH<sub>4</sub>, and Ta filament current. Single and multi-layer SiN<sub>x</sub> films grown (the latter with intermediate Ar plasma treatment steps). Excess Si in Si-rich SiN<sub>x</sub> films controlled by varying the NH<sub>3</sub>/SiH<sub>4</sub> flow ratio between 0.45 to 1.0. | 23, 22 |
| HW-CVD reactor with Ta filament Glow-discharge (PECVD) chamber for sequences of SiN<sub>x</sub> single layers with Ar plasma surface treatment between individual layers deposition steps | PET substrates | 100 | varied | 2 | 54 | 360 | 25 × 10<sup>-3</sup> | 0.35 W/cm<sup>2</sup> (for Ar plasma treatment @50 mTorr only) | 50 | None reported | For multilayered SiN<sub>x</sub> depositions, samples transferred back and forth between HWCVD to PECVD chamber without breaking vacuum between deposition steps. For Ar treatment, samples were clamped to top electrode and heated to 100°C and bottom electrode was RF-powered. Optimal SiN<sub>x</sub> growth conditions achieved by varying 3 parameters: Hydrogen dilution, ratio of NH<sub>3</sub> to SiH<sub>4</sub>, and Ta filament current. Single and multi-layer SiN<sub>x</sub> films grown (the latter with intermediate Ar plasma treatment steps). Excess Si in Si-rich SiN<sub>x</sub> films controlled by varying the NH<sub>3</sub>/SiH<sub>4</sub> flow ratio between 0.45 to 1.0. | 20 |
| Remote-controlled PE-CVD chamber | (100) p-type Si substrates | 300 | varied (6.3 to 14 sccm) | 14 | N/A | 1800 | N/A | N/A | N/A | SiN<sub>x</sub> samples transferred from PECVD to conventional furnace with vacuum break SiN<sub>x</sub> films annealed in N<sub>2</sub> flow. Annealing temperature: varied from 700–1100°C. Annealing Duration: 30–60 mins | | 32 |
### Appendix A. Continued.

| Reactor Type                                    | Subs. Type                              | Subs. T (°C) | NH₃ Flow Rate (sccm) | SiH₄ Flow Rate (sccm) | H₂ Flow Rate (sccm) | Duration of Deposit (sec) | Working Pressure (torr) | RF Power (W) or Power Density (W/cm²) | Film Thick. (nm) | Post Deposition Treatment | Pertinent Details                                                                 |
|------------------------------------------------|-----------------------------------------|--------------|----------------------|-----------------------|----------------------|--------------------------|--------------------------|----------------------------------------|----------------|---------------------------|----------------------------------------------------------------------------------|
| Low-pressure CVD standard reactor               | p-type (100) Si substrates              | 750          | N/A                  | None SiCl₂H₂ used as Si source (flow rate: N/A) | None N₂ used (flow rate: N/A) | N/A                       | 0.6                       | 100                                | 33–231        | None reported              | SiNₓ films were deposited directly on a 5 nm-thick SiO₂ thin films on p-type (100) Si |
| PE-CVD standard chamber with a working frequency of 2.45 GHz | a-Si:H substrates                      | N/A          | N/A                  | N/A                   | N/A                  | 25 × 10⁻³                 | 1000                     | 80                            | None reported   | SiNₓ films with refractive index of 1.5–1.8 were used as antireflection coating |
| PE-CVD Chamber                                  | HF solution rinsed Si(100) wafers        | 200–400      | N/A                  | N/A                   | N/A                  | 0.6                      | 100                      | 100–500                   | None reported   | RF Sputtered SiNₓ films were of higher density than their PECVD counterparts |
| Linear microwave plasma batch processing system with a working frequency of 2.45 GHz Two deposition modes: Low total flow rate and high total flow rate | c-Si, UV cured acrylates and PEN substrates | 100          | Low total flow rate (400 sccm) \( R = \frac{\text{SiH}_4}{\text{NH}_3} \text{ flow ratio} = 0.05–0.5 \) | None Ar used (flow rate: 200 sccm) | 180–1020 secs \( 6 \times 10^{-2} \) | 1000                     | 79–100                   | None reported             | The films were a-SiNₓ:H          |
