

Dissolution Behaviors and Applications of Silicon Oxides and Nitrides in Transient Electronics

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Silicon oxides and nitrides are key materials for dielectrics and encapsulation layers in a class of silicon-based high performance electronics that has ability to completely dissolve in a controlled fashion with programmable rates, when submerged in bio-fluids and/or relevant solutions. This type of technology, referred to as "transient electronics", has potential applications in biomedical implants, environmental sensors, and other envisioned areas. The results presented here provide comprehensive studies of transient behaviors of thin films of silicon oxides and nitrides in diverse aqueous solutions at different pH scales and temperatures. The kinetics of hydrolysis of these materials depends not only on pH levels/ion concentrations of solutions and temperatures, but also on the morphology and chemistry of the films, as determined by the deposition methods and conditions. Encapsulation strategies with a combination of layers demonstrate enhancement of the lifetime of transient electronic devices, by reducing water/vapor permeation through the defects.

1. Introduction

Materials for insulation, passivation and encapsulation in microelectronics are critically important for proper operation of the devices. Silicon oxides and nitrides are in widespread use not only for digital and analog circuits but also for thin film display electronics and others, due to their excellent properties as



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gate and interlayer dielectrics, passivation coatings,^[1-3] and barriers against water penetration.^[4,5] This paper explores the materials aspects of use of these films in a different, emerging class of electronics, whose defining characteristic is solubility in water, with environmentally and biologically benign end products. This type of technology, sometimes referred to as a class of transient electronics, could be important for temporary biomedical implants, resorbable sensors and monitors for the enviroment, 'green' disposable consumer devices and other systems that are not well served by conventional electronics, which last for decades and involve biologically and environmentally harmful materials. Initial demonstrations relied either on miniaturized, non-degradable inorganic components integrated with

resorbable silk substrates and encapsulating layers,^[6,7] or on synthetic and/or nature-inspired organic active and passive materials.^[8-10] An important advance followed from the observation that monocrystalline, device-grade silicon in ultrathin forms (i.e., nanomembranes), can dissolve, at various rates, in different types of biofluids as well as in seawater and other naturally occurring forms of water, all of relevance to envisioned applications.^[11,13] The end product, silicic acid, is biocompatible and environmentally benign at the low levels of concentration that are associated with small nanomembranes of silicon. Examples of demonstration devices include high performance complementary metal-oxide-semiconductor (CMOS) transistors and simple circuits, solar cells, strain/temperature sensors, digital imaging devices, wireless power scavenging systems and others.^[11-13] Additional inorganic semiconductor options include ZnO, of interest in part due to its piezoelectric properties, for transient mechanical energy harvesters, actuators and others.^[14] In most of these examples, MgO, which undergoes hydrolysis to Mg(OH)2, serves as the dielectric and encapsulation layer. Initial observations suggested that SiO2 might provide another option. Here, we study this material in detail, and also present evidence that SiN_x represents another alternative.

2. Dissolution Studies of Different Types of Oxides

Previous work on bulk materials establishes that the mechanism for hydrolysis of silicon oxides is SiO₂ + $2H_2O \rightarrow$ Si(OH)₄.^[15-17] Because OH⁻ initiates this reaction, the concentration of OH- (pH of solution) strongly influences the





Figure 1. Schematic illustration, images and data from a structure for testing the dissolution of thin (\approx 100 nm thick) square pads of SiO₂ formed by plasma-enhanced chemical vapor deposition (PECVD). a) Schematic illustration of the test structure, which consists of an array of square pads (3 μ m × 3 μ m × 100 nm) of PECVD SiO₂ deposited at 350 °C on a thermally grown oxide (tg-oxide) on a silicon (100) wafer, with inset optical micrograph. b) AFM topographical images and c) profiles of a representative pad at different stages of hydrolysis in buffer solution (pH 12) at physiological temperature (37 °C).

dissolution rate, as observed in studies of the dissolution kinetics of quartz and amorphous silica.^[15-18] Here, we examine materials in forms and with chemistries widely utilized in the semiconductor industry, as thin films grown/deposited using standard or slightly modified techniques. The results reveal essential aspects of hydrolysis in such cases, including the influence of morphology and chemistry, as defined by the conditions and methods for deposition. To examine the dependence of the dissolution rate on pH and type of oxide, systematic studies were performed in buffer solutions with pH between 7.4 to 12, and at different temperatures. Three different classes of materials were examined: thin films of oxides formed by 1) growth using dry (O_2 gas) and wet (H_2O vapor) thermal oxidation (tg-oxide), 2) plasma enhanced chemical vapor deposition (PECVD oxide), and 3) electron-beam evaporation (E-beam oxide).

