

Electronic Materials and Processing Division Room 611 - Session EM2-ThA

Silicon Carbide and Dielectrics on Si

Moderator: R.M. Feenstra, Carnegie Mellon University

2:00pm EM2-ThA1 Silicon Carbide: Material of the 21st Century?, P.G. Soukiassian, Université de Paris-Sud/Orsay, France **INVITED**

Silicon carbide (SiC) is a refractory material belonging, with diamond and nitrides, to the wide band gap semiconductor class. SiC has a strong technological interest especially in high temperature, high speed, high voltage and high power semiconductor devices and sensors. Furthermore, rather inert chemically, its ability to resist to radiation damages makes SiC very suitable for hostile environments. In addition, SiC has very interesting mechanical properties and is one of the best biocompatible material. These exceptional properties are driving forces into the present fast growing interest in surfaces and interfaces of this advanced material. The surfaces and interfaces of cubic and hexagonal SiC are investigated by atom-resolved variable temperature scanning tunneling microscopy and spectroscopy and photoemission spectroscopies using synchrotron radiation. Such important issues as the atomic scale self-propagated surface oxidation and SiO₂/SiC initial interface formation will be addressed. In addition, the discovery of highly stable self-organized Si and C atomic lines having fascinating characteristics and their dynamics will also be described. The Si nanostructure number and spacing could be mediated by annealing time and temperature leading to ordering ranging from a single isolated Si atomic line to large superlattices of "massively parallel" atomic chains. One discovers also a sp² to sp³ temperature-controlled diamond-like transformation which could potentially be useful in diamond growth. All these characteristics are unprecedented and show a very novel and interesting aspect of SiC in its ability to also be a very suitable material in nanoscience. Semond, P. Soukiassian, A. Mayne, G. Dujardin, L. Douillard and C. Jausaud, Phys. Rev. Lett. 77, 2013 (1996). P. Soukiassian, F. Semond, L. Douillard, A. Mayne, G. Dujardin, L. Pizzagalli and C. Joachim, Phys. Rev. Lett. 78, 907 (1997). V. Yu. Aristov, L. Douillard, O. Fauchoux and P. Soukiassian, Phys. Rev. Lett. 79, 3700 (1997). G. Dujardin, A. Mayne, F. Semond, G. Dujardin and P. Soukiassian, Phys. Rev. B 57, Rap. Comm., R 15108 (1998). F. Semond, L. Douillard, P. Soukiassian, D. Dunham, F. Amy and S. Rivillon, Appl. Phys. Lett. 68, 2144 (1996). P. Soukiassian, F. Semond, A. Mayne and G. Dujardin, Phys. Rev. Lett. 79, 2498 (1997). V. Derycke, P. Soukiassian, A. Mayne, G. Dujardin and J. Gautier, Phys. Rev. Lett. 81, 5868 (1998).

2:40pm EM2-ThA3 Characterization of PECVD SiC and its Application in Advanced Reticle Technology-SCALPEL Membrane, S. Han, W.J. Dauksher, P.J.S. Mangat, K.D. Cummings, S.M. Smith, Motorola, Inc.

The material which forms thin membrane layer (1000Å) in Scattering with Angular Limitation Projection Electron Beam Lithography (SCALPEL) mask technology should satisfy a handful of rigid requirements such as stress controllability, high mechanical stiffness and good chemical etch resistance for wet processing. We have demonstrated that amorphous PECVD SiC can be an excellent choice of material that satisfies the criteria above. SiC potentially could be a better candidate for the membrane layer than silicon nitride, which is currently recommended. Furthermore, it has the possibility of better membrane yield and improved image placement because the elastic modulus for SiC is almost twice that for silicon nitride. Amorphous SiC films were prepared by PECVD using SiH₄ and CH₄ chemistries. The as-deposited intrinsic stress can be varied from mid-compressive to weak tensile depending on the deposition conditions. Furthermore, we have shown that the magnitude and sign of the as-deposited stress in the film can be modulated by RTA anneal cycle. Stress level in the films can be modified to our level of interest (about 1e9 dynes/cm² tensile.) In addition, the etch resistance in KOH etchant, an important criteria, is improved after the post annealing cycle. This is associated with hydrogen evolution during the annealing, which reduces the density of hydrogen bonds with C and Si. Results will include the yield impact of controlling stress on the membrane by deposition conditions or by post annealing. In addition, characterization results of films using FTIR and RBS for hydrogen bonding and atomic ratio, respectively will be included. In summary, this paper addresses comprehensive information on

a uniform, low stress PECVD SiC that can be used as a membrane material for SCALPEL mask technology.

