Sol-gel silicate thin-film electronic properties
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INTRODUCTION

Silicon dioxide thin films are extensively used in micro-electronic devices as the gate and field oxides in metal-oxide-semiconductor-field-effect transistors (MOSFETs), passivation layers, diffusion and oxidation barriers, and scratch-resistant coatings. Currently, thermally grown silicon dioxide films on silicon (typical growth temperatures range from 800 to 1100 °C) are the best insulators and exhibit the lowest interface trap densities; they are the heart and soul of modern day microelectronic devices and are the standard by which other dielectrics are judged. In recent years, however, there has been a considerable amount of interest in the development of lower-temperature shorter-time dielectric deposition schemes. Some applications include III-V compound semiconductor MOSFET processing as well as primary dielectrics for thin-film transistors.

In this study we have explored the electronic and physical properties of sol-gel dielectric thin films on silicon. 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 a relatively short annealing time. Perhaps most importantly, the sol-gel process allows the use of multicomponent systems; one may also apply this fundamental understanding of sol-gel chemistry to control 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, one may also apply this fundamental understanding of sol-gel chemistry to control the electronic properties of the sol-gel films.

We have investigated how various processing parameters affect the dielectric integrity of the silicate gel thin films on silicon. In doing so we have been able to identify factors that affect the electronic properties of the silicate gel thin films. We find that (1) the water to silicon alkoxide ratio strongly affects the film's electronic and physical properties, (2) the film's properties are relatively independent of the annealing ambient, and (3) a rather short (5 min) anneal time at \( T > 800 \) °C is necessary to obtain sufficient insulating properties. Our results illustrate that sol-gel thin films on silicon can be of high quality; they exhibit low interface trap densities (\(< 10^{11} \text{cm}^{-2} \text{eV}^{-1} \) at mid-gap) and fairly good insulating properties (\( > 6 \text{MV/cm} \)), indicating that sol-gel oxides may be of considerable benefit to the microelectronics community.

EXPERIMENTAL PROCEDURE

Sol-gel processing uses metal alkoxides, \( M(\text{OR})_n \), (where \( M \) is Si, Al, B, P, etc. and \( R \) is often an alkyl group, \( \text{C}_n\text{H}_{2n+1} \)) as monomeric oxide precursors. In alcohol solutions the alkoxide is hydrolyzed by the addition of water causing the replacement of alkoxyl groups (OH) as shown for a silicon alkoxide [Si(OR)_x].

\[
\text{(OR)}_4\text{Si} + \text{H}_2\text{O} \rightarrow \text{(OR)}_3\text{SiOH} + \text{ROH}.
\]

Subsequent condensation reactions involving the hydroxyl groups result in the formation of inorganic polymers composed of M-O-M bonds.

\[
\text{(OR)}_3\text{SiOH} + \text{HOSi(OR)}_3 \rightarrow \text{(OR)}_2\text{Si-O-Si(OR)}_3 + \text{H}_2\text{O}.
\]

Many factors influence the structure of the inorganic polymers. The most important are the water to alkoxide ratio, pH, and aging conditions of the initial solutions. Film porosity is largely determined by the polymer structure. For example, weakly branched species are fairly compliant and form denser oxides; however, highly cross-linked polymers resist the compressive forces of surface tension during drying, leading to larger pores that are only removed at higher temperatures by sintering.

The sol-gel solutions were prepared with varying water to silicon alkoxide ratios; the ratios investigated were 2.5, 5.0, 7.5, 10.0, 12.5, 15.0, and 20.0 to 1. Details regarding further solution preparation can be found in Ref. 5. The solutions were deposited on n-type (100) Si substrates with resistivities of 1–10 Ω cm. The substrates were cleaned using a standard RCA procedure. The substrates were then immediately coated using either a dip coating apparatus or a commercial spinner. In dip coating, a constant withdrawal speed

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We have explored the effects of various processing parameters on the dielectric and electronic integrity of sol-gel-derived silicate thin films and have identified several factors that strongly affect the thin-film electronic properties. We find that sol-gel dielectrics can exhibit excellent dielectric integrity: viz., low interface trap densities and fairly good insulating properties approaching those of a thermally grown silicon dioxide film on silicon.
Two factors that degrade MOSFET performance are interface traps (with either fast or slow time constants) at the silicon-oxide interface and large leakage currents through the dielectric. To evaluate the interface trap densities MOS high-frequency (1 MHz) and quasi-static CV measurements were performed. The mid-gap interface trap densities were calculated using the Terman and combined high-low frequency methods.