Spectroscopic ellipsometry (J. A. Wooldman Co. Inc., USA) revealed the dissolution rate as a time dependent change in

thickness. Atomic force microscopy (AFM, Asylum Research MFP-3D, USA) provided information on the surface topography as well as independent measurements of thickness. Test structures of PECVD and E-beam materials for AFM measurements consisted of arrays of isolated square films (3 $\mu m \times$ 3 $\mu m \times$ 100 nm) patterned on tg-oxide, whose dissolution rate is much slower than that of other materials, as shown subsequently. Figure 1a presents a schematic illustration of a test structure, and an optical micrograph in the inset. Figure 1b,c provides AFM images and thickness profiles at several stages of immersion in aqueous buffer solution (pH 12) at 37 °C. (Additional AFM images appear in Figure S1 and S2, Supporting Information.) These results indicate that the oxides dissolve in a uniform fashion, without any significant change in surface topography, formation of flakes or other non-ideal behaviors like those observed, for example, in transient metals under similar conditions.^[19] In all cases, samples were immersed in ≈50 mL of aqueous solutions, removed, rinsed and dried, and



then measured (spectroscopic ellipsometry; AFM). After measurements (total times of several hours), samples were placed back into fresh solutions. The solutions were replaced every other day. (The dissolution rates, for all cases examined in this paper, did not change substantially for various time intervals for solution replacement (e.g., for every 1, 2, 4, or 7 days). Details appear in the experimental section.)

Figure 2a–c and Figure S3 provide the dissolution kinetics of tg-oxide (dry and wet oxidation), PECVD oxide and E-beam oxide in terms of the change in thickness as a function of time in buffer solutions (pH 7.4 to 12) at room temperature (RT) and 37 °C. The tg-oxides and E-beam oxide exhibit the slowest and fastest rates, respectively, under the same conditions. Four main factors affect the rate: temperature, pH, and ionic content of the solutions, and chemical/morphological properties of the films. The dissolution rate of each oxide increases with temperature, with an expected Arrhenius dependence, consistent with previous studies.^[17,20]

Figure 2d shows a linear dependence of the dissolution rate for each type of oxide in buffer solutions with different pH at 37 °C (see more details at RT in Figure S4, Supporting Information), similar to related observations.^[15–17] The relationship can be written log r = a + n [pH], where r is the dissolution rate, and *a* and *n* are constants $(n = 0.33 \text{ for quartz when } r \text{ is in mol } m^{-2} \text{ s}^{-1}).^{[16]}$ The values of n for the data in Figure 2d and Figure S4 (Supporting Information) are between 0.31 to 0.44 (at 37 °C) and 0.22 to 0.62 (at RT), respectively. The kinetics can also be influenced by the concentration of ions in the solution.^[21,22] As an example, bovine serum (pH ~ 7.4) and sea water (pH ~ 7.8) show rates that are ≈ 9 and ≈ 4 times higher than those observed at similar pH in buffer solution, respectively, likely due to the presence of additional ions (e.g., K⁺, Na⁺, Ca²⁺, and Mg²⁺) in these liquids.^[21,22]

The dissolution rate can also be affected, of course, by the physical and chemical properties of the films, which in turn depend on growth/deposition methods and conditions. Thermal oxide is known to be uniformly dense.^[23] Oxide created by PECVD can show different stoichiometries and densities, due to by-products from the SiH₄ source gas as it reacts with Si to form Si–H. Such effects can be particularly important for low temperature deposition.^[24] E-beam oxide formed from a pure source of SiO₂ (i.e., pellets) can involve nanoscale fragmentation during evaporation,