3:00pm EM2-ThA4 Contact Properties of Cerium Ultrathin Film on SiC, W.J. Lu, D.T. Shi, T. Crenshaw, A. Burger, W.E. Collins, Fisk University

Cerium (Ce) is well known as an excellent catalyst for NO_x conversion in environmental and automobile exhaust gas control. It has a strong adsorption capability for oxygen containing gases. Ce/SiC has a great potential as a chemical sensing materials for NO_x which can be operated at high temperature. To the best of our knowledge, the electrical contact properties of Ce/SiC on SiC have not been reported. In this work, the morphology and interfacial composition of Ce ultra-thin films on 6H-SiC and 4H-SiC are investigated after thermal annealing using atomic force microscopy and X-ray photoelectron spectroscopy. The Ce ultra-thin films of about 3 nm thickness are deposited by RF sputtering. The samples are annealed at the evaluated temperatures for 30 minutes in air. The Ce ultra-thin film on 6H-SiC and 4H-SiC has a good uniformity as deposited, and there are no significant morphological changes for both samples after annealing. The Ce on SiC contact is a Schottky contact, and the Schottky barrier heights for Ce/6H-SiC and Ce/4H-SiC as deposited are 1.43 eV and 1.77 eV, respectively. The Ce film is oxidized to be a Ce oxide film after thermal annealing in air. The morphology and the interfacial compositions after annealing will be presented. Key Words: SiC, Ce, AFM, XPS, and Schottky barrier height.

3:20pm EM2-ThA5 A Thermodynamic Analysis of Silicide and Carbide Formation and Stability of W, Co, V, and Zr Thin Films on Single-Crystal SiC, W.F. Seng, M.J. Bozack, P.A. Barnes, Auburn University; S.A. Catledge, Y.K. Vohra, University of Alabama at Birmingham

Electronic devices capable of operation at elevated temperatures require understanding of the chemical reactions which occur at the metal-semiconductor interface. Phases predicted from equilibrium thermodynamics are presented in the forms of both Ellingham and Gibbs ternary diagrams to understand the temperature sequence of silicide and carbide formation and stability of the phases formed at the metal-SiC interface. W, Co, V, and Zr were deposited on single-crystal SiC by electron-beam deposition and annealed to temperatures approaching 1000 °C. Resulting phases were identified by AES, XPS, and XRD and compared to the phases predicted by thermodynamic analysis. Limitations of the thermodynamic approach are also discussed.

3:40pm EM2-ThA6 Deposition of Yttrium Oxide by Yttrium Sputter/Thermal Oxidation and Reactive Sputtering for Advanced High k Gate Dielectrics, J.J. Chambers, G.N. Parsons, North Carolina State University