| Standard PE-CVD chamber                         | N/A                                     | N/A          | N/A                  | N/A                   | N/A                  | N/A                      | N/A                      | N/A                         | None reported   | Excellent reliability shown for vanadyl-phthalocyanine (VOPc) thin film transistors (TFTs) with SiNₓ as gate insulator |
| Pulsed RF with a low frequency (200 Hz) square wave envelope PECDV chamber Pulsed-RF supply generated by modulating a continuous wave (CW) RF supply using the 200 Hz signal generator with 50% duty cycle | c-Si substrates                          | 150          | 40                   | 4                     | 120                   | N/A                      | 0.8                      | 130 mW/cm²                  | N/A            | None reported              | 200 Hz modulation used to ensure that the duration of the off-cycle (2.5 ms) is significantly shorter than the gas residence time (~1s) and achieve a growth rate that is \( \frac{1}{2} \) of that for CW-RF growth |
| Reactor Type                     | Subs. Type                                                                 | Subs. T (°C) | NH₃ Flow Rate (sccm) | SiH₄ Flow Rate (sccm) | H₂ Flow Rate (sccm) | Duration of Deposit (sec) | Working Pressure (torr) | RF Power (W) or Power Density (W/cm²) | Film Thick. (nm) | Post Deposition Treatment | Pertinent Details                                                                 |
|---------------------------------|------------------------------------------------------------------------------|---------------|----------------------|----------------------|---------------------|---------------------------|------------------------|--------------------------------------|----------------|--------------------------|-----------------------------------------------------------------------------------|
| Standard PE-CVD chamber         | 4-inch GaAs bare and device wafers                                            | N/A           | 14–16                | 14                   | 0                   | 240–300                   | N/A                    | N/A                                  | 40–60 | Rapid thermal annealing (RTA) in ambient consisting of: Ar only, Ar with 20% O₂ and Ar with 50% O₂ RTA T: 850°C, 900°C, 950°C and 1050°C SiNₓ samples annealed at 830°C for better hydrogen passivation and reduced leakage current | Films consisted of Si nanometer size inclusions (Si-ni) in Si-rich SiNₓ matrix      |
| Standard PE-CVD chamber         | p-doped (100) oriented Fz-wafers with a resistivity of 1 Ω-cm               | 200–400       | N/A                  | N/A                  | N/A                 | N/A                       | N/A                    | N/A                                  | N/A          | CV measurements in crystalline solar cells showed that interfacial trap density and fixed charges are higher for PECVD SiNₓ than thermal SiO₂ and PECVD SiO₂ | SiNₓ samples annealed at 830°C for better hydrogen passivation and reduced leakage current | 36                          |
| Standard PE-CVD chamber         | Oxidized (111) p-type Si substrates                                          | 300–340       | (2% SiH₄ diluted in N₂ flow rate: 285 sccm) | 15                   | None                | 60–600                    | 0.4                    | 15 W                                 | 50             | None reported             | A high (SiH₂:N₂)/NH₃ flow ratio was employed in order to obtain high-refractive-index SiNₓ film (Single and multilayered SiNₓ films were deposited using the same processing parameters) | 24                          |
| Standard PE-CVD chamber         | 4-inch GaAs bare and device wafers                                            | 300           | 15                   | 15                   | N₂ used As diluent gas | N/A                       | N/A                    | Comb. of both high frequency (HF) and low frequency (LF) power | 50–70 |                                                                                       |                                                                                             | 16                          |