The breakdown strengths (the electric field at which substantial leakage currents flow through the oxide) were evaluated using a corona discharge apparatus. The corona ions charge the films surface; by measuring the potential across the film's surface using a Kelvin probe and electrostatic voltmeter several minutes after charging, we evaluate an arbitrarily defined breakdown field corresponding to a current density about 10 x 10^{-10} A/cm. The etch-rate experiments were performed using a buffered HF solution which etches a thermal oxide around 1 A/s. 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 at 700 °C etches eight times faster than a thermal oxide.

Refractive index experiments were made using a Rudolf Auto-ELIV ellipsometer. Again higher refractive indices are generally indicative of a denser oxide. For comparison, the refractive index of a thermal oxide was measured to be 1.461 ± 0.002.

RESULTS

In Figs. 1 and 2 we illustrate the breakdown strength and etch rate of silicate gel thin films prepared using solutions with different water to silicon alkoxide ratios annealed in either oxygen (Fig. 1) or an argon (Fig. 2) ambient. Comparing Figs. 1 and 2 we noted that the film's properties are relatively independent of the annealing ambient. Although, the remaining data presented in this paper are for films annealed in oxygen for 5 min at T = 800 °C.

Fig. 2. At very low (r < 5:1) or very high (r > 15:1) ratios film properties are significantly degraded. The low refractive indices and low breakdown strengths of the films prepared using solutions with lower water to silicon alkoxide ratios, came as a surprise. It is well documented that bulk monolithic silicates prepared using solutions with low water ratios form more weakly branched polymers; these species are quite compliant and during drying form denser oxides with small pores that collapse at lower temperatures via viscous sintering. Highly cross-linked polymers formed at higher r values are sufficiently stiff to resist the compressive forces of surface tension during annealing, leading to larger pore sizes that sinter only at higher temperatures. The larger pore sizes will increase film porosity generally leading to lower refractive indices and lower breakdown strengths.

![Graph of breakdown strength and etch rate vs. water to silicon alkoxide ratio](image-url)
However, in this thin-film study we find (1) that films prepared using solutions with low $r$ values ($r < 7.5:1$) are more porous dielectrics (lower refractive indices, lower breakdown strengths, and faster etch rates), (2) films prepared with intermediate water to silicon alkoxide ratio solutions ($10:1$ to $15:1$) are the densest oxides, and (3) films prepared using solutions with ratios $r > 15:1$ tend to again become porous. A possible explanation for our results is provided by the work of Hurd et al. who observed the drying front of a dip coated film using imaging ellipsometry. Their results on water alcohol mixtures demonstrate that during dip coating, water becomes concentrated near the drying line. Since all solutions contain excess water ($r > 2$ according to Eq. (1)) and since water has a factor of 3 greater surface tension than alcohol, the capillary pressure exerted on the solid phase at the final stage of drying is larger for greater water to alkoxide ratios.

Our work strongly suggests that it is this additional “compacting” force in the films prepared using solutions with $r$ values between 10 and 15 that leads to higher densities, smaller pores, and lower sintering temperatures. This compacting force can be as high as 1000 atm. In contrast, larger $r$ values ($> 15$) apparently promote aging leading to much stiffer structures that resist collapse by additional capillary pressure. This would explain the increase in porosity of the films prepared using the highest water ratios. These results strongly demonstrate that the polymer structure and deposition conditions affect the thin-film properties and furthermore illustrate that one may employ different water to silicon alkoxide ratios to tailor the refractive index.