The advent of 50nm MOSFET devices will require an equivalent SiO₂ thickness (t_{ox,eq}) of 10Å. Direct tunneling through SiO₂ becomes problematic below about 15Å. To maintain low tunneling, the gate thickness must be >15Å, which requires an insulator with k>3.9. We form yttrium oxide on Si by: 1) yttrium sputtering followed by thermal oxidation; and 2) reactive sputtering of yttrium. Conditions for the sputter/thermal oxidation process were yttrium sputter in 4.3mTorr Ar at 25°C then ex-situ furnace oxidation in 1 atm N₂/O₂ at 900°C. Conditions for reactive sputtering of yttrium were 4.3mTorr, 25-500°C and an Ar/N₂/O₂ flow ratio of 0.5. Infrared absorption peaks from 400-600cm⁻¹ are present in the FTIR transmission spectra of the sputter/thermal oxidation and reactive sputtered films. These peaks are consistent with the 467, 562 and 698cm⁻¹ absorption peaks present in the spectrum of a 99.9% pure Y₂O₃ standard. CV and IV electrical measurements have been performed on films from both processes. Leakage current at 2V of 0.1μA/cm² has been measured for sputter/thermal oxidation (t_{ox,eq}=50Å) and reactive sputtered (t_{ox,eq}=100Å) films. Using optical thickness measured with spectroscopic ellipsometry, effective dielectric constants are approximately 8.0 for films from both processes. Bulk Y₂O₃ has k=14-17, which suggests that the films described here have a reduced k in their thin film form, some yttrium silicate formation and/or an underlying SiO₂ layer. Under some deposition conditions, inert gas annealing increased inversion capacitance in the CV trace, possibly due to interfacial silicide formation. We will discuss the affects of pre-deposition N₂ and N₂/O₂ plasma surface treatments on the electrical properties of these films. The chemical and structural changes upon annealing will be investigated using XPS, AFM and RHEED.

Thursday Afternoon, October 28, 1999

4:00pm **EM2-ThA7 Bi@sub 4@Ti@sub 3@O@sub 12@ Ferroelectric Thin Films Deposited on Silicon by Pulse Injection Metal-Organic Chemical Vapor Deposition**, S.K. Lee, H.J. Kim, Seoul National University, Korea

Bi@sub 4@Ti@sub 3@O@sub 12@ is one of the well-known bismuth-based layered perovskite materials. This compound has attracted much attention because of its characteristic anisotropic property. Especially, the low coercive field along c-axis, about 3.5 kV/cm, has made Bi@sub 4@Ti@sub 3@O@sub 12@ thin film a very promising gate dielectric for a ferroelectric field effect memory device. For this application, ferroelectric thin film has to be fabricated at low temperature in order to keep the abrupt interface with the semiconductor substrate and the composition of the film has to be uniform. By these requirements, metal-organic chemical vapor deposition (MOCVD) was taken as the fabrication method of Bi@sub 4@Ti@sub 3@O@sub 12@ thin film on p-type (100) silicon substrate. Solid Bi(C@sub 6@H@sub 5@)@sub 3@ and liquid Ti(OC@sub 3@H@sub 7@)@sub 4@ were chosen as precursors of bismuth and titanium, respectively, because of their good stability and complete decomposition ability. However, the great difference in formation kinetics of TiO@sub 2@ and Bi@sub 2@O@sub 3@ made it very difficult to control the Bi@sub 4@Ti@sub 3@O@sub 12@ /Si interface and the film composition. In order to overcome this problem, pulse injection method was introduced, in which input precursors were varied periodically during deposition for compensating the lower reactivity of Bi(C@sub 6@H@sub 5@)@sub 3@ with oxygen. By this pulse injection method, abrupt Bi@sub 4@Ti@sub 3@O@sub 12@ /Si interface was attained and the composition of Bi@sub 4@Ti@sub 3@O@sub 12@ thin film was also very uniform. The properties of Bi@sub 4@Ti@sub 3@O@sub 12@ thin films were strongly dependent on the substrate temperature and pulse injection conditions.

4:20pm **EM2-ThA8 Film-Formation Mechanisms and Step Coverage of (Ba,Sr)TiO@sub 3@ Films Grown by MOCVD**, Y. Gao, T.T. Tran, S. Thevuthasan, M.H. Engelhard, Pacific Northwest National Laboratory; P. Alluri, Motorola, Inc.

