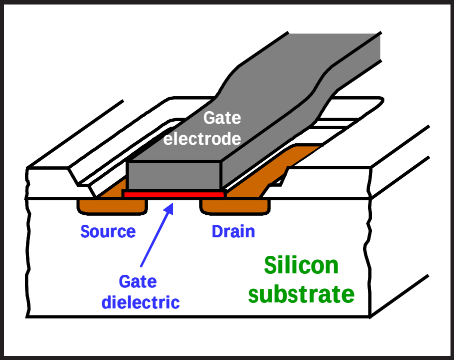
Combinatorial Measurement Methods for Inorganic Materials

Objective

Our goal is to develop novel, combinatorially-compatible measurement methods and metrologies, as well as comprehensive and consistent data sets, that will enable manufacturers of devices based on inorganic functional materials to select new materials more rapidly and intelligently. For example, the silicon microelectronics industry is currently materials-limited; the traditional transistor and capacitor formation materials — silicon, silicon dioxide, and polysilicon — have been pushed to their fundamental material limits, and continued scaling will require the introduction of novel materials.

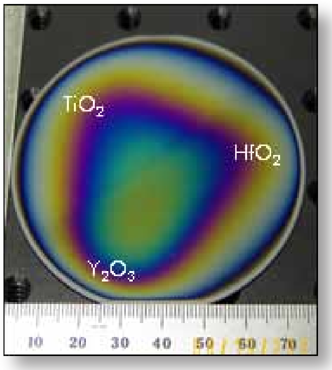


Impact and Customers

- The silicon (Si) microelectronics industry and the consumer electronics and information revolution that it fuels is, at $750 billion, one of the largest sectors of the U.S. (and global) economy. The development of materials with superior properties that will enable device scaling (dimensional shrinkage of integrated circuit device elements according to Moore's Law) and enhanced device performance is critical to continued innovation in Si microelectronics.
- Currently, there are no rapid measurement techniques to determine the critical properties of novel functional materials, e.g., the work functions of metal gate electrodes for metal-oxide-semiconductor-field-effect-transistor (MOSFET) devices, or the Seebeck coefficients of thermoelectric materials for vehicular waste heat recovery devices. Development of such methods would enable more rapid selection, optimization, and commercialization of systems incorporating these devices.
- Key customers include Sematech and major U.S. semiconductor manufacturers such as Intel and Micron, as well as GM and Honda for the use of thermoelectrics for vehicular waste heat recovery applications. We are very active in promoting the use of combinatorial methodologies with our customers.

Approach

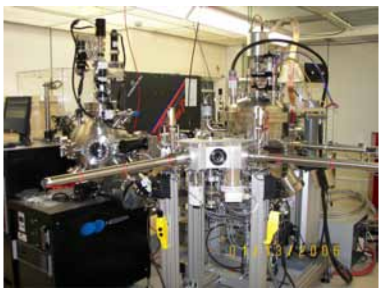
Our approach is to develop a novel metrology for interrogating the property of interest in the combinatorial library film. A good example of the application of this approach is the advanced gate stack of the integrated circuit MOSFET device. The traditional gate stack layers (SiO_2 gate dielectric and polycrystalline Si gate electrode) in current Si microelectronic devices must be replaced with a high dielectric constant (high-κ) gate dielectric, and a metal gate electrode. We will develop combinatorial methodologies to: (1) fabricate compositionally graded thin film libraries of novel gate metal electrode/high-κ gate dielectric/substrate combinations ("gate stack" structures); and (2) measure the key electronic properties (e.g., work function) and thermal stability of such libraries. Comprehensive data sets of electronic properties as a function of composition will be generated for materials systems identified as high priority by the microelectronics industry. In addition, first-principles modeling techniques will be used to predict the electronic properties of such systems.



CERAMICS

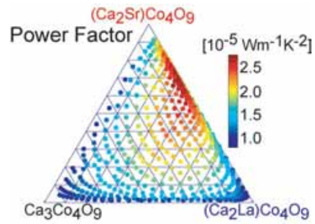
Accomplishments

We commissioned a state-of-the-art combinatorial tool capable of producing thin film libraries by reactive sputtering or pulsed laser deposition (PLD). Both chambers are equipped with multiple targets, allowing for the deposition of ternary films of metals and nitrides (by sputtering) and oxides (by PLD) with monolayer (0.5 nm) thickness control. At present, this tool produces library films for our thermoelectric materials and advanced MOS gate stack materials projects.