## Appendix B. Summary of SiNx Sputtering Parameters and Post Processing Treatments.

| Reactor Type | Subs. Type | Subs. T (°C) | Sputtering Gas | Duration of Deposit. (sec) | Working Pressure (torr) | Density (W/cm²) | Film Thick. (nm) | Post Deposition Treatment | Pertinent Details | Reference |
|--------------|------------|--------------|---------------|---------------------------|-------------------------|----------------|----------------|------------------------|---------------------|-----------|
| RF Magnetron Sputtering System | Double-side polished, single crystalline n-type (P doped) (100) CZ-Si wafers (p > 50 Ωcm) | R.T. | Ar + N₂ mixture 20 60 | N/A | 2.25–6.75 × 10⁻³ | 300–900 W (RF power density of 1.5–4.5 W/cm²) | 500 | None reported | Pre-deposition Si wafer inverse sputter etching clean step in same reactor: Substrate temperature: N/A Sputtering gas: Ar Ar flow rate: 20 sccm N₂ flow rate: 0 sccm RF Power: 200W Working Pressure: 4.0 × 10⁻³ torr | 116 |
| DC Magnetron Sputtering System (same as one used for RF sputtering above) | Double-side polished, single crystalline n-type (P doped) (100) CZ-Si wafers (p > 50 Ωcm) | R.T. | None Used 60 | 2.25–6.75 × 10⁻³ | 300–900W (DC power density of 1.5–4.5 W/cm²) | 500 | None reported | Pre-deposition Si wafer inverse sputter etching clean step in same reactor: Substrate temperature: N/A Sputtering gas: Ar Ar flow rate: N/A N₂ flow rate: 0 sccm DC Power: 200W Working Pressure: ⁿ⁻³ torr | 74 |
| RF Magnetron Sputtering Reactor | p-type (100) Si substrates (p = 15 Ωcm) | 500 | Ar + N₂ mixture N/A N/A | N/A | N/A | N/A | 3 | Half of the samples annealed at 800°C for 15s in continuous N₂ flow | The RMS SiNx films were deposited on p-type Si with x = 0.8 (Si-rich SiNx) | 75 |
| Standard RMS Reactor | Hydrofluoric acid (HF) solution rinsed Si(100) wafers | R.T. to 300 | Ar + N₂ mixture N/A | N/A | N/A | 50 | 100–500 | None reported | RF Sputtered SiNx films were of higher density than their PECVD counterparts Films consisted of 25 alternating layers of Si-rich SiNx and 1 nm SiNx Films capped with a sputtered SiNx capping layer of ~10 nm to prevent moisture and oxidation during thermal annealing | 25 |
| Magnetron co-sputtering system @ 5 × 10⁻⁹ base pressure | Two targets used: Si and SiNₓ | R.T. | N/A 0 | N/A | 1.5 × 10⁻² | 50 W (SiNx target RF power) 6 W (Si target DC power) 5 nm (Si-rich SiNx) and 1 nm (SiNx) Samples annealed in conventional quartz-tube furnace for 1 h at 900, 1000 and 1100°C in N₂ | N/A | None reported | | | 31 |
