

Monday Afternoon, October 19, 2015

Electronic Materials and Processing

Room: 210E - Session EM+NS+PS-MoA

More Moore! II

Moderator: Christopher Hinkle, University of Texas at Dallas, Andrew C. Kummel, University of California at San Diego

2:20pm **EM+NS+PS-MoA1 Effect of Ex Situ and In Situ Surface Cleaning on the Quality of Al₂O₃-SiGe(001) Interfaces.** *K. Sardashti, Kai-Ting Hu*, UC San Diego, *S. Madiseti*, College of Nanoscale Science and Engineering, Albany-SUNY, *K. Tang*, Stanford University, *S. Oktyabrsky*, College of Nanoscale Science and Engineering, Albany-SUNY, *P.C. McIntyre*, Stanford University, *S. Siddiqui*, B. GeOx, Globalfoundries, *N. Yoshida*, *J. Kachian*, Applied Materials Inc., *A.C. Kummel*, UC San Diego

Silicon-Germanium has shown a great promise for future CMOS technology by combining the high hole and electron mobility of Ge with the ability to have both tensile and compressive strain by fabrication of alloys of higher and lower Ge content. In contrast to Si, SiGe native oxide is a combination of SiO₂ and GeO₂, SiGeOx, which has low interface quality and stability in comparison with SiO₂ due to the presence of the GeOx. Therefore, instead of thermal oxide growth, it is necessary to employ atomic layer deposition (ALD) for gate oxide deposition in SiGe MOS devices. The effects of the ex-situ wet chemical clean (such as HF and (NH₄)₂S dip) and in-situ NH₃ plasma clean prior to ALD, were determined on Al₂O₃/SiGe; interface quality quantified by oxide leakage, interfacial trap density, and near-interface trap density. MOS capacitors fabricated by Al₂O₃ ALD at 120°C. Compared to HF clean, both ex-situ (NH₄)₂S clean and in-situ NH₃ plasma resulted in smaller density of interface and smaller leakage current in accumulation. Furthermore, both methods resulted in high surface stability in air; queue times up to an hour could be tolerated. Angle-resolved X-ray photoelectron spectroscopy (AR-XPS) measurements on SiGe(001) with 0.8nm thick Al₂O₃ showed that (NH₄)₂S clean significantly reduces the amount of GeOx at the in Al₂O₃/SiGe(001) interface, compared to HF clean.

2:40pm **EM+NS+PS-MoA2 Surface Passivation for ALD-Al₂O₃/SiGe MOS Devices.** *Liangliang Zhang*, Stanford University, *V. Hassan*, *C. Lo*, *C. Olsen*, *M.A. Foad*, Applied Materials Inc., *P.C. McIntyre*, Stanford University

We report a study of passivation of the SiGe surface, a critical challenge for future SiGe MOSFET technology. Epitaxially grown p-type SiGe films on lightly doped Si substrates are investigated. The layered surface structures of native oxide coated, as-received SiGe samples are characterized using soft x-ray synchrotron photoemission electron spectroscopy (PES). It is observed that the surface of as-received SiGe wafers have a mixed SiO_x/GeO_x oxide layer. Angle-resolved PES shows that this layer is SiO_x-rich at the top surface and GeO_x-rich below. Lab source x-ray photoelectron spectroscopy (XPS), hard x-ray PES and x-ray reflectivity (XRR) are used to characterize the interface region between atomic layer deposited (ALD) Al₂O₃ gate dielectrics and SiGe. Prior to ALD, 2% HF(aq) solution is used to remove the surface oxides, and a high quality Al₂O₃ layer on the SiGe substrate is deposited with the help of efficient sites for Al(CH₃)₃ (TMA) precursor adsorption produced by H₂O oxidant pre-dosing of the SiGe surface immediately prior to the TMA/H₂O ALD process. It is observed from XPS and PES that there is an increase of the SiO_x peak intensity after Al₂O₃ deposition, while there is little or no detectable Ge core level feature associated with GeO_x. The thermodynamic preference of Si (compared to Ge) atoms bonding to oxygen agrees well with the identity of the layered oxide structures extracted by fitting measured XRR data from the processed samples.

