

# Deposition of High Quality Sol-Gel Oxides on Silicon

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We have fabricated high quality sol-gel derived silicate and aluminoborosilicate thin films deposited on silicon substrates. From capacitance vs voltage measurements we observe low interface trap densities ( $<10^{11}/\text{cm}^2\text{eV}$ ) and very low densities of slow interface state ( $<10^{10}/\text{cm}^2$ ) in most films investigated. We have been able to make significant improvements over previous sol-gel derived oxides on silicon by controlling some of the key factors which effect the structure of the sol-gel derived thin films.

**Key words:** Sol-gel, oxides on Si, interface trap densities

## INTRODUCTION

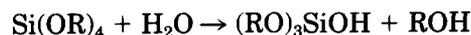
Even though thermally grown oxides on silicon are the best insulators, there is a growing interest in low temperature and short time deposition techniques for thin film dielectrics to reduce the thermal budget.<sup>1-3</sup> Some potential applications include secondary passivation layers, interlayer isolation, III-V compound semiconductor structures, and thin film transistors. To date, a number of techniques have been utilized to deposit insulating films, including chemical vapor deposition (CVD), plasma enhanced CVD, wet chemical anodization and sputtering. In this study we explore oxides derived by the sol-gel process, and find that their electronic properties are at least comparable to other films prepared by a number of other low temperature techniques.<sup>4,5</sup>

Oxides formed by the sol-gel process are of considerable technological interest for a variety of reasons: the technique is (1) inexpensive, (2) simple, and (3) requires relatively low temperature processing for short times. Perhaps most importantly, the sol-gel process allows the use of multicomponent systems; one may tailor the electronic properties of the oxide by varying its chemical composition. Furthermore, since the sol-gel process chemistry has been extensively explored in the literature,<sup>6-13</sup> one may also apply this fundamental understanding of sol-gel chemistry to control the electronic properties of the sol-gel films. In this study we have investigated silicate and aluminoborosilicate dielectric thin films. The electronic properties of the sol-gel films are of high quality: they exhibit low fast and slow interface trap densities and have fairly good insulating properties.

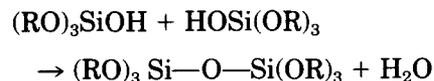
## EXPERIMENTAL DETAILS

Sol-gel processing uses metal alkoxides,  $M(\text{OR})_4$  (where M is Si, Al, B, P etc. and R is often an alkyl

group,  $(\text{C}_x\text{H}_{2x+1})$ ), as monomeric (or oligomeric) oxide precursors. In alcohol solutions the alkoxide is hydrolyzed by the addition of water causing the replacement of alkoxy groups (OR) by hydroxyl groups (OH) as shown for a silicon alkoxide . . .



Subsequent condensation reactions involving the hydroxyl groups result in the formation of inorganic polymers composed of  $\text{M}-\text{O}-\text{M}$  bonds . . .



The structures of the resulting inorganic polymers are influenced by many factors such as the water to alkoxide ratio, the solution pH, aging conditions and the specific metal alkoxide precursors.<sup>6-13</sup> For example, it is possible to vary the structure of the sol-gel derived silicates from linear or weakly branched polymers to highly condensed  $\text{SiO}_2$  particulates.<sup>7</sup>

Film porosity is largely determined by the structure of the inorganic precursors (polymers). For example, weakly branched species are quite compliant and form denser oxides;<sup>12</sup> with small pores that collapse at low temperature via viscous sintering Fig. 1(a). By comparison, highly crosslinked polymers are sufficiently robust to resist the compressive forces of surface tension during annealing;<sup>12</sup> leading to larger pore sizes that collapse at higher temperatures Fig. 1(b).

We have investigated silicate and aluminoborosilicate sol-gel films. A promising feature of the sol-gel process is its ability to fabricate multicomponent films; making it possible to tailor the oxide and interface.