Combinatorial thin film tool

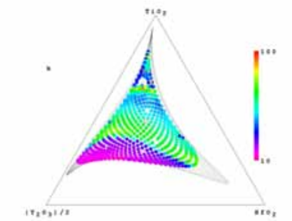
Thermoelectric materials have a major application for vehicular waste heat recovery, which could result in a 10% improvement in fuel efficiency, as well as a decrease in CO_2 emissions. There is currently no screening tool to measure the Power Factor (equal to the square of the Seebeck coefficient multiplied by the electrical conductivity), an important indicator of energy conversion efficiency of thermoelectric thin films. If applied to combinatorial thin film libraries, it would accelerate material selection and optimization. In the example shown, the power factor is plotted as a function of composition for La and Sr substituted $Ca_3Co_4O_9$ thermoelectric materials. Several hundred data points were automatically probed on this library film in about 2 hours. It can be seen that the power factor "sweet spot" is approximately at the composition $(Ca_2Sr_{0.7}La_{0.3})Co_4O_9$.



Power factor of La and Sr substituted $Ca_3Co_4O_9$ thermoelectric materials

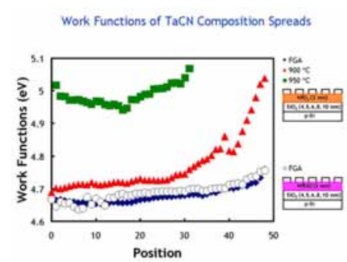
Another driver for our combinatorial project is the MOS gate stack (gate dielectric and gate metal electrode), which must be replaced by advanced materials if scaling is to continue. The microelectronics industry has identified HfO_2, among other high-k gate dielectrics, as the leading candidate replacement materials for the SiO_2 gate dielectric. However, dielectrics with dielectric constants even greater than HfO_2 (k = 20), i.e., between the range of 50 and 100, are now needed. We have investigated the HfO_2-TiO_2-Y_2O_3 ternary oxide system, and determined that there are many compositions with dielectric constants between 50 and 100, notably TiO_2-rich oxides containing about 30% Y_2O_3 and 15% HfO_2.

We have also studied the other gate stack layer, the gate metal electrode. The selection of gate electrode materials to replace polysilcon is not as far along as for the gate dielectric case. Recently, we



Dielectric constants of HfO_2-TiO_2-Y_2O_3 alloys

have focused our efforts on gate electrode materials, specifically metalloids such as the Ta-C-N ternary system. We have developed high throughput, automated methods to measure current-voltage (I-V) and capacitance-voltage (C-V) properties of gate stack structures. From these measurements, the work function (ϕ_m) and leakage current density (J_L) can be determined. Shadow masks are used during thin film deposition, so etching is not needed to produce capacitor pillars. Each capacitor is individually addressable; the properties of 700 capacitors can be measured in about 5 hours. Our work function results on the Ta-C-N system are the first reported comprehensive measurements of the dependence of work function on composition for this metalloid system deposited on high-κ dielectrics.



Work function as a function of position (i.e., composition) on a Ta-C-N library film

Learn More

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Publications

Chang K-S, Green ML, Hattrick-Simpers J, Suehle J, Takeuchi I, Celik O and DeGendt S *Determination of Work Functions in the $Ta_{1-x}Al_xN_y/HfO_2$ Advanced Gate Stack Using Combinatorial Methodology* IEEE Trans. Electron Devices, 55: 2641 (2008)

Schenck PK, Klamo JL, Bassim ND, Burke PG, Gerbig YB and Green ML *Combinatorial Study of the Crystallinity Boundary in the HfO_2–TiO_2–Y_2O_3 System Using Pulsed Laser Deposition Library Thin Films* Thin Solid Films, 517: 691 (2008)

Otani M, Lowhorn ND, Schenck PK, Wong-Ng W, Green ML, Itaka K and Koinuma H *A High-throughput Thermoelectric Power-Factor Screening Tool for Rapid Construction of Thermoelectric Property Diagrams* Applied Physics Letters, 91: 132102 (2007)