Enhancement of the electrical characteristics of MOS capacitors by reducing the organic content of H$_2$O-diluted Spin–On–Glass based oxides

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A B S T R A C T

In this work, the physical, chemical and electrical properties of Metal-Oxide-Semiconductor (MOS) capacitors with Spin-On-Glass (SOG)-based thin films as gate dielectric have been investigated. Experiments of SOG diluted with two different solvents (2-propanol and deionized water) were done in order to reduce the viscosity of the SOG solution so that thinner films (down to ~20 nm) could be obtained and their general characteristics compared. Thin films of SOG were deposited on silicon by the sol–gel technique and they were thermally annealed using conventional oxidation furnace and Rapid Thermal Processing (RTP) systems within $N_2$, ambient and vacuum condition. SOG films diluted with organic solvent and deionized water and further annealing (at relatively high temperatures >450°C) are important processes intended to reduce the organic content of the films. Fourier-Transform Infrared (FTIR) Spectroscopy results have shown that water-diluted SOG films have a significant reduction in their organic content after increasing annealing temperature and/or dilution percentage when compared to those of undiluted SOG films. Both current–voltage ($I–V$) and capacitance–voltage ($C–V$) measurements show better electrical characteristics for SOG-films diluted in deionized water compared to those diluted in 2-propanol (which is an organic solvent). The electrical characteristics of H$_2$O-diluted SOG thin films are very similar to those obtained from high quality thermal oxides so that their application as gate dielectrics in MOS devices is promising. Finally, it has been demonstrated that by reducing the organic content of SOG-based thin films, it is possible to obtain MOS devices with better electrical properties.

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1. Introduction

Since state-of-the-art MOSFET devices are continuously shrinking in dimensions to deep-submicron scale, they are now facing serious issues like higher gate leakage currents ($I_{leak}$), a more complex and expensive fabrication processing, poor reliability characteristics, etc. [1]. As an example, measuring the leakage current flowing through the gate of a 70 μm (channel length) MOSFET will produce its characteristic low $I_{leak}$ levels; for a 70 nm MOSFET however, $I_{leak}$ increases several orders of magnitude because of a reduction in thickness of its gate oxide (see Fig. 1). In order to reduce the high $I_{leak}$ levels present in modern MOSFET devices, high-dielectric constant (high-k) materials have been introduced by the semiconductor industry at a price that involves more complex deposition techniques and which require sophisticated and expensive deposition systems. In this work, we apply one of the simplest thin-film deposition techniques for obtaining gate oxide materials so that fabrication and evaluation of MOS devices containing SOG-based oxides can be realized. The sol–gel deposition method offers great versatility for the deposition of different materials by spinning; additionally, it is one of the simplest and cheapest methods to fabricate MOS structures since the chemicals used for oxide formation are commonly used by the semiconductor industry (for planarization and inter-level dielectric isolation, see for example [2,3]) and they are SOG-based materials. SOG are siloxane- and silicate-based polymers; the silicate-based materials are able to form hard films of pure SiO$_2$ while the siloxane-based materials (containing significant amounts of silanol Si–OH groups) produce oxides with electrical properties inferior to oxides deposited by other methods [4]. Because of the potential use of silicate-based SOG oxides as gate dielectrics, correlating the film composition to device performance of SOG-based MOS devices is important due to the advantages already exposed. Additionally, thermal stability of ultra-thin SOG-based oxides and their subsequent compositional changes after annealing are subjects that require further investigation since former studies have only considered thicker films not useful for gate oxide applications [5,6]. This work then correlates the chemical composition of SOG-based thin oxide films to their electrical characteristics after fabrication of MOS devices. Specifically, understanding the influence of organic based compounds in the physical and electrical $C–V$ and $I–V$ characteristics of SOG-
based MOS devices is of primary importance in order to assess their utility as gate oxide materials. On the other hand, the need for gate oxides as thin as possible (less than 100 nm) is desired since the thinner the oxide, the greater the field effect at its gate. For this purpose, the reduction in the viscosity of SOG-solutions is explored using two different solvents which produce SOG-oxides with different chemical and electrical characteristics. By correlating both chemical and electrical characteristics for this material, ways to enhance the electrical performance of even thinner SOG-based oxide films could be found in order to produce high-quality thin oxide films after a quite simple and cheap spin-coating technique so that their application in some electronic applications like FET-based memory devices could be systematically explored. The great versatility of SOG provide applications that go beyond their conventional uses, so that producing low-cost, simple and reproducible gate oxide materials for MOS devices could be achieved and high-k Spin-On-Dielectrics could be further developed.