Figure 4 illustrates some of our $CV$ measurements for a sol-gel thin film annealed at 800 °C for 5 min in an argon ambient using a water to silicon alkoxide ratio of 12.5:1. Curves 4(a) and 4(b) are typical high-frequency and quasi-static $CV$ curves respectively, for sol-gel films on silicon annealed at $T > 725$ °C in any ambient as long as the water to alkoxide ratio is between 10:1 and 15:1. The mid-gap interface trap densities are always quite low ($\approx 8 \times 10^{10}$ cm$^{-2}$ eV$^{-1}$); the films exhibit strong accumulation and inversion characteristics, and there is very little fixed net charge in the dielectric. All these properties are indicative of a fairly high-quality dielectric. Figure 5 illustrates that the mid-gap interface trap densities are quite low ($\approx 8 \times 10^{10}$ cm$^{-2}$ eV$^{-1}$) for various anneal temperatures in an argon ambient. For comparison, we measure the mid-gap interface trap density of a high-quality thermal oxide to be $\approx 2 \times 10^{10}$ cm$^{-2}$ eV$^{-1}$, the detection limit of our apparatus. We measure the mid-gap interface trap densities using the combined high–low frequency method. Interface trap densities $< 1 \times 10^{10}$ cm$^{-2}$ eV$^{-1}$ are typical for high-quality thermally grown silicon dioxide films on silicon after a forming gas or post-metallization anneal.

The breakdown strengths and etch rates of silicate gel thin films vs anneal time are illustrated in Fig. 6. As demonstrated in Fig. 6 only a relatively short anneal time (5 min) is
FIG. 6. Breakdown strength and etch rates of sol-gel thin films on silicon annealed for different times in an argon ambient at 900 °C. The solution's water to silicon alkoxide ratio was 12.5:1.

needed to optimize the film's properties; longer anneal times did not generally improve the film's properties. This observation may be of considerable interest to applications that can withstand high temperatures for only short times. A sol-gel-derived thin film would be a viable candidate.

The films illustrated in Fig. 6 were all annealed in an argon ambient. The film thicknesses annealed for 5, 15, or 30 min were all identical (± 4 Å). This is consistent with the premise that we are not growing a thermal oxide. However, it is conceivable that some of the absorbed water in the films react at the Si/SiO₂ interface forming a very small thermal oxide, i.e., a few angstrons at most.

In Fig. 7 we show the corona current density versus electric field measurements for the silicate gel films annealed in argon at various temperatures. The results are compared to a thermal oxide. As shown, the films annealed at $T = 800 °C$ exhibit fairly good insulating properties. The sol-gel films annealed at 900 °C and 1000 °C for 5 min are nearly identical to a thermal oxide structure.

The refractive index of the silicate gel thin films versus anneal temperature is illustrated in Fig. 8. The anomalously high refractive indices at lower temperatures ($T < 650 °C$) are most likely due to retained organics in the films. As the anneal temperature is increased ($T > 725 °C$) the refractive index increases, indicative of a denser dielectric. The refractive index measurements agree quite well with the breakdown strength and etch rate of the sol-gel thin films annealed at different temperatures (Fig. 9). Figures 8 and 9 show that

FIG. 7. Current-density vs electric field measurements for sol-gel thin films annealed at (a) 500, (b) 650, (c) 725, (d) 800, (e) 900, and (f) 1000 °C for 5 min in an argon ambient. Curve (g) is for a thermal oxide grown in steam at 1050 °C to a thickness of 2500 Å.

FIG. 8. Refractive index ($n$) of silicate gel films annealed at different temperatures. All anneals were for 5 min in an argon ambient. The solution's water ratio to silicon alkoxide was 12.5:1.

FIG. 9. Breakdown strength and etch rate of sol-gel films annealed at different temperatures. The anneals were performed in an argon ambient for 5 min. The solution's water to silicon alkoxide ratio was 12.5:1.
the films need to be annealed at $T > 800 \, ^\circ C$ in order to exhibit fairly good breakdown characteristics and to obtain fairly dense dielectrics, i.e., higher refractive indices and lower etch rates.

**OBSERVATIONS AND CONCLUSIONS**

In summary, we have been able to fabricate high-quality sol-gel silicate thin films on silicon. We have been able to successfully fabricate sol-gel silicate thin films that exhibit low interface trap densities, low etch rates, and fairly high breakdown strengths. By systematic variation of processing parameters, we have been able to provide insight for fabricating silicate gel films of high dielectric integrity. We find (1) that the sol-gel film properties are strongly affected by the water to silicon alkoxide ratio, (2) that film properties are independent of annealing ambient, and (3) that a relatively short anneal (5 min) at temperatures $> 800 \, ^\circ C$ is needed to obtain sufficient densification and insulating properties.