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Figure 2. Dissolution kinetics, as defined by the rate of change of film thicknesses, of different silicon oxides in various aqueous solutions, with different values of pH at room and physiological temperatures. a) Calculated (lines) and measured (symbols) values for the time-dependent dissolution of thermally grown SiO₂ (dry oxidation) in buffer solutions (black, pH 7.4; red, pH 8; blue, pH 10; magenta, pH 12) at room (left) and physiological (right, 37 °C) temperatures. b) Calculated (lines) and measured (symbols) dissolution behaviors of PECVD SiO₂ in diverse aqueous solutions with different pH at room (left) and physiological (right, 37 °C) temperatures. c) Calculated (lines) and experimental (symbols) results of dissolution studies on E-beam SiO₂ in aqueous solutions at different pH and temperature. d) Dependence of dissolution kinetics of silicon oxide films on pH (black, tg-oxide (dry); red, tg-oxide (wet); blue, PECVD SiO₂; magenta, E-beam SiO₂) at physiological temperature (37 °C) corresponding to experimental data (symbol) and numerical fits (line). e) Measurements of dissolution rates of silicon oxides as a function of film density in buffer solution (pH 7.4) at room (black) and physiological (red, 37 °C) temperatures.



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which can potentially lead to alterations in the stoichiometry and reductions in density. $\ensuremath{^{[25]}}$

X-ray photoelectron spectroscopy (XPS) and X-ray reflectometry (XRR) reveal the stoichiometries, atomic bond configurations and densities. The tg-oxide (dry oxidation) and PECVD oxide have chemistries close to SiO_2 (i.e., Si : O = 1 : 2), while the E-beam oxide is oxygen rich, at $SiO_{2,2}$ (Si : O = 1 : 2.2), as shown in Table S1 (Supporting Information). The Si 2P spectra (Figure S6) indicate that the Si-O bond energies are almost identical for the three oxides. Figure 2e and Figure S7 (Supporting Information) show the dependence of the dissolution rate on the film density (≈ 2.3 g cm⁻³ for tg-oxides, ≈ 2.1 g cm⁻³ for PECVD oxide, ≈ 1.9 g cm⁻³ for E-beam oxide). Reduced density can enhance the ability of aqueous solutions to diffuse into the material, thereby to accelerate the hydrolysis reaction by increasing the reactive surface area.^[11,19,26] Previous research^[11,19,26] suggests that a reactive diffusion model can capture some of the behaviors. A modified version of this model, assuming applicability of continuum physics, provides a simple, approximate means to incorporate the effect of density variations associated with porosity. Here, the concentration of water *w* in the porous material is first determined from the partial differential equation for reactive diffusion $D_t \partial^2 w / \partial z^2 - kw = \partial w / \partial t$, where z is the coordinate in the film thickness direction, t is the time, k and D_e are the reaction constant and the diffusivity in the porous media, respectively. Since the mass of the air pore is negligible compared with that of the porous material, the effective density $ho_{
m eff}$ of the porous material is related to the density $\rho_{\rm s}$ of the fully dense material as

$$\rho_{\rm eff} = \frac{V_{\rm s}}{V_{\rm air} + V_{\rm s}} \,\rho_{\rm s} \tag{1}$$

where V_s and V_{air} are the volumes of material and air pore, respectively. At time t = 0, the air pores are filled with water, or $w|_{t=0} = w_0(\rho_s - \rho_{eff})/\rho_s$ ($0 \le z \le h_0$). The water concentration is constant at the top surface of the material $w|_{z=h_0} = w_0$ ($w_0 = 1 \text{ g cm}^{-3}$) and the water flux is zero at the bottom surface $\partial w/\partial z|_{z=0} = 0$. By the method of separation of variables, the water concentration field can be written

$$w(z,t) = w_0 \left\{ \frac{\cosh\left(\sqrt{\frac{kh_0^2}{D_e}} \frac{z}{h_0}\right)}{\cosh\sqrt{\frac{kh_0^2}{D_e}}} + 2\pi \sum_{n=1}^{\infty} B_n (-1)^n \times \left(n - \frac{1}{2}\right) e^{-\frac{kh_0^2}{D_e} \left(n - \frac{1}{2}\right)^2 \pi^2 \frac{D_e t}{h_0^2}} \cos\left[\left(n - \frac{1}{2}\right) \pi \frac{z}{h_0}\right]\right\},$$
(2)

where B_n is

$$B_{n} = \frac{1}{\frac{kh_{0}^{2}}{D_{e}} + \left(n - \frac{1}{2}\right)^{2}\pi^{2}} + \frac{\frac{\rho_{\text{eff}}}{\rho_{s}} - 1}{\left(n - \frac{1}{2}\right)^{2}\pi^{2}}$$
(3)

