Sol-gel silicate thin-film electronic properties

W. L. Warren, P. M. Lenahan, C. J. Brinker, C. S. Ashley, S. T. Reed, and G. R. Shaffer

Articles you may be interested in

Effect of sol-age on the surface and optical properties of sol-gel derived mesoporous zirconia thin films
AIP Advances **1**, 022111 (2011); 10.1063/1.3590744

Alcohol Sensing Properties of Sol-gel Derived TiO 2 Thin Film
AIP Conf. Proc. **1203**, 528 (2010); 10.1063/1.3322502

Dielectric properties of SiO 2 thin films prepared by the sol–gel technique
J. Vac. Sci. Technol. B **18**, 288 (2000); 10.1116/1.591185

Semiconducting properties of sol-gel derived vanadium silicate glasses
Appl. Phys. Lett. **59**, 855 (1991); 10.1063/1.105258

Application of sol-gel techniques to thin-film superconductor systems
AIP Conf. Proc. **200**, 157 (1990); 10.1063/1.39037

Sol-gel silicate thin-film electronic properties

W. L. Warren[a] and P. M. Lenahan
The Pennsylvania State University, University Park, Pennsylvania 16802

C. J. Brinker, C. S. Ashley, and S. T. Reed
Sandia National Laboratories, Albuquerque, New Mexico 87185

G. R. Shaffer[b]
The Pennsylvania State University, University Park, Pennsylvania 16802

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.

INTRODUCTION

Silicon dioxide thin films are extensively used in microelectronic 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[1-4]. 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 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,[5-9] 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 ($< 10^{11}$ cm^{-2} eV^{-1} at mid-gap) and fairly good insulating properties (> 6 MV/cm), indicating that sol-gel oxides may be of considerable benefit to the microelectronics community.

EXPERIMENTAL PROCEDURE

Sol-gel processing uses metal alkoxides, $M(OR)_n$ (where M is Si, Al, B, P, etc. and R is often an alkyl group, $C_x H_{2x+1}$) as monomeric oxide precursors. In alcohol solutions the alkoxide is hydrolyzed by the addition of water causing the replacement of alkoxy groups (OR) with hydroxyl groups (OH) as shown for a silicon alkoxide [Si(OR)$_4$]

$$(OR)_4 Si + H_2 O \text{---} (OR)_3 SiOH + ROH.$$
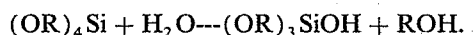
Subsequent condensation reactions involving the hydroxyl groups result in the formation of inorganic polymers composed of M-O-M bonds.

$$(OR)_3 SiOH + HOSi(OR)_3 \text{--} (OR)_3 Si\text{-}O\text{-}Si(OR)_3 + H_2 O.$$
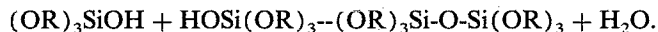
Many factors influence the structure of the inorganic polymers. The most important are the water to alkoxide ratio, pH, and aging conditions[5-9] of the initial solutions. Film porosity is largely determined by the polymer structure. For example, weakly branched species are fairly compliant and form 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.[10] The substrates were then immediately coated using either a dip coating apparatus or a commercial spinner. In dip coating, a constant withdrawal speed

insures a uniform thickness which can be controlled by the pull rate and/or multiple dippings. During film deposition, the evaporation of solvent produces a rigid porous silicate layer. After deposition, the thin porous silicate layers were heat treated in air at 80 °C to help burn off some of the residual organics and adsorbed water, followed by an anneal at higher temperatures in either an argon, air, or oxygen ambient. The annealing temperatures investigated were 500, 650, 725, 800, 900, and 1000 °C. After the anneal Al was deposited on the films using an electron beam evaporator and a standard post-metallization anneal (5% H_2/95% N_2) at 400 °C for 30 min was performed.

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[11] and combined high-low[12] frequency methods.

The breakdown strengths (the electric field at which substantial leakage currents flow through the oxide) were evaluated using a corona discharge apparatus.[13] 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 10×10^{-10} A/cm.[2]

The etch-rate experiments were performed using a buffered HF solution which etches a thermal oxide around 1 Å/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.[14]

Refractive index experiments were made using a Rudolf Auto-ELIV ellipsometer. Again higher refractive indicies are generally indicitive of a denser oxide[15]. 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 an argon ambient, very similar results were also obtained for films annealed in air or oxygen ambients.

