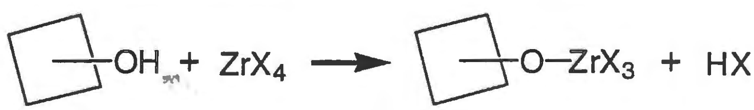
Chemical and Electrical Properties of Zirconia on Silicon

Jason Lee Final Seminar April 12, 2002

Advances in computer technology have been realized by continuous miniaturization of transistors, diodes, resistors, and capacitors on integrated circuits.[1,2] Decreasing dimensions make it possible to operate integrated circuits at higher speeds at constant power per unit area. As a result, the number of transistors per integrated circuit has roughly doubled every 18 months from the introduction of Intel's 4004 processor in 1971 with 2,250 transistors to Intel's Pentium 4 processor in 2000 with approximately 42,000,000 transistors.[3] However, as the dimensions of the transistor continue to decrease, problems arise due to physical limitations since individual components must also scale accordingly.[4] One component that poses serious scaling problems is the gate insulator which is used to maintain capacitance between the gate electrode and silicon channel. While SiO_2 has been the material of choice for the gate insulator because it readily forms on the silicon substrate by oxidation,[5] SiO_2 gate insulator thickness cannot be reduced to less than about 0.8 nm due to excessive leakage currents.[6] In future generation Metal-Oxide-Semiconductor Field Effect Transistor (MOSFET) devices, capacitance (C) will be maintained with smaller gate insulator area (A) according to the relationship, $C=\kappa\varepsilon_0 A/t$, by increasing the value of the dielectric constant (κ) with an alternative gate insulator material to keep thickness (t) above 0.8 nm and minimize leakage current. The permittivity of free space (ε_0) is 8.85×10^{-14} F/cm.

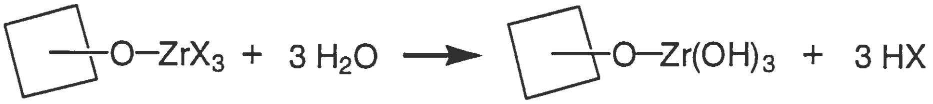
There are a wide range of candidates for replacement gate insulators,[7] but ZrO_2 is one of the few high-κ materials that has proved to be compatible with silicon. For example, deposition of ZrO_2 films on Si by reactive sputtering yields insulating films displaying an equivalent oxide thickness of less than 11 Å and leakage currents less than 1.9×10^{-3} A/cm^2.[8] Many other high-κ materials such as Ta_2O_5 and TiO_2 are believed to oxidize Si upon annealing to form SiO_2 and reduced oxides and/or silicates.[7,9] These materials form separate phases that adversely affect dielectric properties.[7,9] In contrast, ZrO_2 does not react with Si at temperatures less than 900 °C.[10]

Atomic layer deposition (ALD) has found widespread application for the vapor deposition of ZrO_2 on silicon for gate oxide applications. This process involves the use of chemical vapor deposition in a series of alternating surface-saturating reactions. Surface hydroxyl groups provide initial sites for condensation. The reaction between ZrX_4, where X is Cl,[10-13] OBu^t,[14] or $OCH_2C(CH_3)_3$,[15] and the hydroxyl groups on the surface yield a single layer of adsorbed $-OZrX_3$ according to Equation **1**.



1

The adsorbed layer is "protected" from multilayer formation by the remaining unreacted X groups. The adsorbed $-OZrX_3$ species is then "deprotected" by hydrolysis according to Equation **2**.



2

A second exposure to ZrX_4 results in further surface condensation as in Equation **1**. Through repeated condensation-hydrolysis cycling, a robust zirconia film is formed layer by layer.

Ultrathin films of zirconia were grown on Si(111) substrates using ALD. However, instead of using a conventional precursor for vapor deposition, chemical solutions containing $Zr_4(OPr^n)_{16}$ in methylcyclohexane were employed. In previous work, regular growth using $Zr(OPr^n)_4$ in a 1:1 toluene:propanol solution was observed on surface-activated gold substrates but only at low temperatures.[16] While most precursors for the deposition of ZrO_2 are single metal-center complexes, a precursor with multiple metal centers arranged in a metal-oxide framework analogous to ZrO_2 might result in a more efficient film deposition process. Through the repeated cycling using $Zr_4(OPr^n)_{16}$ in methylcyclohexane and H_2O in *n*-propanol, a zirconia film was deposited at a rate of 9.7×10^{13} to 1.7×10^{14} Zr atoms/cm^2 per cycle. These films were chemically and physically characterized using Rutherford backscattering spectrometry, X-ray photoelectron spectroscopy, and transmission electron microscopy. Metal-insulator-semiconductor capacitors were fabricated using zirconia films on p-Si with an Au top electrode and Au backside ohmic contact. Figures 1 and 2 are current-voltage (I-V) and capacitance-voltage (C-V) curves, respectively. Preliminary results show that these zirconia films have a leakage current density at -1 V in the range of 10^{-3} to 10^{-4} Amps/cm^2 and equivalent SiO_2 thicknesses below 2 nm.

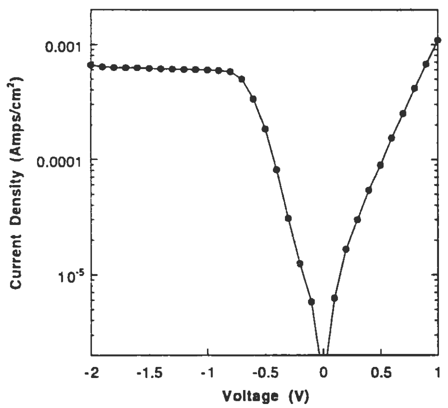


Figure 1

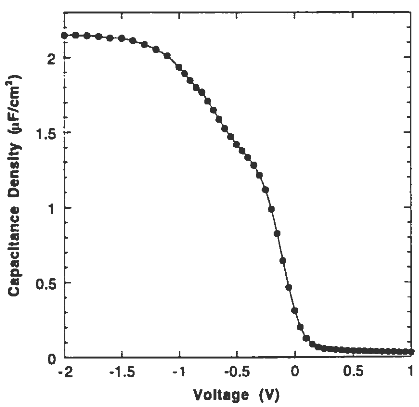


Figure 2

To reduce the number of reaction cycles and therefore improve the quality of zirconia films, a robust polynuclear zirconate precursor would offer advantages relative to $Zr_4(OPr^n)_{16}$. The triskaidecazirconate $[Zr_{13}O_8](OH)_{12}(OPr^n)_{24}$ has a metal-oxide framework analogous to that of crystalline ZrO_2, and its application as a precursor to thin film growth will be examined in the near future.

References

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