Electronic properties of sol-gel-derived oxides on silicon

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Sol-gel-derived SiO_2, borosilicate, and aluminosilicate thin films deposited on silicon and heated for 5 min at temperatures of 1000 °C or lower exhibit dielectric strength as great as 5 MV/cm and interface state densities as low as $\sim 1 \times 10^{11}/\text{cm}^2$ eV. These values represent significant improvements over previous sol-gel-derived oxides on semiconductors and indicate that sol-gel processing can provide device quality oxides in situations where native oxides are unavailable or exhibit poor dielectric behavior, e.g., amorphous, hydrogenated silicon or III-V compound semiconductors.

A need exists for low-temperature alternatives to thermally grown oxide films in metal-oxide-semiconductor field-effect transistor (MOSFET) technologies.[1-14] Potential applications requiring low-temperature processing include amorphous hydrogenated silicon[2-5] and III-V compound semiconductor[6-9] MOSFET processing. In addition, microelectronic sensors may utilize porous silica obtainable by sol-gel processing rather than dense, thermally grown SiO_2.[10-11]

Sol-gel-derived oxides provide a low-temperature alternative to thermal oxides.[15] Sol-gel processing uses metal alkoxides $M(OR)_n$ (where M is Si, B, Al, P, etc., and R is often an alkyl group, C_xH_{2x+1}) as monomeric oxide precursors. In alcohol solutions the alkoxide is hydrolyzed and condensed to form inorganic oxide polymers composed of M–O–M bonds as shown by the net reaction to form silica:

$$n\text{Si}(\text{O}R)_4 + 2n\text{H}_2\text{O} \rightarrow n\text{SiO}_2 + 4nR\text{OH}. \quad (1)$$

The resulting solutions (containing polymeric silicates, borosilicates, aluminosilicates, etc.) may be deposited on virtually any substrate by conventional spinning or dipping methods. The as-deposited film is porous. Moderate heat treatments (400–1000 °C for a few minutes) are employed for their consolidation.

There are several advantages of sol-gel-processed oxides over thermal oxides: (1) the composition and microstructure of the oxide may be precisely tailored and are independent of the composition of the substrate; (2) sol-gel films may be deposited at room temperature on any substrate; (3) film thickness is controlled by the deposition process, therefore, although moderately high temperatures (400–1000 °C) are employed for consolidation, minutes rather than hours are spent at elevated temperatures; (4) multilayer films, consisting, e.g., of alternating layers of two different compositions, are easily obtained by multiple spinning or dipping operations. To date, however, the potential advantages of sol-gel-processed oxides have yet to be exploited in any area of MOSFET technology. In order to assess the potential of sol-gel processing in MOSFET applications, one must establish whether or not the process is capable of yielding highly insulating films on semiconductors with low densities of interface states at the semiconductor/insulator surface.[16,17]

Several earlier studies, for the most part utilizing commercially available sol-gel SiO_2 preparations, have shown that sol-gel-derived oxides exhibit electronic properties significantly inferior to those of thermal SiO_2 on silicon.[9,12-14] Lam and Lam[12,13] and Carmen[14] observed interface state densities in the range of $10^{12}/\text{cm}^2$ eV and current versus voltage behavior quite inferior to that of thermal SiO_2. In this investigation, we establish that sol-gel-derived oxides can be excellent insulators, exhibiting in one case (SiO_2 processed at 1000 °C for 5 min) current versus voltage characteristics nearly identical to thermal SiO_2 on silicon. We furthermore find that sol-gel-derived oxide/silicon structures may exhibit quite low interface state densities ($\sim 1 \times 10^{11}/\text{cm}^2$ eV).

This investigation extends the earlier work in three significant respects. First, we utilize films prepared with rigorous control of reagent purity. Second, we explore the electronic properties of several multicomponent oxides containing Al_2O_3, B_2O_3, and BaO in addition to SiO_2. Third, we utilize a corona discharge technique[18] to evaluate current versus voltage characteristics of the films. Weinberg *et al.*[19,20] pointed out that the corona technique is quite insensitive to the effects of local weak spots; one might anticipate weak spots in sol-gel films which have not been processed in the dust-free environment of a microelectronic processing clean room. If extrinsic effects due to the processing environment are eliminated, we can then study the intrinsic properties of sol-gel-derived oxides which have characteristic pore dimensions of less than 10 nm.