### Appendix C. Summary of SiN$_x$ Atomic Layer Deposition Parameters and Post Processing Treatments.

| Reactor Type                  | Subs. Type                     | Subs. T (°C) | Si Source (Vapor Pressure. torr) | Si Source Pulse Exposure | N Source (flow rate) | N Source Pulse Duration (sec) | Purge Gas | Purge Pulse Duration (sec) | Plasma Type | Working Pressure (torr) | Film Thick. (nm) | Pertinent Details                                                                 | Reference |
|-------------------------------|--------------------------------|--------------|---------------------------------|--------------------------|----------------------|-------------------------------|-----------|----------------------------|-------------|-------------------------|-----------------|----------------------------------------------------------------------------------------------------------------------------------|-----------|
| Thermal ALD reactor           | Insulators (e.g., SiO$_2$, HfO$_2$); conductor; semiconductors | 175–250      | SiI$_4$ (N/A)                   | N/A                      | NH$_3$ or t-butyl hydrazine (C$_4$H$_9$N$_2$) | N/A                          | He, Ar, or N$_2$ | N/A                       | None         | 0.1–1.0                 | ~1.3 per cycle    | −3 h, in-situ, remote plasma post-treatment in H$_2$ flow rate of 100 sccm and plasma pressure of H$_2$ mixed with Ar of 300 mTorr (@substrate temperature of 350 °C) to remove residual carbon | 100       |
| PE-ALD in a hot-wall reactor | Single crystal Si (100) wafers  | 350          | 3DMAS 7.1 @R.T.                 | 0.4s                     | N$_2$ (40 sccm)      | 15.0                          | Ar        | 10                         | Remote ICP plasma (300 W @ 13.56 MHz) | ~12         | Films used for ab initio density functional theory calculations of the reactivity of different β-Si$_3$N$_4$ surface sites with SiCl$_4$ and Si$_2$Cl$_6$ precursors | 80        |
| Hot-wall reactor and cold-wall reactor | Single crystal Si (100) wafers  | 350          | 3DMAS, TSA, DCS               | Varied function of Si source | NH$_3$ or H$_2$ + N$_2$ plasma | 15                            | N$_2$     | 3                         | Remote ICP plasma (300 W @ 13.56 MHz for hot-wall reactor and 400 W for cold-wall reactor) | N/A         | Films used for ab initio density functional theory calculations of the reactivity of different β-Si$_3$N$_4$ surface sites with SiCl$_4$ and Si$_2$Cl$_6$ precursors | 81        |
| Traveling-wave-type cold-wall reactor | β-Si$_3$N$_4$ | 300          | HCDS                           | 1 torr.s – 50 torr.s      | NH$_3$ | 10$^3$ torr.s | Ar | N/A                       | Remote ICP plasma (100W @ 13.56 MHz) | 1.5            | −16.5 | Energies of adsorption and reaction of DTBN2-H2 with SiN$_x$ surface were also calculated by density functional theory | 82        |
| Traveling-wave-type cold-wall reactor | N/A | 200–500       | DTDN2-H2 1.0@60°C | 3.0s | N$_2$ | 12.0 | N$_2$ | 16s | Remote ICP plasma 100W @ 13.56 MHz | N/A | ~16.5 | Energies of adsorption and reaction of DTBN2-H2 with SiN$_x$ surface were also calculated by density functional theory | 83        |
### Appendix C. Continued.

| Reactor Type                          | Subs. Type | Subs. T (°C) | Si Source (Vapor Pressure, torr) | Si Source Pulse Exposure | N Source (flow rate) | N Source Pulse Duration (sec) | Purge Gas | Purge Pulse Duration (sec) | Plasma Type               | Working Pressure (torr) | Film Thick. (nm) | Pertinent Details                                                                 |
|--------------------------------------|------------|--------------|----------------------------------|--------------------------|----------------------|-----------------------------|-----------|---------------------------|--------------------------|----------------------|-----------------|----------------------------------------------------------------------------------|
| Capacitively coupled plasma reactor  | Si         | 325          | BDEAS, TEAS, TIPAS, DIPAS        | N/A                      | NH₃                  | N/A                         | Ar        | N/A                       | Direct capacitively coupled plasma (CCP) 100–300 W @ 13.56 MHz Direct plasma @ 13.56 MHz | 3                      | ~1.5–1.8        | Additional plasma steps were employed after Si precursor purge to improve efficiency of precursor adsorption and lower deposition temperature | 84                    |
