

## Dielectrics

### Room 312 - Session DI+EL+MS-ThA

#### High K Dielectrics: Perovskites

**Moderator:** J.N. Kidder, University of Maryland

#### 2:00pm DI+EL+MS-ThA1 High Density Thin Film Ferroelectric Nonvolatile Memories, **R. Ramesh**, University of Maryland **INVITED**

Over the past two years, we have focused considerable effort on understanding the deposition and characterization of conducting barrier layers for the direct integration of ferroelectric capacitors on a poly-Si plug. Our specific focus has been on the materials science of the barrier layers to understand the role of crystallinity and process parameters on the structural and chemical integrity of the barrier layers during the subsequent growth of the ferroelectric capacitor stack. We are using the PZT system with conducting oxide electrodes as a prototypical test system for which at least two different conducting barrier materials systems have been successfully developed. Using both epitaxial and polycrystalline capacitors on these conducting barriers as test vehicles, we have been carrying out systematic studies on the effect of composition, point defect chemistry, strain and other processing variables on the structural integrity and ferroelectric properties. A novel aspect of our work is the use of scanning electric force microscopy techniques to understand the microscopic influence of film microstructure on the ferroelectric properties. In this presentation, we will present results of our progress on the process integration, device properties, specifically, polarization switching and relaxation dynamics and microscopic observations of ferroelectric properties and time dependent changes ; stress effects on fundamental properties. This work is supported by the NSF-MRSEC under Grant No. DMR- 96-32521 and by Bellcore.

#### 2:40pm DI+EL+MS-ThA3 Process Window Extension of TiN Diffusion Barrier using Pre-oxidation of Ru and RuO<sub>2</sub> Film for (Ba,Sr)TiO<sub>3</sub> Dielectric Film, **H.J. Kim, S. Kim**, Hyundai Electronics Industries Co. Ltd., Korea

(Ba,Sr)TiO<sub>3</sub> (BST) thin film and other high dielectric oxides have attracted considerable attention due to their possible application in dynamic random access memories. However, serious integration issues are faced with in many cases because BST films need to be grown at rather high deposition or post-annealing temperatures of above 600°C in an oxidizing ambient. Deterioration of capacitor performance may result from interdiffusion and oxidation. Therefore, a diffusion barrier for oxygen should be developed for high-density DRAM device. In order to extend the process window of conventional sputtered TiN diffusion barrier and find out a proper electrode, in this experiment, the effect of pre-annealing method on the oxidation behavior of TiN barrier during 2 step annealing for BST dielectric film. Rapid thermal annealing in oxygen ambient (RTO) and N<sub>2</sub>/O<sub>2</sub> plasma oxidation was respectively introduced to form a thin RuO<sub>2</sub> layer and bond between oxygen and Ru at the surface of each Ru and RuO<sub>2</sub> film. It is expected that a thin RuO<sub>2</sub> layer be formed at the surface of each film by RTO and N<sub>2</sub>/O<sub>2</sub> plasma. This can be retarded the oxygen interdiffusion through Ru and RuO<sub>2</sub> layer at high temperature due to complex diffusion paths and strongly stuffed along the grain boundaries as well as matrix. Two steps annealing for BST dielectric film is recently introduced to minimize the oxidation of diffusion barrier. In this work, a role of thin RuO<sub>2</sub> oxidized layer formed at the surface of each Ru and RuO<sub>2</sub> film by different pre-annealing methods prepared with/without BST deposition is investigated during two steps annealing.

#### 3:00pm DI+EL+MS-ThA4 Atomic Polarization and Screening Charge by Variable Temperature Scanning Probe Microscopy of Ferroelectric Surfaces, **S.V. Kalinin, D.A. Bonnell**, University of Pennsylvania

Atomic force microscopy (AFM), electrostatic force microscopy (EFM), scanning surface potential microscopy (SSPM) and piezoresponse imaging (PRI) are applied to the BaTiO<sub>3</sub> (100) phase transition. The imaging mechanism for non-contact microscopies (EFM and SSPM) based on an analytical solution for potential and field above the surface is discussed. The PRI imaging mechanism on a ferroelectric surface is analyzed in terms of the solution of the combined electrostatic-piezoelectric indentation problem. The relationship between SPM signal and screened and unscreened charge density is established. Quantification of force and force gradient-distance dependencies indicate that polarization bound charge is screened on this surface when imaged in ambient environments. The

absolute value of the measured potential difference between domains of opposite polarity suggests that surface adsorbates play the governing role in surface potential. This conclusion is corroborated by a direct measurement of the phase transition and by observations of domain wall motion. The influence of tip shape effects and mobile surface charges on effective domain wall width is also discussed. The contribution of electrostatic forces to piezoresponse contrast is extracted from force-distance measurements and its influence of the local hysteresis loops is estimated. Considerations regarding the polarization switching by the tip are presented. Based on the experimental observations for this and other systems the dominant role of electromechanical vs. electrostatic effects in PRI imaging mechanism is established.

