

Balancing Reactor Fluid Dynamics and Deposition  
Kinetics to Achieve Compositional Variation in  
Combinatorial Chemical Vapor Depositions

Wayne L. Gladfelter  
Bin Xia  
Feng Chen  
Stephen A. Campbell  
Jeffrey T. Roberts

Departments of Chemistry and Electrical and Computer  
Engineering  
University of Minnesota  
207 Pleasant St., SE  
Minneapolis, MN 55455  
USA

There is much interest in developing high-throughput methods for identification of new materials. The first use of chemical vapor deposition (CVD) to produce compositional spreads (CS) in multicomponent oxides produced mixtures of  $\text{TiO}_2$ ,  $\text{HfO}_2$  and  $\text{SnO}_2$  that were studied as possible replacements for  $\text{SiO}_2$  as the gate dielectric in field effect transistors (FET).(1) The first two oxides in the above mixture were chosen because of their higher dielectric constants while the  $\text{SnO}_2$  was added to minimize crystallization at the lower deposition temperatures. Atomically smooth surfaces having few grain boundaries are desirable features for the FET application. One of the goals of the research described in this paper is to minimize the reaction between the metal oxide layer and the silicon substrate by replacing  $\text{TiO}_2$  with  $\text{ZrO}_2$ . The anhydrous metal nitrates  $\text{Hf}(\text{NO}_3)_4$  (HN)  $\text{Sn}(\text{NO}_3)_4$  (SnN) and  $\text{Zr}(\text{NO}_3)_4$  (ZN) have been established previously as single source CVD precursors to the pure metal dioxide films and are used in this study.(2-6)

Films were deposited in a low pressure CVD reactor that was modified to locate three parallel precursor outlets approximately 1 cm above the substrate surface. The outlets were positioned at the apices of an equilateral triangle having an edge length of 1.5 cm. Two deposition temperatures (400 and 450 °C) were used in this study.

Rutherford backscattering spectrometry was used to map the elemental composition, and ellipsometry was used to map the film thickness and refractive index. Standard lithographic procedures were used to pattern 100 x 100  $\mu\text{m}$  squares of platinum (to act as the top electrode of a capacitor) over the entire substrate. X-Ray microdiffraction was used to map the phase.

X-ray microdiffraction of the 400 °C CS film showed that, with the exception of the areas immediately beneath the  $\text{Zr}(\text{NO}_3)_4$  and  $\text{Hf}(\text{NO}_3)_4$  precursor outlets, the as-deposited films were amorphous. Film composition (atomic %), which ranged from 3 to 83% for Zr, 5 to 92% for Hf and 3 to 85% for Sn was mapped using a 10 x 10 array of data points. The film thickness ranged from 150 to 480 Å for films grown for RBS and electrical measurements. For XRD analysis the thickness range was increased to 1200 to 3000 Å.

The films deposited at 450°C exhibited a similar compositional spread, however, diffraction indicated that most of the sample was polycrystalline. The X-ray microdiffraction patterns obtained for the 450 °C CS film confirm that the regions of the sample directly below the

ZN, SnN, and HN injectors yielded peaks corresponding to the thermodynamically stable forms of the corresponding oxides. In the area bordering between both the ZN and SnN injectors and the HN and SnN injectors, the observed reflections were assigned to an  $\alpha\text{-PbO}_2$  phase for material having the composition range represented by the formula  $(\text{Zr}_x\text{Hf}_{1-x})_{0.5-0.8}\text{Sn}_{0.2-0.5}\text{O}_2$ , where x can range from 0 to 1.

Based on measurements of the capacitance, the value of  $\kappa_{\text{eff}}$  was mapped as a function of composition for the 450 °C CS sample. The effective dielectric constant increased as the relative amount of Zr in the film increased. The composition that gave the highest  $\kappa_{\text{eff}}$  value (~22) was  $\text{Zr}_{0.77}\text{Sn}_{0.06}\text{Hf}_{0.17}\text{O}_2$ .

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