When one mole of material reacts with q moles of water, then integration of materials dissolved at each location through

the thickness and over time leads to an expression for the remaining thickness h, normalized by its initial thickness h_0 as

$$\frac{h}{h_{0}} = 1 - \frac{w_{0}M}{q\rho_{\text{eff}}M_{\text{H}_{2}\text{O}}} \frac{kh_{0}^{2}}{D_{e}} \\ \left\{ \frac{D_{e}t}{h_{0}^{2}} \frac{\tanh\sqrt{\frac{kh_{0}^{2}}{D_{e}}}}{\sqrt{\frac{kh_{0}^{2}}{D_{e}}}} - 2\sum_{n=1}^{\infty} B_{n} \frac{1 - e^{-\left[\frac{kh_{0}^{2}}{D_{e}} + \left(n - \frac{1}{2}\right)^{2}\pi^{2}\right]\frac{D_{e}t}{h_{0}^{2}}}}{\left[\frac{kh_{0}^{2}}{D_{e}} + \left(n - \frac{1}{2}\right)^{2}\pi^{2}\right]} \right\}$$
(4)

where *M* and $M_{\rm H_{2}O}$ are the molar masses of porous material and water, respectively. The effective diffusivity of water in a porous medium is linearly proportional to the pores available for the transport, which is equivalent to the air fraction in the porous medium

$$D_e \propto \frac{V_{\rm air}}{V_{\rm air} + V_{\rm s}} = \frac{\rho_{\rm s} - \rho_{\rm eff}}{\rho_{\rm s}}$$
(5)

The density of SiO₂ is 2.33 g cm⁻³, 2.10 g cm⁻³, and 1.90 g cm⁻³ for the case of thermally grown, PECVD and E-beam oxides, respectively. If SiO₂ with a density of 2.34 g cm⁻³ has a diffusivity of 8×10^{-16} cm² s⁻¹ at body temperature, then the diffusivities for PECVD SiO₂ and E-beam SiO₂ can be calculated from Equation 5 as 1.6×10^{-14} cm² s⁻¹ and 2.92×10^{-14} cm² s⁻¹. Reaction constants are fitted to the experimental data and the dissolution rate, -dh/dt, is then estimated from

$$-\frac{\mathrm{d}h}{\mathrm{d}t} = \frac{w_0 M}{q\rho_{\mathrm{eff}} M_{\mathrm{H}_{2}\mathrm{O}}} kh_0 \left\{ \frac{\tanh\sqrt{\frac{kh_0^2}{D_e}}}{\sqrt{\frac{kh_0^2}{D_e}}} - 2\sum_{n=1}^{\infty} B_n e^{-\left[\frac{kh_0^2}{D_e} + \left(n-\frac{1}{2}\right)^2 \pi^2\right] \frac{D_e t}{h_0^2}} \right\}$$
(6)

which can be simplified to

$$-\frac{\mathrm{d}h}{\mathrm{d}t} = \frac{w_0 M}{q \rho_{\mathrm{eff}} M_{\mathrm{H}_{2}\mathrm{O}}} k h_0 \frac{\tanh \sqrt{\frac{k h_0^2}{D_e}}}{\sqrt{\frac{k h_0^2}{D_e}}}$$
(7)

In Figure 2a–c, the reaction constants (k) are 1.7×10^{-9} (tg-oxide with dry oxidation), 1.6×10^{-8} (PECVD oxide), and 1.3×10^{-9} (E-beam oxide) s⁻¹ in buffer solution with pH 7.4 at 37 °C. The results suggest that density influences the dissolution rate not only through changes in rates for diffusion into the material, but also through differences in reactivity. One possibility is that dissolution can occur not just at a molecular level, but also through removal of nanoscale pieces of material that might be released from the film as narrow regions of the porous matrix disappear by hydrolysis. Careful transmission electron microscopy (TEM, JEOL 2010F, USA) studies (Figure S8, Supporting Information) suggest, however, that the porous structures in the PE-CVD and E-beam oxides do not involve voids with dimensions larger than one or two nanometers. AFM observation of surfaces with sub-nanometer roughness (average roughness < 0.4 nm, Figure S9, Supporting Information) throughout the course of the dissolution process also supports the notion that the film disappears uniformly and gradually,



at the molecular level, without the release of pieces of material. Possible mechanisms, such as bond strengths, kinetics and other effects could affect the reaction constant associated with different oxides. Additional work is necessary to uncover an atomic level understanding of the dependence of reactivity on these various oxides.