We have evaluated the electronic properties of sol-gel-derived oxide films on (100) oriented n-type ($\rho \sim 3$–6 Ω cm) silicon substrates. The oxides were deposited by spinning solutions of polymerized metal alkoxides. Three film compositions were utilized: SiO_2, a four-component oxide containing SiO_2, Al_2O_3, B_2O_3, and BaO, and a two-component Al_2O_3, SiO_2 oxide. Ellipsometric measurements established that the as-deposited films were 2000–3000 Å thick with refractive indices near 1.42 (less than 10 vol % porosity). All the samples were coated in a glove box with 5% relative humidity in a nitrogen atmosphere in order to ensure

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uniform and reproducible hydrolysis and condensation conditions. To consolidate the initially porous films, 5-min anneals in dry nitrogen at temperatures ranging from 600 to 1000 °C were employed.

We have measured the density of interface states in the middle half band gap for the three different film compositions. Interface state density was determined from a Terman analysis[17] of 1-MHz capacitance versus voltage (CV) measurements; the analysis took into account differences in the dielectric constants which varied from 3 to 6. In Fig. 1 we illustrate the results. Surprisingly, the highest interface state densities were observed in the pure SiO_2 films. To the best of our knowledge, the lower interface state densities of Fig. 1 ($\sim 1 \times 10^{11}/cm^2$ eV) are the best ever reported for low-temperature ($T < 1000$ °C) processed sol-gel oxides.

Current density versus voltage was measured using a corona discharge technique[18-20] in which a large (~ 7000 V) potential is applied to a sharp needle point several centimeters from the bare oxide surface. Corona ions drift down to the oxide surface, providing a potential drop across the film. The corona needle is then removed and a Kelvin probe electrostatic voltmeter (Monroe 170) is utilized to measure surface potential versus time. From the decay in surface potential versus time one may easily obtain current versus voltage ($CdV/dt = dQ/dt = i$).

The results of several corona measurements are illustrated in Fig. 2. In addition to the sol-gel film data, we also present a curve for device quality thermal SiO_2 on silicon. The behavior of the sol-gel SiO_2 annealed at 1000 °C closely matches that of thermal oxide; the others clearly do not.

Weinberg *et al.*[19] showed that, if the thin-film current versus voltage characteristics were dominated by Fowler–Nordheim[21] tunneling of electrons from the silicon into the oxide, one would expect a plot of log time versus reciprocal field to yield a straight line. The slope of this line is used to approximately determine the barrier to electron tunneling, i.e., the energy difference between the conduction-band edges of Si and the oxide. In Fig. 3 we present such a plot. The behavior of sol-gel-derived SiO_2 annealed at 1000 °C closely resembles that of thermal SiO_2. The linear relationship is indicative of Fowler–Nordheim[21] tunneling. The characteristics of the other films do not yield straight line plots, and thus the conductivity must be dominated by an alternative process. Analysis of the 1000 °C anneal SiO_2 plot yields a barrier height of approximately 2.5 eV. The thermal SiO_2/Si barrier is about 3.1 eV.[22] (We have made similar corona biasing measurements with thermal SiO_2 on silicon and consistently obtain a barrier height in the range of 2.5–2.8 eV; thus, within the limits of our experimental technique we find that the sol-gel films annealed at 1000 °C have current versus voltage characteristics identical to thermal SiO_2 on silicon.)