Figures 1 and 2 also illustrate that the solutions water to silicon alkoxide ratio strongly affects the insulating properties (density) of the sol-gel thin films. Figure 3 further demonstrates the effect of the water to silicon alkoxide ratio (r) on the refractive index of the films. When r is between 10 to 15:1, the film's refractive index (and density) is about maximized. The refractive index measurements correlate extrememly well with the breakdown strength and etch rates of
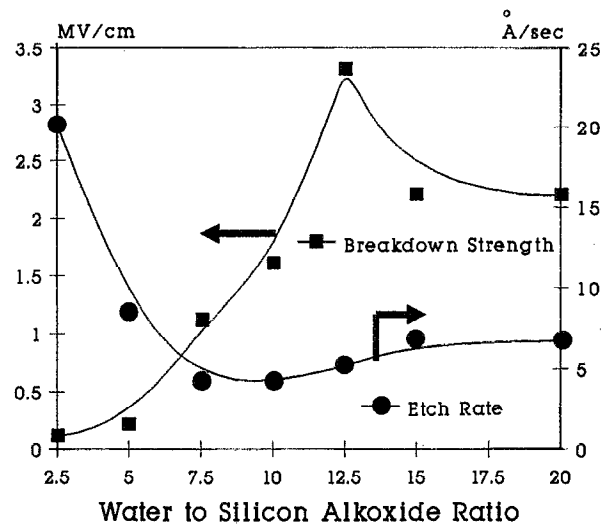

FIG. 1. Breakdown strength and etch rate of sol-gel films on silicon prepared using solutions with different water to silicon alkoxide ratios. All films were annealed in oxygen for 5 min at $T = 800$ °C.

Fig. 2. At very low ($r < 5$:1) or very high ($r > 15$:1) ratios film properties are significantly degraded. The low refractive indicies 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 monolith silicates prepared using solutions with low water ratios form more weakly branched polymers;[9,16] 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 indicies and lower breakdown strengths.
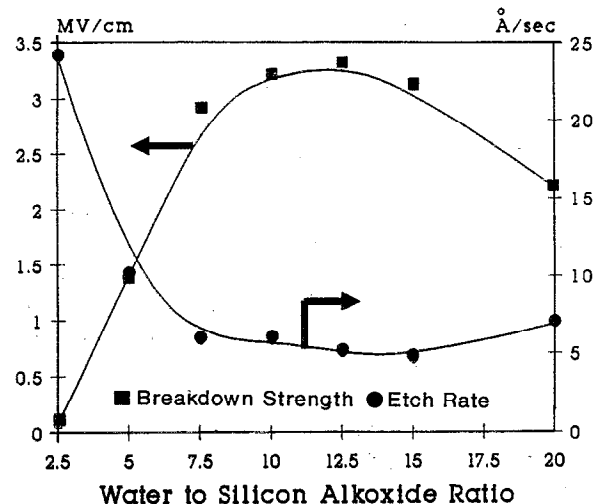

FIG. 2. Breakdown strength and etch rate of sol-gel films on silicon prepared using solutions with different water to silicon alkoxide ratios. All films were annealed in argon for 5 min at $T = 800$ °C.
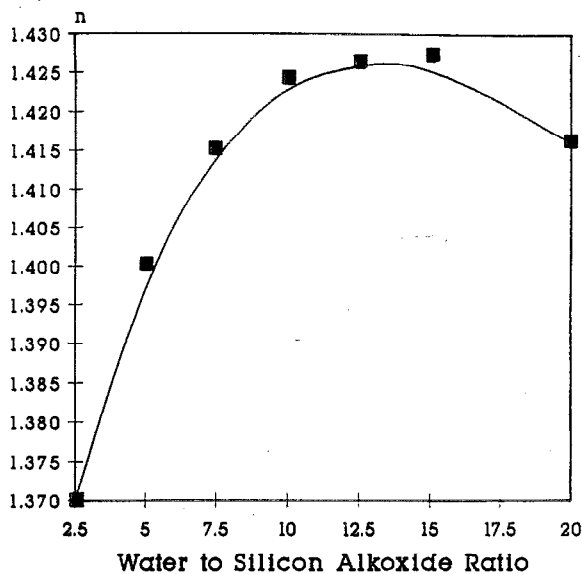
FIG. 3. Refractive index of sol-gel films (n) on silicon prepared using solutions with different water to silicon alkoxide ratios. All films were annealed in argon for 5 min at 800 °C.