3. Dissolution Studies of Various Classes of Nitrides

Studies of the dissolution kinetics of silicon nitrides were performed in procedures and under conditions similar to those for the silicon oxides. Silicon nitride hydrolyzes in aqueous solution in two steps: 1) oxidation into silicon oxide $(Si_3N_4 + 6H_2O \rightarrow 3SiO_2 +$ 4NH₃) and 2) hydrolysis of silicon oxide $(SiO_2 + 2H_2O \rightarrow Si(OH)_4)$, where the overall reaction is $Si_3N_4 + 12H_2O \rightarrow 3Si(OH)_4 +$ 4NH₃.^[27-29] Because silicon dioxide serves as an intermediate product in these reactions, the dependence of rate on pH might be expected to be similar to that observed in the oxides. The dissolution rates of the intermediate oxide products are difficult to determine separately. Low pressure chemical vapor deposition (LPCVD) and PECVD techniques were used to form the silicon nitrides studied here. For PECVD nitrides, two different frequency modes were employed to vary the properties of the films, including residual stress. Spectroscopic ellipsometry revealed the changes in thickness of films deposited on silicon substrates.

Figure 3a–c shows the dissolution behavior of LPCVD nitride, PECVD-LF nitride (low frequency, LF) and PECVD-HF nitride (high frequency, HF) in buffer solutions (pH 7.4 to 12) at RT and 37 °C. Here, three factors (temperature, pH and film characteristics) were considered. The dissolution rate increases with temperature, as expected. Figure 3d and Figure S10 show the pH dependence, which is similar to that observed in the oxides. The kinetics suggests a linear relationship between dissolution rate and pH according to $\log r = a + n [pH]$, where *n* ranges from 0.11 to 0.28 for 37 °C and 0.26 to 0.31 for RT. As with the oxides, the nitrides were studied in bovine serum at 37 °C and sea water at RT; the rates are ≈ 8 times and ≈ 4 times higher than those at similar pH in buffer solution, likely due to chemical substances in the serum and sea water (Figure S11, Supporting Information).

Effects of stoichiometry and density were also investigated. Table S2 shows that the $% \left({{{\rm{S}}_{\rm{B}}}} \right)$

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Figure 3. Dissolution kinetics via hydrolysis of various silicon nitrides in aqueous solutions at different pH and temperature. a) Calculated (lines) and measured (symbols) values for the dissolution of Si₃N₄ formed by low-pressure chemical-vapor deposition (LPCVD) in buffer solutions (black, pH 7.4; red, pH 8; blue, pH 10; magenta, pH 12) at room (left) and physiological (right, 37 °C) temperatures. b) Calculated (lines) and measured (symbols) dissolution behaviors of PECVD Si₃N₄ (low-frequency mode) in diverse aqueous solutions with different pH at room (left) and physiological (right, 37 °C) temperatures. c) Calculated (lines) and experimental (symbols) results of dissolution study on PECVD Si₃N₄ (high-frequency mode) in aqueous solutions at different pH and temperature. d) Calculated (lines) and experimental (symbols) results of the dependence of dissolution kinetics of silicon nitride films on pH (black, LP-CVD Si₃N₄; red, PE-CVD Si₃N₄ (low frequency); blue, PE-CVD Si₃N₄ (high frequency)) at physiological temperature (37 °C). e) Measured dissolution nitride s a function of film density in buffer solution (pH 7.4) at room (black) and physiological (red, 37 °C) temperatures.



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stoichiometry of the LPCVD film is Si₃N_{3.9}, while that of the PECVD films is Si₃N_{4.3} (LF) and Si₃N_{3.3} (HF). Figure 3e and Figure S12 (Supporting Information) show the dependence of the dissolution rate on average film density. The densities are 3.1 g cm⁻³ for LPCVD, 3.0 g cm⁻³ for PECVD-LF, and 2.5 g cm⁻³ for PECVD-HF. The results suggest that LPCVD nitride exhibits the lowest dissolution rate, at least partly due to its favorable stoichiometry and high density. PECVD-HF nitride shows the fastest dissolution rate due to its non-stoichiometric chemistry and its low density. The modified reactive diffusion model described previously can provide some utility in capturing the effects of porosity, subject to limitations associated with its approximations. From the results of Figure 3a-c, the reaction constants (k) were found to be 8.0×10^{-8} , 4.5×10^{-7} , and 4.0×10^{-7} s⁻¹ for LPCVD nitride, PECVD-LF nitride, and PECVD-HF nitride, respectively, in buffer solution (pH 7.4) at 37 °C by modified reactive diffusion model where the density of closely packed amorphous nitrides was 3.16 g cm^{-3} .