2. Experimental

For all experiments, we used a silicate-type SOG material (from Filmtronics, 700A). Silicon wafers were 2" diameter, N and P type (100) with a resistivity range of 5–10 Ω cm. These wafers followed standard RCA-cleaning procedures resulting in HF-last surfaces. A dropper was used to apply SOG solution directly on the wafer surfaces. After SOG application, spinning speeds ranging from 4000 to 7500 rpm were used in order to obtain different oxide thicknesses. All deposited films were initially baked at 200°C (10 min in N2 ambient) in order to evaporate most of the SOG organic solvents. N2 ambient was used for all subsequent thermal annealing treatments of the films at T>200°C so that better densification could be obtained (30 min for all curing treatments). All oxide films were metalized with aluminum (1 μm) by evaporation and a gate capacitor area of 13.34e–4 cm² was used for all MOS devices. On the other hand, different dilution percentages of SOG with C2H4O (2-propanol) and H2O (DI water) were done in order to reduce both the SOG organic content and its viscosity so that thinner films could be obtained. A high-quality dry thermal oxide grown on silicon (~60 nm) was used as a monitor so that chemical and electrical characteristics of SOG-based oxides were compared against it. This thermal oxide was grown on Si(100) within dry-O2/TCE ambient at 1000°C for ~100 min. The films’ compositional analysis was done with a Bruker Vector 22 system in order to obtain the FTIR spectrum of each sample. Both refractive indexes and thicknesses for all films were measured with a Gaertner ellipsometer L117 equipment. Finally, C–V and I–V measurements were done using a Keithley Model 82–DOS Simultaneous C–V system and an HP 4156B Semiconductor Parameter Analyzer, respectively.

3. Results and discussion

Since spinning undiluted SOG produces oxides whose thicknesses are well above the requirements of gate oxide dielectrics (a few nm for most submicron MOS technologies), obtaining thinner oxide films is of primary importance. By increasing the spinning velocity, a linear trend in oxide thickness reduction is obtained as expected (see Fig. 2). In this figure, we can see that by increasing the spinning velocity from 4000 rpm up to 7000 rpm, the oxide thickness (after a 200°C bake in N2, 10 min) lowers from 280 nm to 240 nm, which is quite a moderate reduction indeed, not enough to produce thinner films suitable for the gate of a MOSFET device. On the other hand, the refractive index for these films is kept within 1.45–1.47, which is an indicator of the films’ low porosity and whose magnitude is quite close to the refractive index of high-quality thermal SiO2, 1.46 [7]. Since baking the undiluted

![Fig. 1. Gate leakage current versus gate voltage (Ig–VG) characteristic for MOSFET devices with channel lengths of 70 nm and 70 μm, gate oxide thickness is 2 nm and 14 nm, respectively.](image1)