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 indicies, 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,[17,18] who observed the drying front of a dip coated film using imaging ellipsometry. Their results[18] 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 about 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 an-
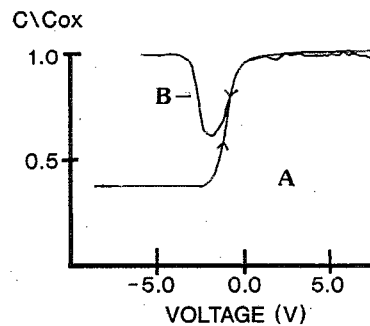

FIG. 4. High-frequency (A) and quasi-static (B) CV measurements for a silicate gel film annealed in argon for 5 min at 800 °C. The water ratio is 12.5:1.

nealed 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^{-1} 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
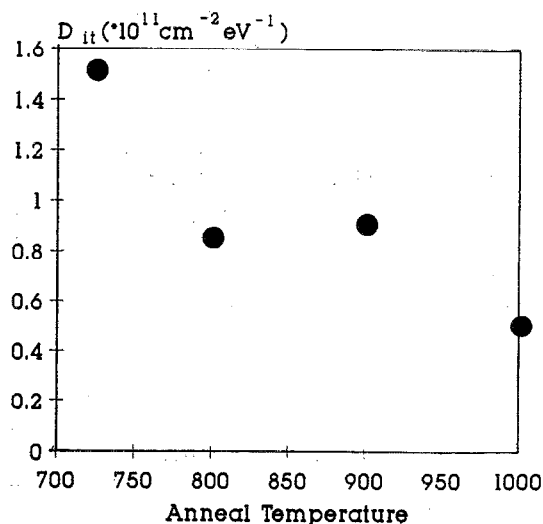

FIG. 5. Mid-gap interface trap densities of sol-gel silicate thin films on silicon annealed at different temperatures. All anneals were performed in argon for 5 min. The films were prepared using solutions with a 12.5:1 water to silicon alkoxide ratio.
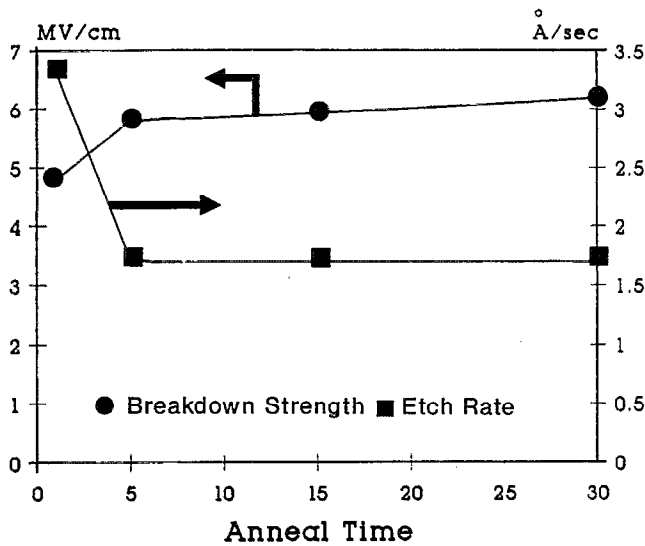
FIG. 6. Breakdown strength and etch rates of sol-gel thin films on silicon annealed for different times in an argon ambient at 900 °C. The solution's water to silicon alkoxide ratio was 12.5:1

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.

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/SiO$_2$ 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 ° 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 indicies at lower temperatures ($T < 650$ °C) are most likely due to retained organics in the films. As the anneal temperature is increased ($T \geqslant 725$ °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
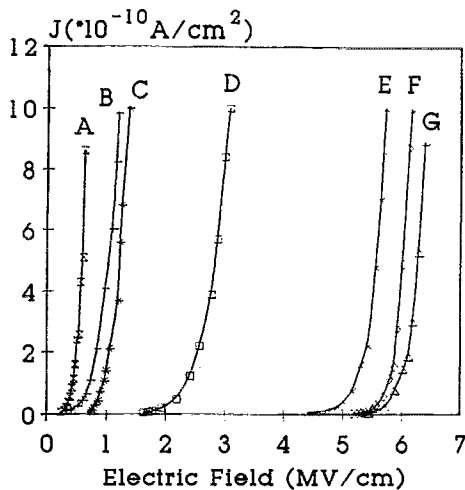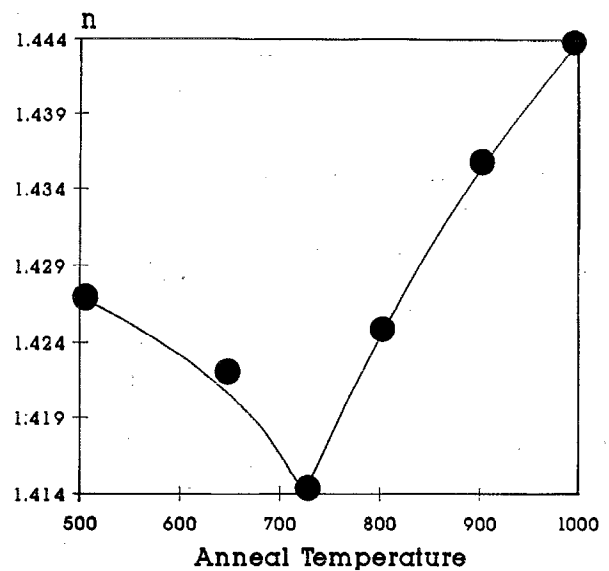