4. Encapsulation Strategy with Inorganic Layers

In addition to their use as gate and interlayer dielectrics, silicon oxides and nitrides can be considered as transient passivation/encapsulation layers. These materials are well known to be good barrier materials for permeation of water vapor in conventional electronics.^[4,5,30,31] Previous research^[4,31] on encapsulation with PECVD oxide and nitride in organic lightemitting diode (OLED) devices indicates that defects, such as pinholes, are a primary cause of leakage of vapors or fluids. We show here that multilayer structures of both silicon oxides and nitrides can reduce such defects and that these materials can be used in transient electronics.

As shown in Figure 4a (left), a combination of multiple different layers, that is, SiO2 and Si3N4, improves the performance of the encapsulation. Multiple layers with different materials can reduce water/vapor permeation through an underlying layer, by cooperative elimination of defects.^[4,31] Atomic layer deposition (ALD) provides a complementary strategy to reduce effects arising from defects.^[32,33] A double layer of PECVD SiO₂ (or PECVD-LF Si₃N₄) and ALD SiO₂ represents effective means of encapsulation, even with thin layers (Figure 4a, right). The dissolution rate of a single layer of ALD SiO₂ is 0.08 nm per day in buffer solution (0.1 M, pH 7.4) at 37 °C (Figure S13, Supporting Information), similar to that of PECVD SiO₂ in the same conditions.

Figure 4b presents measured changes in resistance of a serpentine-shaped Mg trace (≈300 nm), with several encapsulation approaches at various times for immersion in deionized water at room temperature. Samples with a single layer of ALD SiO₂ (\approx 20 nm), PECVD SiO₂, or Si₃N₄ (\approx 1 µm) show increases in resistance after just a few hours of immersion. A combination of PECVD SiO₂ (≈500 nm) and Si₃N₄ (≈500 nm) extends this time to ≈1 day. Triple layers of PECVD SiO₂ and Si₃N₄ (~200 nm/200 nm/200 nm/200 nm/100 nm/100 nm, total thickness $\approx 1 \text{ }\mu\text{m}$) extend to $\approx 10 \text{ days}$. Combinations of PECVD SiO₂/ALD SiO₂ (\approx 500/20 nm) and PECVD Si₃N₄/ALD SiO₂ (\approx 500/20 nm) show characteristic times of \approx 5 and \approx 7 days, respectively. These results suggest that the ALD SiO₂ layer has



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Figure 4. Encapsulation approaches with transient materials. a) Schematic illustrations of encapsulation methods for transient electronic devices, showing defects (e.g., pinholes) covered by a bilayer of SiO₂/ Si₃N₄ (left); ALD provides a defect-free layer (right). b) Measurements of changes in resistance of Mg traces (≈300 nm thick) encapsulated with different materials and thicknesses while immersed in deionized (DI) water at room temperature. A single layer of PECVD SiO₂ (black, 1 µm), PECVD-LF Si₃N₄ (red, 1 μ m) and ALD SiO₂ (orange, 20 nm), a double layer of PECVD SiO₂/PECVD-LF Si₃N₄ (blue, 500/500 nm), PECVD SiO₂/ ALD SiO₂ (magenta, 500/20 nm), PECVD-LF Si₃N₄/ALD SiO₂ (purple, 500/20 nm), and a triple layer of PECVD SiO_2/PECVD-LF Si_3N_4 (Cyan, 200/200/200/200/100/100 nm) were used for the encapsulation. c) A series of micrographs of a serpentine trace of Mg (initially ≈300 nm thick) during dissolution in DI water at room temperature. Dissolution begins from local defects, then rapidly propagates outward.