![Fig. 2. Oxide thickness and refractive index dependence with spinning velocity. A linear trend in oxide thickness reduction with spinning velocity is observed while keeping refractive index between 1.45 and 1.47.](image2)
was slightly above 240 nm, increasing the curing temperature up to 1000 °C can produce oxide films as thin as ~120 nm (half the previous thickness), and having a refractive index quite close to that of pure SiO$_2$. Fig. 4 shows the FTIR spectrum (taken from 4000 to 400 cm$^{-1}$, in absorbance mode) for these samples with the characteristic Si–O peak found at 1070 cm$^{-1}$ (stretching mode) and the peak related to alcohols and other carbon-related compounds found at 1139 cm$^{-1}$ [8], those are peak numbers 5 and 6, respectively. A summary of the main chemical-bonds composing these films is shown in Table 1. In Fig. 4, we notice that peak number 6 gets smaller as the curing temperatures increases for the samples, thus making evident the reduction in the density of organic compounds for SOG cured at higher temperatures. These A1–A4 oxide films were then metalized in order to obtain their C–V and I–V electrical characteristics. Depending on the curing temperature, the oxide film’s thickness will change accordingly and so will the accumulation capacitance Cox of that MOS capacitor, so that comparing all C–V curves of samples A1–A4 from accumulation to inversion regions is somewhat difficult. In order to simultaneously compare the C–V characteristics for all samples, normalization of all curves to Cox was realized and the results are shown in Fig. 5. There, we notice that depending on the curing temperature, different slopes for the accumulation to inversion transition will be obtained, which is a sign of the strong influence the final thermal treatment has on the properties of the SiO$_2$–Si interface. For the sample annealed at 800 °C (sample A3), we also notice an anomalous increase in the C/Cox relation at negative Vg or inversion regime and this could be related to a weak re-oxidation mechanism triggered from this particular temperature since the refractive index for these films increases once the annealing temperature goes from 800 °C to 1000 °C (see Fig. 3). A weak re-oxidation mechanism would increase fixed charge density (without significantly increasing oxide thickness for these relatively thick samples) thus shifting flat-band voltage Vfb to more negative values while screening out some of the electric field needed for charge depletion. Since we are focused on samples annealed at 1000 °C in this work, this important effect requires further and detailed study. Fig. 6 shows the I–V characteristics for the same samples. Although samples annealed at 450 °C and 600 °C (A1–A2) were thicker than those annealed at 800 °C and 1000 °C (A3–A4), we notice that the gate leakage current in both inversion and accumulation is higher for A1–A2 samples. This is somewhat expected since higher curing temperatures are able to enhance the densification of the films, turning into more insulating or resistant to electronic conduction and closer to the structure and properties of thermal oxide as well [9].

Up to now, our thinnest oxide film (~120 nm) was obtained after a 7000 rpm spinning velocity, an initial baking at 200 °C and a final

<table>
<thead>
<tr>
<th>Wavenumber</th>
<th>450</th>
<th>584</th>
<th>642</th>
<th>800</th>
<th>1070</th>
<th>1139</th>
<th>1500–1675</th>
<th>2346</th>
<th>3000–3800</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond type</td>
<td>Si–O rocking</td>
<td>CS-rings</td>
<td>CS-rings</td>
<td>Si–O stretching</td>
<td>Alcohols, ethers</td>
<td>AQ group</td>
<td>CO$_2$</td>
<td>HDX groups</td>
<td></td>
</tr>
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Table 1: Main chemical-bonds found for SOG films after high-temperature annealing in N$_2$.
cure thermal treatment at 1000 °C, both in N2. Because of its still poor electrical characteristics and thicker dimensions, this oxide cannot be useful as a gate dielectric in any standard MOS technology. On the other hand, this oxide was obtained after using a SOG solution that was not diluted with any specific solvent previously. In order to obtain thinner oxides, diluting the SOG solution with 2-propanol or DI water (C3H8O or H2O) reduces the viscosity of the SOG prior to spinning and this proved to be an effective way to produce oxides well below 100 nm. For the thinnest oxides, Fig. 7 shows that H2O is a better solvent for SOG as compared to 2-propanol (C3H8O). A ∼40 nm oxide is obtained after diluting the SOG solution down to a 50% in volume with H2O and after the initial baking in N2 at 200 °C. Such a thin oxide could be obtained without need to apply a high temperature curing treatment. On the other hand, Fig. 8 shows that compared to H2O-diluted SOG samples, the FTIR spectrum of C3H8O-diluted samples present higher peaks related to chemical bonds that are associated to Si atoms bonded to C-based molecules like CH3 and C6H5 (band between 500 and 750 cm−1) [8]. By evaluating the C–V characteristics of C3H8O-diluted SOG oxides, we notice that a highly organic-based oxide produces poor electrical characteristics as shown in Fig. 9, where lots of electrical defects are observed from the accumulation to depletion regimes like huge spreading of the accumulation capacitance and lateral shifts in Vfb. Nonetheless, C50 at the strong inversion regime was almost the same thus suggesting uniform distribution of the depletion layer under the oxide after C–V measurements at 1 MHz. For this specific sample, even though an additional RTP-based high temperature annealing was applied in N2 ambient (so that most of the organic solvents could be evaporated out of the oxide), its electrical behavior could not be recovered.