| Direct plasma reactor                 | Si (100) wafers | 250–300     | NPS                              | 1.0s                     | Direct N₂ plasma     | 2–30                        | Ar        | 15                        | Direct plasma @ 13.56 MHz | 0.56                  | 0.14 per cycle | Additional plasma steps were employed after Si precursor purge to improve efficiency of precursor adsorption and lower deposition temperature | 85                    |
| Thermal ALD reactor                   | Si, SiO₂, strained Si, Si on insulator (SOI), GaAs, Ge, metals, SiNₓ, p-type Si wafers | 350–600°C | Si halides containing Br and/or I halogens (e.g., SiₓBrₙ, SiBrₙ₋₁Iₓ (x = 1–3); SiₓXₓ₋₂ₓ (y > 2, and X is one or more Br or I)) | ~5.0                     | N-containing reactant (e.g., NH₃) | ~30.0                      | Ar        | 20.0                      | Thermal                  | N/A                  | ~8.0            | Substrate exposure to Ar plasma prior to SiNₓ ALD led to significantly lower SiNₓ wet etch rates | 86                    |
| Thermal ALD reactor                   | p-type Si wafers | 310–500     | OCTS                             | 2–15                     | NH₃                  | 2–30                        | N/A       | 15 @ 500 sccm             | N/A                      | 0.7                   | 15–35           | SiNₓ films deposited in ALD mode using 600 deposition cycles Film thickness controlled by deposition temperature | 87                    |
| Reactor Type | Subs. Type | Subs. T (°C) | Si Source (Vapor Pressure, torr) | Si. Source Pulse Exposure (sec) | N Source (flow rate) | N Source Pulse Duration (sec) | Purge Gas | Purge Pulse Duration (sec) | Plasma Type | Working Pressure (torr) | Film Thick. (nm) | Pertinent Details | Reference |
|-------------|------------|--------------|---------------------------------|-------------------------------|----------------------|----------------------------|----------|----------------------------|-------------|------------------------|--------------|----------------------|-----------|
| Remote PA-ALD reactor | ZnSe internal reflection crystal (IRC) | 350–450 | HCDS | 5–30 | NH₃ plasma | 5–45 | Ar | 30 @ 100 sccm | NH₃ | 0.7–1 | 30 | Surface reactions during Si₂Cl₆ and NH₃ plasma half-cycles were observed using in situ attenuated total reflection FTIR to identify surface reactive sites, and elucidate H incorporation mechanism in SiNx. Properties dependent on plasma exposure time, pressure and substrate temperature. Comparison of the effects of NH₃, N₂, or H₂ + N₂ plasma on SiNx growth rates. Thin films of SiNx deposited at low temperatures. | 89 |
| Remote PA-ALD reactor | c-Si with thin oxide layer | R.T.-500 | BTBAS | 0.15–3.0 | N₂ | 10 | Ar | 1 @ 100 sccm | Remote ICP plasma 600 W @ 13.56 MHz | N/A | 10⁻⁶ | N/A | N/A | | 89 |
| Remote PA-ALD reactor | N/A | N/A | BTBAS | N/A | NH₃ or N₂, H₂ + N₂ plasma | N/A | N/A | N/A | Remote ICP plasma 600 W @ 13.56 MHz | N/A | N/A | | 90 |
| Remote Plasma reactor | c-Si with thin oxide layer | 80–200 | BTBAS | 0.15–3.0 | N₂ | 10 | Ar | | Remote ICP plasma 600 W @ 13.56 MHz | 0.8 | 10 | | 91 |
| Remote PA-ALD reactor | N/A | 200–400 | BTBAS | 0.15–3.0 | N₂ | 10 | Ar | 10 @ 100 sccm | Remote ICP plasma 600 W @ 13.56 MHz | 0.2–0.4 | 30 | Re-deposition controlled by gas residence time during the plasma step. | 89 |
| Reactor Type                        | Subs. Type | Subs. Type | Subs. T (°C) | Si Source (Vapor Pressure, torr) | Si Source Pulse Exposure | N Source (flow rate) | N Source Pulse Duration (sec) | Purge Gas | Purge Pulse Duration (sec) | Plasma Type | Working Pressure (torr) | Film Thick. (nm) | Pertinent Details                                                                 |
|-----------------------------------|------------|------------|--------------|----------------------------------|--------------------------|----------------------|-------------------------------|-----------|---------------------------|-------------|--------------------------|----------------|-----------------------------------------------------------------------------|