much few defects than PECVD SiO₂ or Si₃N₄. A single layer of ALD (~20 nm) provides similar timescale as a single layer of SiO₂ or Si₃N₄ (\approx 1 µm). Although combined use of PECVD SiO₂ and ALD SiO₂ shows extended lifetimes, a single layer of ALD SiO₂ itself is not sufficiently thick to cover uniformly the sorts of structures found in transient electronics, with the Mg resistor (≈300 nm) as a simple example. These dissolution behaviors lead to two-stage kinetics in the functional transience of this test structure: i) encapsulation layers define the first time period, that is, stable operation with negligible changes in electrical properties, ii) the Mg defines the second, that is, rapid degradation in function. The optical microscope images in Figure 4c clearly reveal that the dissolution of Mg begins



with leakage of water from local defects, followed by fast lateral propagation. These results suggest that an efficient encapsulation strategy is critically important in removing these leakage pathways, to increase the time for stable operation. Also, encapsulation with these inorganic materials can be improved by combined use of biodegradable polymers as suggested in previous encapsulation study in OLED devices.[31,34]

5. Conclusion

The results reported here provide a foundation of understanding of hydrolysis in silicon oxides and nitrides for applications in transient electronics, and their dependence on temperature, pH and film properties. An appealing aspect of these materials for these applications is that they are already well developed and widely used in conventional electronics. Opportunities range not only from gate and interlayer dielectrics to passivation and encapsulation layers but also to window layers and antireflection coatings in photovoltaics or optoelectronics systems.

6. Experimental Section

Test Structures for Silicon Oxides and Nitrides: Thin layers of silicon oxides (SiO₂) were prepared in three different ways, all on silicon wafers (University Wafer): 1) Thermally grown (tg-oxides) (dry and wet oxidation), 2) plasma-enhanced chemical vapor deposited from precursor gases (PECVD, Trion Technology, USA) at 350 $^\circ\text{C}$, and 3) electron beam (E-beam) evaporated from SiO₂ pellets (99.99%, Kurt J. Lesker Company, USA). The nitrides were deposited onto similar wafers. The films were formed by low-pressure chemical vapor deposition (LPCVD) and by PECVD (Surface Technology Systems, Newport, UK) at 300 °C using low frequency (LF, 380 kHz) and high frequency (HF, 13.56 MHz). In all cases, the thickness was controlled at ≈100 nm. The test structures for measurement by atomic force microscope (AFM) consisted of arrays of square pads (3 μ m \times 3 μ m \times 100 nm), fabricated by photolithography and reactive ion etching (RIE).

Dissolution Experiments: Samples were placed into 50 mL of aqueous buffer solutions with different pH (pH 7.4–12, Sigma-Aldrich, USA) at either room temperature (RT) or physiological temperature (37 °C). Studies also involved bovine serum (pH ≈7.4, Sigma-Aldrich, USA) at 37 °C and sea water (pH \approx 7.8) at room temperature. In all cases, the samples were removed from the solutions, rinsed with DI water, and measured by spectroscopic ellipsometry (J. A. Wooldman Co. Inc., USA) to determine thickness and/or atomic force microscopy (AFM, Asylum Research MFP-3D, USA) to determine both the thickness and surface morphology. After such measurements, each of which lasted a few hours, the samples were returned to the solutions. The solutions were replaced every other day.

Characterization of Film Properties: Film density was measured using an X-ray reflectometry (XRR, X'pert MRD System, Netherlands). X-ray photoelectron spectroscopy was performed with a system from Axis ULTRA, UK. To avoid surface oxidation of the nitrides, the measurements were conducted shortly after oxide removal in buffered oxide etchant (BOE, 6:1, Transene Company Inc., USA) for a few seconds. Transmission electron microscopy (TEM, JEOL 2010F (S)TEM, USA) was used to study the porous microstructure of the PECVD and E-beam oxides.

Encapsulation Tests: Serpentine traces of Mg (~300 nm thick) were defined by E-beam evaporation and liftoff using a patterned layer of photoresist (AZ 2070, MicroChem, USA) on a glass substrate. Each trace was then encapsulated with various overcoats of PECVD SiO₂,

PECVD-LF Si₃N₄, and ALD SiO₂ (Savannah, Cambridge Nanotech, USA). Encapsulation layers at both ends of the trace were removed by RIE, to allow continuous measurement of changes in resistance while immersed in aqueous solutions.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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