In conclusion, we find that some sol-gel-derived oxides on silicon exhibit relatively low interface state densities, and some films also are fairly good to excellent insulators. To the best of our knowledge, we report herein the lowest interface

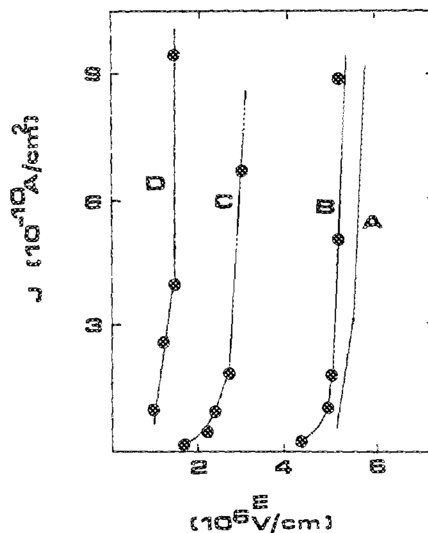

FIG. 2. Current density vs electric field. (A) Thermal SiO_2 film. (B) SiO_2 film annealed at 1000 °C. (C) SiO_2 film annealed at 800 °C. (D) Four-component (SiO_2, Al_2O_3, B_2O_3, BaO) film annealed at 1000 °C.

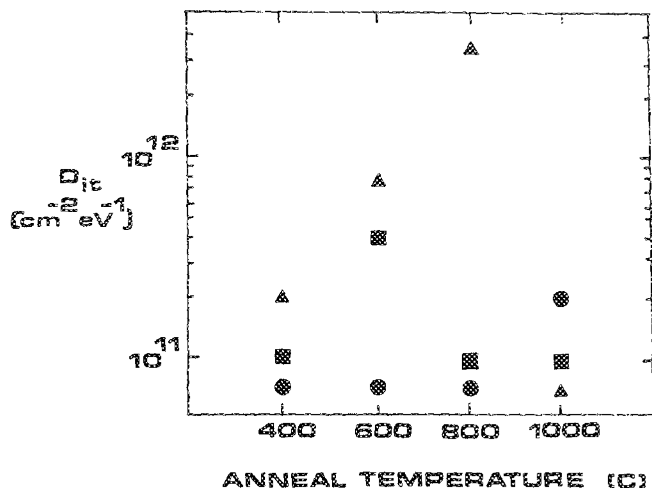

FIG. 1. Interface state density vs annealing temperature. Four-component (SiO_2, Al_2O_3, B_2O_3, BaO) film (●), two-component (SiO_2, Al_2O_3) film (■), pure SiO_2 film (▲).

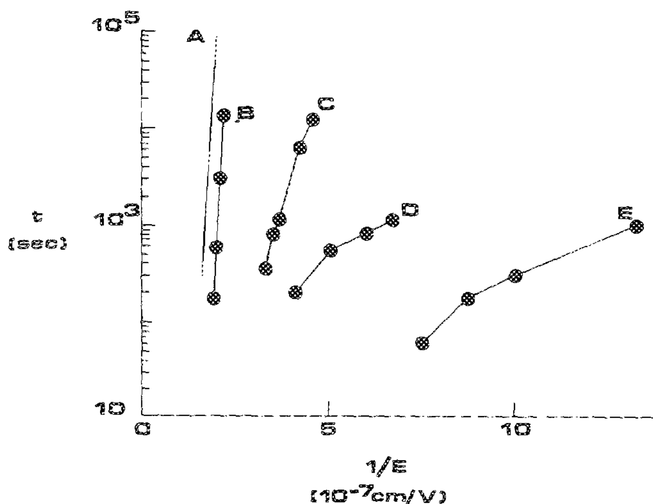

FIG. 3. Semilog plot of time vs reciprocal of field for sol-gel-derived films and device quality thermal SiO_2 on silicon. (A) Thermal SiO_2 on silicon; (B) sol-gel SiO_2 annealed at 1000 °C; (C) sol-gel SiO_2 annealed at 800 °C; (D) four-component (SiO_2, Al_2O_3, B_2O_3, BaO) oxide annealed at 1000 °C; (E) four-component (SiO_2, Al_2O_3, B_2O_3, BaO) oxide annealed at 800 °C.

state densities and best insulating behavior ever reported for sol-gel oxides on a semiconductor. Our observations suggest that sol-gel processing of insulating films may be useful in MOSFET applications in which thermally grown oxides cannot be utilized.

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