| Direct plasma reactor             | Poly-Si/TiN/HfO₂ stacks | 400 or 500 | DCS, MCS    | N/A                              | Ionized NH₃              | N/A                  | N/A                           | N/A       | N/A                       | Direct plasma | N/A                      | <5 nm          | DCS used for SiNx gate encapsulation applications @ 500°C; MCS used for SiNx for spacer applications @ 400°C SiNx thin film characteristics controlled by dep. temp. to adjust the defect density for charge trap flash memory applications |
| Remote PA-ALD reactor             | p-type Si (100) | 50–400     | TSA @ 12°C (315 torr @ R.T.) | 0.2 | NH₃ | 5 | Ar | 15 | Remote plasma 100W@13.56 MHz | 0.3 | 4–25                 | First principles study using density functional theory to model the growth of a Si₁ₓN₂ surface in a full ALD cycle |
| Thermal ALD reactor               | Bare β-Si₃N₄ surface | N/A        | BDEAS, BTBAS | N/A                              | NH₃                      | N/A                  | N/A                           | N/A       | N/A                       | N/A                      | N/A                      | N/A          | First principles study using density functional theory to probe differences between ALD O₂ and Si₁ₓN₂ using various theoretical approaches, including model reaction pathways, acidity/basicity of the oxide vs nitride surfaces and overall energetics as a function of precursor functional group |

**Appendix C. Continued.**
| Reactor Type                     | Subs. Type | Subs. T (°C) | Si Source (Vapor Pressure, torr) | Si Source Pulse Exposure | N Source (flow rate) | N Source Pulse Duration | Purge Gas       | Purge Pulse Duration (sec) | Plasma Type | Working Pressure (torr) | Film Thick. (nm) | Pertinent Details                                                                 |
|--------------------------------|------------|--------------|----------------------------------|--------------------------|----------------------|------------------------|-----------------|--------------------------|--------------|--------------------------|-----------------|------------------------------------------------------------------|
| Thermal or PE-ALD reactor      | Si structures | 400          | Si precursors containing an iodine ligand such as HSiI₃, H₂SiI₂, H₃SiI, H₂Si₂I₄, H₄Si₂I₂, H₅Si₂I (1) | 0.05–5.0                | NH₃, N₂H₄, N₂       | 0.1–10                 | N₂, Ar or He     | 0.1–10                   | Remote or direct plasma @10–1000 W | N/A          | N/A                     | SiNx films exhibited etch rates in diluted HF that were half of those for SiO₂ | 101               |
| Parallel –plate capacitance PE-ALD reactor | (100) double-sided polished Si with native SiO₂ layer | 400          | SiH₄                               | 0.0–15.0                  | N₂                   | 0.5–90                 | N₂              | 1–5                      | Low frequency (LF) (200–400 kHz) and high frequency (HF) (13.56 MHz) power sources | 2.5          | ~0.5–90                  | PEALD SiNₓ:H growth was performed both on native SiO₂ and on 25 nm PECVD SiNₓ:H and SiO₂ films previously deposited on native oxide of the Si substrate | 11               |
| PE-ALD reactor                 | SiO₂ substrates | 270°C        | TIPAS                             | 0.5–2.0                   | NH₃                  | 8.0                    | Ar              | 10.0                     | Direct 13.56 MHz plasma @100 W | 3            | 100                      | PE-ALD SiNₓ was part of forming RuSiNₓ films as diffusion barrier for Cu interconnects | 97,98             |
| Thermal in traveling-wave-type cold-wall reactor | B-doped Si (100) wafers | ~515–573°C | HCDS                             | 0.1–3.0 × 10⁸L           | NH₃                  | 1.0–10 × 10⁸L       | Ar              | N/A                      | No plasma 1 torr and 10 torr | 20           | 20                      | SiNₓ films were nonstoichiometric and easily oxidized by air exposure to contain 7–8 at.% oxygen | 117             |

*For full descriptions of Si source acronyms used in this Appendix, see Table V.