The sol-gel solutions were deposited on *n*-type (100) Si substrates with resistivities of  $10 \Omega \text{ cm}$ . After cleaning, the substrates were immediately coated using a dip coating apparatus. The substrates were

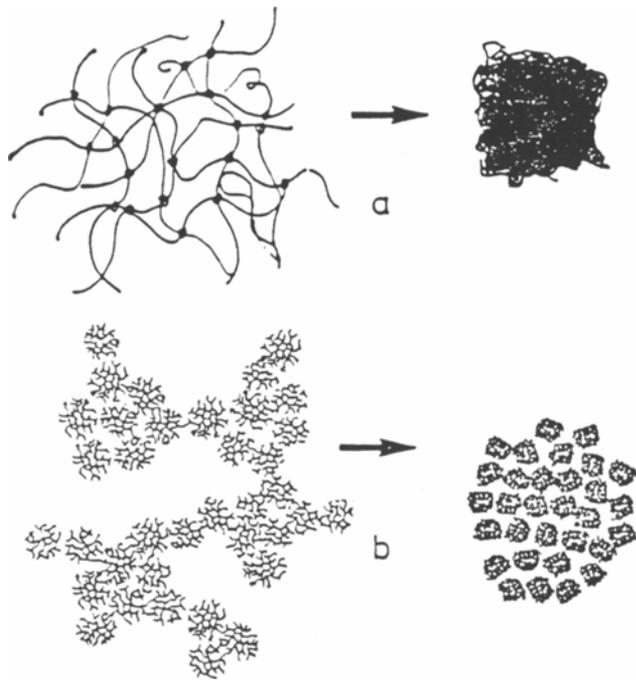


Fig. 1 — Schematic representation of changes in gel structure during annealing for (a) a low water to alkoxide ratio and (b) a high water to alkoxide ratio (from Ref. 12).

cleaned using a standard degreasing procedure. First the wafers were ultrasonically agitated in 1, 1, 1 trichloroethane. Next, they were submerged in a solution consisting of (1) ~80% isopropyl alcohol (2) ~20% deionized water, (3) 0.2% "Renex" 690™ (wetting agent), and (4) 0.05% "Span" 80™ (detergent) followed by a deionized water rinse. Next the wafers were ultrasonically agitated in isopropyl alcohol and blown dry in dry nitrogen. In dip coating, a constant withdrawal speed insures a uniform thickness that can be controlled by the pull rate and/or multiple dippings. During film deposition, the evaporation of solvent produces a rigid porous silicate or aluminoborosilicate layers. The aluminoborosilicate films (designated 4C) are a four component oxide with a nominal solution composition (wt.%) 71% SiO<sub>2</sub>, 18.3%, B<sub>2</sub>O<sub>3</sub>, 7.1% Al<sub>2</sub>O<sub>3</sub> and 3.6% BaO. Details regarding solution preparation can be found in Refs. 7 and 8. After dipping, all specimens were annealed for 5 min at either 800 or 900° C in air, except for the vacuum annealed samples which were annealed at 900° C for one hr. The anneal removes absorbed water and any residual organic substances, densifies the film and increases the extent of bonding between the film and substrate.<sup>14</sup> The film thickness of the annealed samples used in this study ranged from 1900 to 2100 Å as determined by ellipsometry. After the anneal, Al was deposited on the films and a standard postmetallization anneal (5% H<sub>2</sub>/95% N<sub>2</sub>) at 400° C for 30 min was performed.

## RESULTS

The electrical properties of the interfaces between the sol-gel silicate, aluminoborosilicate (4C), thin films on silicon were investigated using high frequency (1 MHz) and quasi-static CV measurements. Using a corona discharge technique we evaluated the current vs voltage (IV) characteristics of the films. This technique is rather insensitive to weak spots on the films surface<sup>15</sup> that may occur since the films were not deposited in a clean room environment.