Using H2O to dilute the SOG, the thinnest oxide films with better properties were obtained. Fig. 10 shows a good linear trend in oxide thickness reduction when the SOG solution has been increasingly diluted with H2O. These oxides were also baked at 200 °C and finally cured at 1000 °C in N2. For a 50–33% of diluted SOG, a ∼30–20 nm oxide can be obtained (thin enough for some long-channel I > 2 μm MOSFET applications). In that same figure, the oxide’s refractive index dependence to H2O dilution percentage shows a refractive index of ∼1.27 for the 33% dilution (well below 1.46 of thermal SiO2), which is close to the refractive index of water.

**Fig. 6.** I–V characteristics showing the gate leakage current density Jg for samples shown in Fig. 3. Jg is smaller for the thinnest films since they were better densified after higher curing temperatures.

**Fig. 7.** Oxide thickness dependence with C3H8O and H2O-based dilution percentage of SOG after annealing in N2 at 200 °C. H2O can be used as a better solvent for SOG in order to obtain thinner films.

**Fig. 8.** FTIR absorbance spectrum for SOG diluted 50% in C3H8O and H2O. Because of the higher organic content of the C3H8O solvent, higher density of peaks related to C-based molecules are found for SOG diluted with this organic solvent.

**Fig. 9.** C–V characteristics for SOG samples diluted in C3H8O. This highly organic-content oxide does not produce good electrical characteristics since lots of electrical defects are observed.
ice 1.3, thus indicating a direct increase of the porosity within the oxide film [10]. The chemical and electrical characteristics of these H2O-diluted oxide samples are shown in Figs. 11 and 12, respectively. The FTIR spectrum shows a “cleaner” material while the peak related to the chemical bonds present in alcohols (shown by the arrow) gets smaller as more solvent is used. The C–V characteristics show an increase in Cox as the oxide gets thinner and a low dispersion in Cox for each set of samples is also shown. Obtaining a low Cox dispersion is indication of the good oxide uniformity throughout the silicon surface. In Fig. 13, the same C–V data of Fig. 12 is presented after taking the average curve of several measurements for the same oxides and normalizing all curves to their correspondent Cox. There, we notice that even the thinnest oxide films (having the highest dilution percentage in H2O) present good C–V electrical characteristics. The slope of the accumulation to inversion transition is greater for a 33% SOG sample compared to 50% and 100% SOG; this is direct consequence of both thinning of the oxide (greater capacity to handle electronic charge for the same applied electric field) and better interface properties with the silicon surface. In this specific case, a 33% diluted SOG–based oxide presents C–V characteristics that are similar to those of thermal oxides grown on silicon (thickness of 60 nm). On the other hand, these samples contain the lowest density of organic components within (see Fig. 11). Fig. 14 compares FTIR spectrums between a dry thermal oxide (~60 nm) and H2O-diluted 66% SOG-oxide (~60 nm), both having similar thicknesses. In that figure, we notice a reduction in the Si–O peaks (1070, 800 and 450 cm⁻¹) for the H2O-diluted film. However, it is clearly shown that a H2O-diluted SOG oxide presents chemical bonds quite similar to those of a dry thermal oxide grown on silicon. Reduction in the organic components of the H2O-diluted films (mainly CH3) is signal of the high quality of the oxide, and this effect is evident after comparing the C–V characteristics already presented in Figs. 12 and 13. Finally, Fig. 15 shows the I–V data for H2O-diluted SOG oxides. Here we notice that even though these were the thinnest oxides obtained (compared to undiluted SOG with thickness down to ~120 nm), electrical conduction processes within these oxides are quite restrained for both inversion and accumulation regimes. These characteristics are quite different from the I–V data presented in Fig. 6 where, although undiluted and thus thicker SOG oxides were cured at temperatures

