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Enhancement of the electrical characteristics of MOS capacitors by reducing the organic content of H_2O-diluted Spin-On-Glass based oxides

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ABSTRACT

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 after deposition. SOG dilution using non-organic solvents like 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_2O-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.

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_g), 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_g levels; for a 70 nm MOSFET however, I_g 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_g 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-

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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 greatest 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.

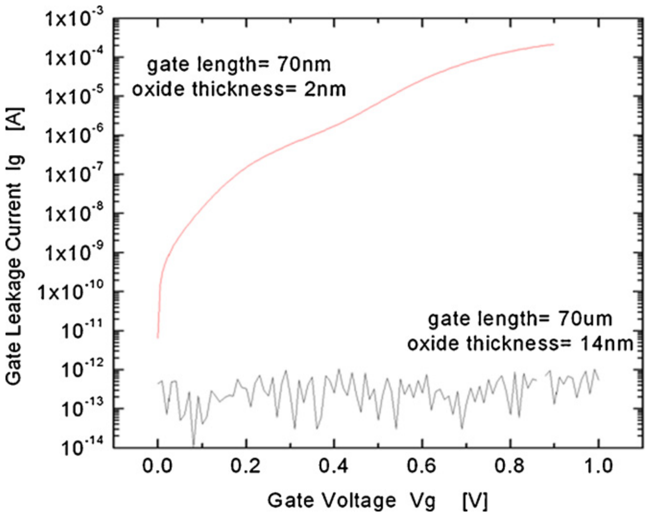

Fig. 1. Gate leakage current versus gate voltage (I_g–V_g) characteristic for MOSFET devices with channel lengths of 70 nm and 70 μm, gate oxide thickness is 2 nm and 14 nm, respectively.

2. Experimental

For all experiments, we used a silicate-type SOG material (from Filmtronics, 700A). Silicon wafers were 2″ diameter, N and P type (1 0 0) 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 N_2 ambient) in order to evaporate most of the SOG organic solvents. N_2 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 cm^2 was used for all MOS devices. On the other hand, different dilution percentages of SOG with C_3H_8O (2-propanol) and H_2O (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(1 0 0) within dry-O_2/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 Keihtley 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 N_2, 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 SiO_2, 1.46 [7]. Since baking the undiluted SOG films at 200 °C produces relatively thick SiO_2 films (no matter how fast we increase the spinning velocity), an additional thermal treatment at higher temperatures or curing, is needed in order to obtain thinner oxides with better physical properties simultaneously (after evaporating most of the remaining organic solvents that can produce poor electrical characteristics). When cured at 425 °C for instance, the dielectric constant of the resulting films is slightly higher than SiO_2 but when the SOG films are cured at higher temperatures, up to 1000 °C, a glass film similar to SiO_2 with superior dielectric characteristics and slower etch rates is obtained [4], so that increasing the final curing temperature will produce oxides with better physical and electrical characteristics. Fig. 3 shows the oxide's thickness and refractive index dependence with increasing curing temperature. For those films, undiluted SOG (100%) was deposited atop Si surfaces with the following conditions for all samples: spin velocity of 7000 rpm followed by a 10 min bake in N_2 at 200 °C. For curing, different temperatures were used: 450, 600, 800 and 1000 °C for samples A1, A2, A3 and A4, respectively. There, better densification and thus, thinning of SOG-based oxides can be observed when cured at higher temperatures while their refractive indexes are kept well above 1.43. Compared to the initial films, where the thinnest oxide produced

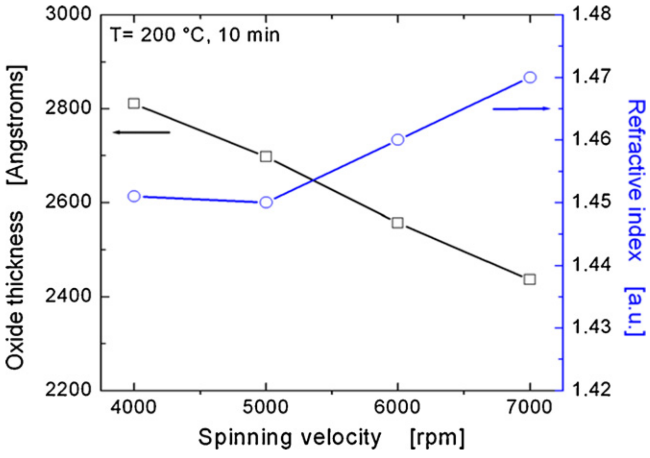

Fig. 2. Oxide thickness and refractive index dependence with spinning velocity. A linear trend in oxide thickness reduction with spinning velocity is observed while keeping refractive index between 1.45 and 1.47.