FIG. 7. Current-density vs electric field measurements for sol-gel thin films annealed at (a) 500, (b) 650, (c) 725, (d) 800, (e) 900, and (f) 1000 °C for 5 min in an argon ambient. Curve (g) is for a thermal oxide grown in steam at 1050 °C to a thickness of 2500 Å.
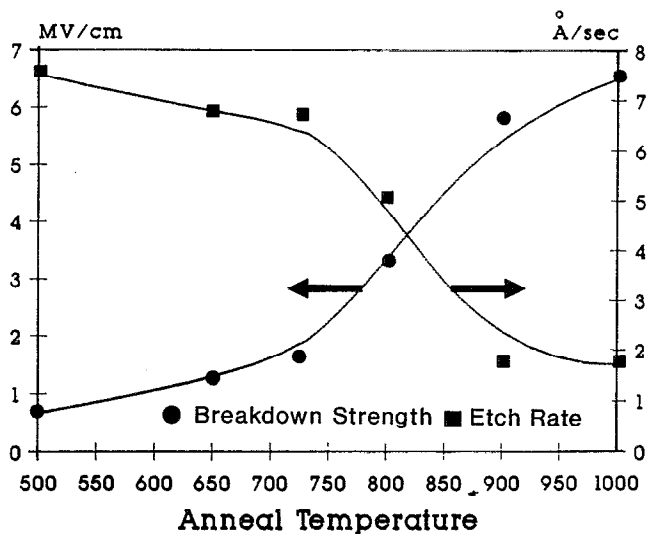

FIG. 9. Breakdown strength and etch rate of sol-gel films annealed at different temperatures. The anneals were performed in an argon ambient for 5 min. The solution's water to silicon alkoxide ratio was 12.5:1.

the films need to be annealed at $T > 800$ °C in order to exhibit fairly good breakdown characteristics and to obtain fairly dense dielectrics, i.e., higher refractive indicies 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 sucessfully 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 °C is needed to obtain sufficient densification and insulating properties.

[1] K. P. Pande and D. Gutierrez, Appl. Phys. Lett. 46, 416 (1985).

[2] J. Batey and E. Tierney, J. Appl. Phys. 60, 3136 (1986).

[3] P. G. LeComber and W. E. Spear, Semiconductors and Semimetals D21, 89 (1984).

[4] J. Lee, I-C Chen, and C. Hu, IEEE Electron. Device Lett. 506 (1986).

[5] C. J. Brinker, K. D. Keefer, D. W. Schafer, R. A. Assink, B. D. Kay, and C. S. Ashley, J. Non-Cryst. Solids 63, 45 (1984).

[6] K. D. Keefer, in Better Ceramics through Chemistry, Materials Research Society Symposium Proceedings, edited by C. J. Brinker, D. E. Clark, and D. R. Ulrich (North Holland, Amsterdam, 1984), Vol. 32, p. 15.

[7] C. J. Brinker, A. J. Hurd, and K. J. Ward, Ultrastructure Processing of Advanced Ceramics (Wiley, New York, 1988), p. 223.

[8] D. W. Schafer, J. E. Martin, K. J. Ward, and K. D. Keefer, in Physics of Finely Divided Matter, edited by N. Boccara and M. Daoud (Springer, Berlin, 1985), p. 13.

[9] S. Sakka, K. Kamiya, K. Makita, and Y. Yamamoto, J. Non-Cryst. Solids 63, 223 (1984).

[10] W. Kern, RCA Eng. 28-4, 3 (1983).

[11] L. M. Terman, Solid State Electron. 5, 289 (1962).

[12] E. H. Nicollian and J R. Brews MOS (Metal Oxide Semiconductor) Physics and Technology (Wiley, New York, 1981), p. 800.

[13] Z. A. Weinberg, W. C. Johnson, and M. A. Lampert, J. Appl. Phys. 47, 248 (1976).

[14] W. A. Pliskin and H. S. Lehman, J. Electrochem. Soc. 112, 1013 (1965).

[15] G. Lucovsky, M. J. Manitini, J. K. Srivastava, and E. A. Irene, J. Vac. Sci. Technol. B 5, 530 (1987).

[16] C. J. Brinker, K. D. Keefer, D. W. Schafer, and C. S. Ashley, J. Non-Cryst. Solids 48, 47 (1982).

[17] A. J. Hurd and C. J. Brinker, Mater. Res. Soc. Symp. Proc. 121, 731 (1988).

[18] C. J. Brinker, A. J. Hurd, D. R. Tallant, and C. S. Ashley, Thin Solid Films (submitted).

4408   J. Appl. Phys., Vol. 69, No. 8, 15 April 1991

Warren et al.   4408