![Graph showing oxide thickness and refractive index dependence](image1)

**Fig. 10.** Oxide thickness and refractive index dependence with H2O-based dilution percentage of SOG after annealing in N2 at 200 °C and 1000 °C. Thinner oxides down to ~20 nm can be obtained.

![Graph showing C-V characteristics](image2)

**Fig. 12.** C–V characteristics for SOG samples diluted in H2O and compared to those of a dry thermal oxide grown on silicon. Good electrical characteristics are observed for all samples, where a low Cox dispersion indicates good oxide thickness uniformity throughout the silicon surface.

![FTIR absorbance spectrum](image3)

**Fig. 11.** FTIR absorbance spectrum for SOG diluted in H2O. The peak related to the chemical bond of organic molecules and alcohols gets proportionally reduced with the H2O dilution percentage.

![Graph showing C-V data normalized to Cox](image4)

**Fig. 13.** C–V data of Fig. 12 normalized to Cox. A 33% diluted SOG-based oxide presents characteristics that exceed those of a thermal oxide. This 33% diluted SOG sample contains the lowest density of organic compounds.
up to 1000°C in N2, they present a highly conductive \( J_g \) behavior. In contrast, thinner H2O-diluted oxides present relatively constant \( I-V \) characteristics so that, as evidenced by their \( C-V \) and \( I-V \) data, H2O-diluted SOG oxides could be further improved in order to assess their real potential as gate dielectrics in long-channel MOSFET devices.

Up to this point, obtaining high-quality and very thin layers (down to ~20 nm) of SOG-based oxides has been demonstrated. The electrical characteristics for these oxides were obtained from MOS capacitors, which are simple devices ideal for the initial evaluation of the quality of the oxide. Nevertheless, the next natural step to evaluate their true potential as gate dielectrics would be inserting these oxides within any CMOS fabrication process and extract all possible gate oxide parameters from MOSFET devices’ performance so that a better assessment of the quality of these dielectrics can be obtained.

4. Conclusions

By adjusting the deposition and processing parameters of SOG-based films, it is possible to obtain thin oxide films (down to 20 nm) with good electrical characteristics for MOS devices. Thick non-diluted SOG-based gate oxides resulted in regular \( C-V \) and \( I-V \) MOS characteristics but these features were both enhanced after diluting the SOG solution in H2O-based solvent. Using C3H6O as a solvent for SOG will produce relatively thick oxide films with highly organic content and poor \( C-V \) characteristics compared to H2O-diluted oxides, where thinner oxides with low Cox dispersion and low gate leakage current for these dielectrics were obtained along with a reduced organic content. On the other hand, the \( C-V \) characteristics for a SOG oxide diluted in H2O at 33% are quite similar to those of a thermal oxide grown on silicon (which was used as a monitor) and the overall enhancement on the electrical characteristics of these oxides is related to a reduction in the organic content of the SOG-based oxides (confirmed after FTIR spectrum measurements showing a reduction in the density of chemical bonds related to organic compounds). Even though the use of SOG-based oxides has been traditionally focused to inter-level dielectric planarization and dopant sources for junction formation processes, it could be possible to use them as good quality gate oxides for the fabrication of MOS devices using a very simple, cheap and yet reproducible spinning technique. Development of Spin-On-Dielectrics could then be explored by just adding the necessary chemicals (in the same way as the H2O-dilution process shown here) in order to obtain for example, high-\( k \) dielectrics needed for advanced MOSFET technologies or even for other electronic applications.

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