In Figs. 2 and 3 we illustrate the high frequency and quasi-static CV curves for a typical silicate (Fig. 2) and aluminosilicate (Fig. 3) film after annealing at 800° C for 5 min. The interface trap densities are quite low ( $<2 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$  at mid-gap) and virtually no hysteresis is observed. The hysteresis was measured using a voltage ramp rate of 50 mV/sec after maintaining the oxide field at  $0.5 \times 10^6 \text{ V/cm}$  for 10 min, then ramping the voltage in the opposite direction and repeating the 50 mV/sec ramp with opposite sign of slope. We define hysteresis as  $C_{ox}\Delta V_{mg}/q$  where  $\Delta V_{mg}$  is the mid-gap voltage shift in the CV curves when ramping the voltage in a positive direction followed by ramping the voltage in the opposite direction,  $C_{ox}$  is the oxide capacitance and  $q$  is the electronic charge. Figure 4 illustrates the sol-gel silicate and aluminoborosilicate (4C) current vs field measurements compared to a high quality thermal oxide.

In Table 1 we summarize our results on the sol-gel silicate, aluminoborosilicate (4C) and thermal oxide thin films evaluating the interface state density, slow state density, etch rate and breakdown strength. The interface trap densities were calculated from high frequency (HF) and quasi-static (QS) CV curves. We calculated the mid-gap interface trap density using both the Terman<sup>16</sup> (high frequency) technique and the combined High-Low<sup>17</sup> technique.

We have also performed etch rate experiments as indicated in Table 1. The etch rates are compared

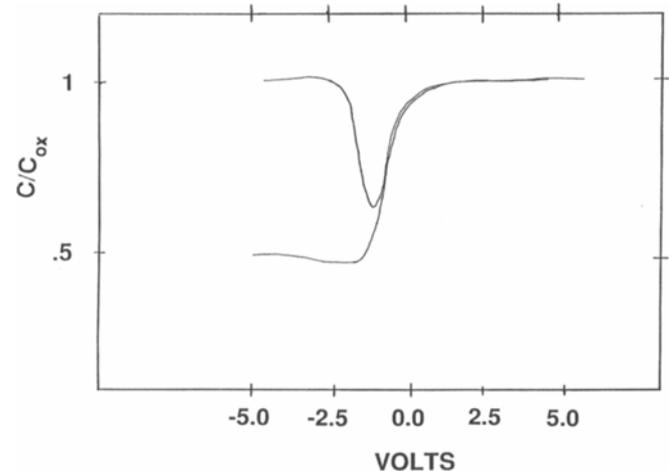


Fig. 2 — High frequency and quasi-static CV curves of a silicate sol-gel oxide annealed at 800° C for five min.

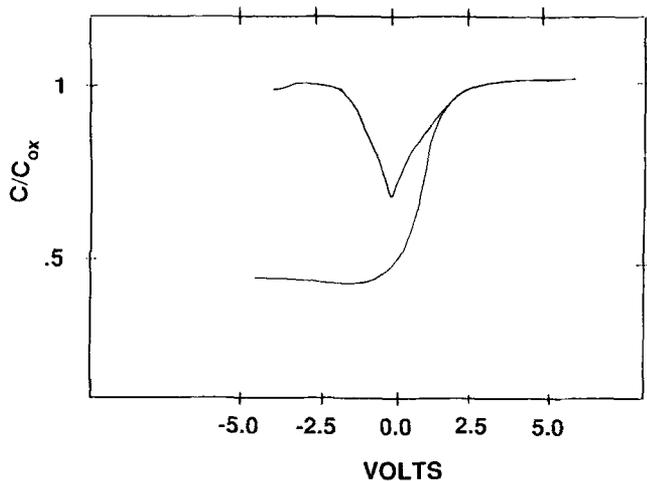


Fig. 3 — High frequency and quasi-static CV curves of an aluminoborosilicate sol-gel oxide annealed at 800° C for five min.