Isotopic labeling experiments (@super 18@O@sub 2@) have been carried out to understand the film-formation reactions in the MOCVD growth of (Ba,Sr)TiO@sub 3@ (BST) thin films using Ba(thd)@sub 2@, Sr(thd)@sub 2@, and Ti(O-iPr)@sub 2@(thd)@sub 2@ as the metalorganic precursors. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) 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 amount of @super 18@O and @super 16@O in these films was also determined by nuclear reaction analysis (NRA). The results are in agreement with the TOF-SIMS data. Thus, the isotopic labeling study reveals two film-formation reactions: oxidation and thermal decomposition of the precursor molecules during the MOCVD growth. The results show that about two thirds of M-O bonds in the original precursors are preserved in the BST films grown at 650 °C in O@sub 2@. However, more precursor molecules are oxidized by O@sub 2@ at 590 °C, indicating that the ligand substitution by O@sub 2@ plays an important role in the film-formation at lower temperatures. Use of a 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 film, indicative direct involvement of N@sub 2@O in the film-formation reactions. Addition of N@sub 2@O in O@sub 2@ also appears to improve film surface morphology and step coverage. The BST films deposited at 650 °C in the 50%O@sub 2@-50%N@sub 2@O mixture exhibit conformal step coverage, excellent crystallinity, and good dielectric properties. The correlation between the film-formation mechanisms, step coverage, crystallinity, and dielectric properties will be discussed in this presentation.

4:40pm **EM2-ThA9 Anhydrous Zirconium (IV) Nitrate as a CVD Precursor for ZrO@sub 2@**, R. Smith, N. Hoelien, C. Taylor, T. Ma, S. Campbell, W.L. Gladfelter, J.T. Roberts, University of Minnesota; M. Copel, D.A. Buchanan, IBM T.J. Watson Research Center; M. Gribelyuk, IBM

We report the chemical vapor deposition (CVD) of ZrO@sub 2@ from the anhydrous metal nitrate, zirconium (IV) nitrate [Zr(NO@sub 3@)@sub 4@]. Zirconia films were deposited onto 100-oriented Si substrates using thermal CVD methods. Measurements of the ZrO@sub 2@ growth kinetics imply an exceedingly low barrier for ZrO@sub 2@ nucleation on a Si(100) surface, as there was essentially no induction period between the onset of CVD and the achievement of steady-state growth. The films were extensively characterized with respect to their suitability as high dielectric constant materials in advanced microelectronic devices. Ion beam methods (Rutherford backscattering, RBS, and medium energy ion scattering spectroscopy, MEIS) suggested that the films were close to the ideal

stoichiometry or slightly oxygen-rich. X-Ray diffraction established that most films were monoclinic ZrO@sub 2@. Cross-sectional transmission electron microscopy (TEM) and MEIS measurements showed that the Si-ZrO@sub 2@ interface consists of a 10-15Å thick interlayer of nearly pure SiO@sub 2@. Finally, electrical characterization measurements established low leakage current densities across the Si-ZrO@sub 2@ interface. This study adds to a growing body of work on the usefulness of volatile, anhydrous metal nitrates as precursors for high electrical quality metal oxide materials.

5:00pm **EM2-ThA10 A New Approach for the Fabrication of Device-Quality Ge/GeO@sub 2@/SiO@sub 2@ Interfaces Using Low Temperature Remote Plasma Processing**, R.S. Johnson, H. Niimi, G. Lucovsky, North Carolina State University

It has been shown that low temperature (300°C) remote plasma enhanced processing can separately and independently control interface formation and bulk oxide deposition on silicon substrates. Plasma processing is followed by a low thermal budget thermal anneal, e.g., 30 s at 900°C. This process has been used for the formation of the device-quality gate dielectrics in both NMOS and PMOS devices. In the new results reported in this paper, this process has been modified and applied to germanium substrates to determine if it can provide a successful pathway to device-quality Ge-dielectric interfaces. The new process is similar low temperature (300°C) three-step process consisting of (i) an O@sub 2@/He plasma-assisted oxidation of the Ge surface to form a superficial germanium-oxide passivating film, (ii) deposition of a SiO@sub 2@ bulk film by remote plasma-enhanced CVD from SiH@sub 4@ and O@sub 2@, and (iii) a post-oxide deposition anneal for chemical and structural relaxation. We track the initial stages of the plasma-assisted oxidation of the germanium substrate using on-line Auger Electron Spectroscopy (AES). We then discuss why the O@sub 2@ /He plasma oxidation is critical for prevention of "subcutaneous" oxidation of GeO@sub 2@ -Ge interface during the deposition step. As in the case of Si devices, the oxidation step is required for formation of a device quality interface.

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