#### 3:20pm DI+EL+MS-ThA5 Film-formation Mechanisms, Microstructure, and Properties of BST Thin Films Grown By MOCVD, **Y. Gao**, Pacific Northwest National Laboratory **INVITED**

A review of MOCVD BST thin films will be presented, focusing on precursor chemistry, film-formation mechanisms, and relationship between film processing, microstructure and dielectric properties. In particular, the precursor chemistry and film-formation reactions have been studied using isotopic labeling experiments (@super 18@O@sub 2@). The precursor chemistry was found to strongly depend on substrate materials. In an oxygen ambient, at least four different reaction processes involved the removal of carb on from the precursor ligands on oxide covered Pt(111). Time-of-flight secondary ion mass spectrometry reveals both M@super 18@O and M@super 16@O (M= Ba, Sr, Ti) in the BST films, indicating that the oxygen in the BST films originates from both the gas phase oxidants (@super 18@O), and the precursor ligands (@super 16@O). The ligand substitution by gas phase O@sub 2@ plays a more prominent role in the film-formation at lower temperatures. On the other hand, the reactive oxygen radicals produced by microwave plasma involved more in breaking the O-C bonds than substituting the precursor ligands for the film formation, resulting in larger surface roughness. Use of the 50%@super 18@O@sub 2@-50%N@sub 2@@super 16@O mixture results in a reduction of @super 18@O incorporation in the BST films, indicative of the direct involvement of N@sub 2@O in the film-formation reactions. The mechanistic studies are essential for understanding the BST precursor properties, and provide useful information to correlate the film microstructure, step coverage, and dielectric properties with the precursor properties. In addition, the study shows that precursor reactivities strongly affect the step coverage on the 3D structure, but little effect on the microstructure, surface morphology, and dielectric properties of the stoichiometric BST films. These properties strongly depend on the film composition, substrate material, and growth temperature.

#### 4:00pm DI+EL+MS-ThA7 Epitaxial (Ba,Sr)TiO<sub>3</sub> on MgO for Room Temperature Microwave Phase Shifters, **C.L. Chen, J. Shen, S.Y. Chen, C.W. Chu**, University of Houston; **F.W. Van Keuls, F. Miranda**, NASA Glenn Research Center; **J.C. Jiang**, Louisiana State University

Single crystalline ferroelectric Ba@sub 0.6@Sr@sub 0.4@TiO@sub 3@ thin films were epitaxially grown on (001) MgO by using pulsed laser ablation. Microstructure studies from x-ray diffraction and electron microscopy suggest that the as-grown films are c-axis oriented with their interface relationship of @sub BSTO@//@sub MO@. Edge dislocations were found through the entire interface in every 8 unit cell length. Microwave property measurements indicated that the room temperature coupled microwave phase shifter have achieved with phase shift over 200@super o@ at 23.675 GHz and a figure of Merit of about 55@super o@/dB. The room temperature dielectric constant and loss tangent were found to be 1688 and 0.008 and the tunability was 33% with 2.5V/μm. The result suggests that the performance of microwave phase shifter based on the epitaxial ferroelectric thin films on (001) MgO are closed to the practical applications in the wireless rf communications.

#### 4:20pm DI+EL+MS-ThA8 High Temperature Etch Processing for FeRAM MFM Capacitor Stack Fabrication, **L.G. Jerde, A. Cofer, R.A. Ditzio, S. Marks, J.A. Meyer, K.A. Olson, S.P. DeOrnellas**, Tegal Corporation

The unique materials utilized in FeRAM MFM capacitor stacks present numerous integrated device fabrication challenges, particularly in the patterning of these materials and the capacitor stacks that utilize them. Many of these patterning challenges are due to the intrinsic involatility of the reaction products formed when etching the elemental constituents of the FeRAM materials (i.e., Pt, Ir, Pb, Zr, Sr and Bi). These challenges have been successfully met for several years by utilizing photoresist etch masks in conjunction with the plasma etch technologies of low pressure, high density and dual frequency. While this technological approach is extendible

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for the foreseeable future of FeRAM capacitor stack definition, the intrinsic involatility of their etch reaction products has recently sparked wide spread interest in utilizing high temperature etch processes to meet the as yet undefined future requirements for these applications. Although there are benefits to this high temperature approach, there are also risks. Among these risks are a number of key considerations that must be dealt with to successfully develop and implement high temperature etch process solutions for FeRAM applications. The first set of these considerations is related to the requirement that the etch tool provides reliable wafer, as opposed to wafer chuck, temperature and temperature uniformity control. In view of the industry trend toward single mask, full stack processes, another set of considerations is the requirement that the etch tool be able to rapidly vary the wafer temperature to accommodate the optimum temperature for each of the FeRAM materials being used. Yet another set of considerations are those related to wafer temperature limitations imposed by the Perovskite structure transition temperature, device damage and thermal budget. We will discuss and illustrate these considerations and present selected high temperature etch process results for various FeRAM films and stacks.

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