to a thermal oxide. The etchant was a buffered HF solution which etched the thermal oxide at a rate of 1Å/sec. The etch rate gives an indication of film porosity and stress; more porous oxides exhibit faster etch rates. Deposited oxides typically etch faster than thermal oxides, for example air pressure chemical vapor deposited SiO<sub>2</sub> deposited at 700° C etches 8 times faster than a thermal oxide.<sup>18</sup> However, as can be seen from Table 1 the sol-gel oxides etch two to three times faster than a thermal oxide when an-

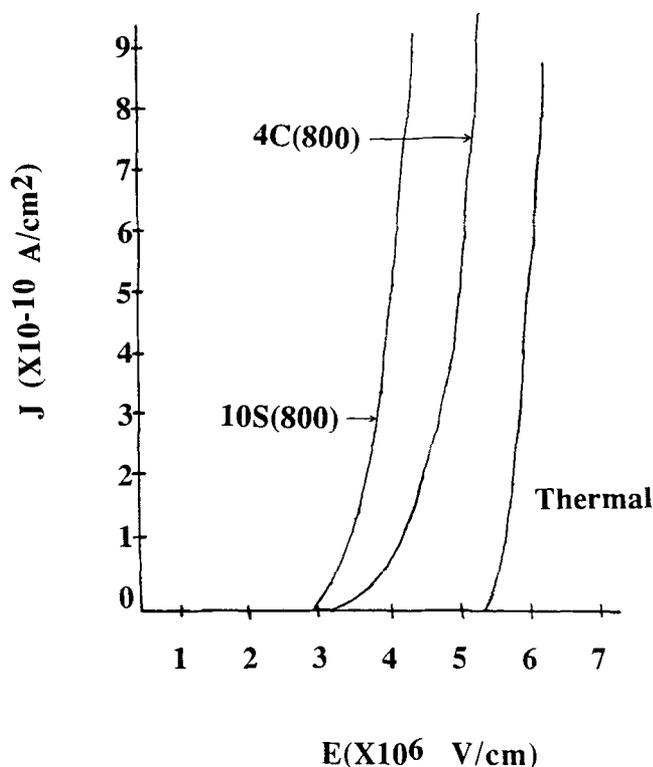


Fig. 4 — Current vs field measurements of sol-gel silicate (10S(800)) and aluminoborosilicate (4C(800)) thin films compares to a thermal oxide. The sol-gel films were deposited using fresh solutions and after coating the films were annealed at 800° C for 5 min.

nealed at 800° C (or 900° C) for simply 5 min. These etch rate experiments indicate that the sol-gel oxides are fairly dense; that is, a 5 min anneal at 800 or 900° C almost completely densifies the film. (The 4C films (aluminoborosilicate) etch at somewhat slower rates than silicate films in a buffered HF solution.<sup>19</sup>

## DISCUSSION

Our results indicate that sol gel films exhibit electronic properties which are at least competitive with the other alternatives to thermal SiO<sub>2</sub>. (1) All films investigated exhibited strong accumulation and inversion characteristics. (2) The interface trap densities, both fast and slow, are very low for all sol-gel films investigated. The values are higher than those obtained in good thermal oxide structures, but are nonetheless very respectable. (3) Comparing the sol-gel samples high frequency CV curve to that of an "ideal" CV curve we find that  $C_{min}$  (capacitance at inversion) and  $C_{max}$  ( $C_{ox}$ ) are in total agreement with the expected values. We also observe very little net fixed charge in the sol-gel oxides. (4) We have evaluated the breakdown strengths of the oxides by charging the films surface with corona ions and measuring the potential across the films using a Kelvin probe and electrostatic voltmeter for several minutes after charging; the arbitrarily defined breakdown field we determine corresponds to a current density of about  $5 \times 10^{-10}$  A/cm<sup>2</sup>. Defining breakdown in this somewhat arbitrary way the corona IV characteristics indicate breakdown strengths of sol-gel films are generally fairly high (3.3-5.3 MV/cm). Defining breakdown strength on a high quality thermal oxide using this technique one finds 5.8 MV/cm.<sup>15</sup>

A previous publication,<sup>20,21</sup> reported some electrical measurements of aluminoborosilicate films; however, the earlier study did not include quasi-static CV data because the oxide was too leaky. We believe that our ability to obtain a quasi-static CV curve (Figs. 2 and 3) in this investigation was possible because the sol-gel solutions used in this study were fresh, not aged. Aging<sup>13</sup> is a process in which the structure of the solution changes with time because small polymers continue to attach to the cluster through a diffusive action. The cluster grows as the aging process continues. In an aged solution, large clusters increase the films porosity in a manner similar to the way in which highly crosslinked polymers increase the films porosity as shown in Fig. 1. Fresh solutions (unaged) form small chains and pack efficiently as they are concentrated via evaporation and collapse by capillary pressure at the final stage of drying.<sup>22</sup> Porosity is manifested in the current vs field measurements; the films deposited from an aged solution were leakier than the films deposited from a fresh solution. Since fresh solutions exhibit better insulating properties than aged solutions (six times higher breakdown field) all sol-

Table I Electrical and Physical Characteristics of Sol-Gel Films on Silicon

Composition and Annealing Conditions	HF ( $\text{cm}^{-2}\text{eV}^{-1}$ )	High-Low ( $\text{cm}^{-2}\text{eV}^{-1}$ )	Breakdown Strength MV/cm	Hysteresis ( $\text{cm}^{-2}$ )	Etch Rate Compared to a Thermal Oxide
10S(800)	$<1 \times 10^{11}$	$8 \times 10^{10}$	3.3	$<5 \times 10^9$	x3.1
10S(900)	$<1 \times 10^{11}$	$7 \times 10^{10}$	4.6	$1 \times 10^{10}$	x2.5
10S(VAC)	$5 \times 10^{11}$	—	4.8	$1 \times 10^{10}$	x3.0
4C(800)	$1 \times 10^{11}$	$2 \times 10^{11}$	5.0	$5 \times 10^9$	x2.2
4C(900)	$<1 \times 10^{11}$	$4 \times 10^{10}$	5.3	$<5 \times 10^9$	x1.7
4C/10S (800)	$<1 \times 10^{11}$	$1 \times 10^{11}$	3.4	$1 \times 10^{11}$	x6.0
Thermal	$<1 \times 10^{11}$	$2 \times 10^{10}$	5.8	$<5 \times 10^9$	x1.0

4C are the aluminoborosilicate films, 10S are the silicate films with a 10:1 water to silicon alkoxide ratio and the 4C/10S films are a double coated sol-gel film with the 4C film coated first followed by the 10S film. The number in parenthesis is the anneal temperature at 5 min, VAC stands for the sample that had a vacuum anneal for 1 hr at 900° C. HF is the high frequency mid-gap interface trap density calculated by the Terman technique and High-Low is the mid-gap interface trap density calculated by the combined High-Low technique. The thermal oxide was grown at 1000° C to a thickness of 1750Å in a steam ambient and then subjected to a forming gas anneal at 400° C.

gel films investigated in this study used fresh solutions. This observation resulted in fairly high breakdown strengths as can be seen in Table 1. (The fresh solutions were prepared less than one week before dipping. Between preparation and deposition the solutions were maintained at 0° C.)

### SUMMARY

In summary, we have been able to fabricate sol-gel thin films on silicon which show very good dielectric integrity. Most films exhibited low fast and slow interface trap densities and fairly good insulating properties. We have also been able to show that in addition to a pure  $\text{SiO}_2$ , a complex four component oxide also yields good electronic properties. Our four component film results suggest that one may be able to vary film chemistry in a controlled manner without destroying its insulating properties. The availability of high quality sol-gel derived films may open up new opportunities for materials engineering amorphous insulating thin films.

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