Both Pt, a metal that is a known catalyst for H₂ dissociation, and Al are investigated as gate metals for ALD-Al₂O₃/SiGe MOS capacitors (MOSCAPs) subjected to post metal forming gas (5% H₂/95% N₂) anneal (FGA). The effects of the identity of the gate metal on post-FGA interfacial oxide composition and interface trap response is studied. Capacitance-voltage analysis of Al/Al₂O₃/p-SiGe MOSCAPs detects minimal frequency dispersion in depletion and accumulation. The extracted density of interface traps is peaked near the valence band, with a maximum value of ~ 3x10¹¹ (eV⁻¹cm⁻²).

3:00pm **EM+NS+PS-MoA3 Harnessing Chemistry to deliver Materials and Process for the Next 10 Years of CMOS Evolution.** *Robert Clark*, TEL Technology Center, America, LLC **INVITED**
Harnessing Chemistry to Deliver Materials and Processes for the Next 10 Years of CMOS Evolution

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The continued scaling of the Integrated Circuits (ICs) according to Moore's law has led to a doubling of the number of devices per unit area in semiconductor microchips approximately every 2 years since 1962. Over the past decade traditional scaling by simple linear shrinking has effectively ceased as IC makers have adopted new 3-dimensional device structures, complex integration schemes and new processes and materials for an expanding number of applications in order to overcome fundamental physical limits. In order to continue Moore's law in the coming decade this trend will not only continue, but intensify as devices are scaled to a level approaching atomic dimensions. Broadly speaking, two major trends are influencing the development of future IC manufacturing processes: the need to harness the third dimension to extend Moore's law; and the need for "self-something" processes. "Self-something" processes refers to processes or schemes that are directed chemically to attain a desired result and includes processes that are self-limited (e.g. ALD or ALE), self-directed (e.g. directed self-assembly or selective deposition), or self-aligned (e.g. self-aligned contacts) in some way that enables device density scaling. "Self-something" processes are required in order to harness the third dimension and make use of new non-planar device architectures (e.g. FinFETs and DRAM capacitors), device arrays/stacking (e.g. 3D NAND and cross-point memory), and 3D integration (e.g. monolithic 3D, and chip stacking). Highly tailored ALD processes are being investigated to fabricate functional material layers. Interspersed treatments and doping may be used to modify the physical and electrical properties of ALD films further in order to optimize the resulting physical or electrical properties. To improve device contacts, ultra-thin dielectric and metal layers may be deposited inside of high aspect ratio contact structures in order to provide lower contact resistivity. Selective deposition processes can be used to deposit functional materials only where they are needed, thus reducing the patterning burden during IC manufacturing. Depositing dopant layers by ALD for thermal solid source doping can be used to conformally dope 3-D device structures without the damage caused by implantation. Examples of these and similar processes will be described and discussed along with the chemical processes and transformations governing film deposition, composition, structure, and interface control.

3:40pm **EM+NS+PS-MoA5 Materials Selection for Oxide-based Resistive Random Access Memory (RRAM).** *John Robertson*, *Y. Guo*, Cambridge University, United Kingdom of Great Britain and Northern Ireland **INVITED**

Resistive random access memory (RRAM) is a main challenger non-volatile memory technology to Flash memory. The favored materials are based on the formation of a conductive filament of oxygen vacancies across a film of a wide gap oxide. However, a wide range of material systems are presently being studied, which use various different switching mechanisms. Materials selection requires us to understand which material properties control each aspect of device performance, such as switching speed, resistance window, retention time and endurance. Here, the energies of various atomic processes in resistive random access memories (RRAM) are calculated for four typical oxides, HfO₂, TiO₂, Ta₂O₅ and Al₂O₃, to define a materials selection process. Oxygen vacancies have the lowest defect formation energy in the O-poor limit, and to dominate the processes. A band diagram defines the operating ranges of Fermi energy and O chemical potential. It is shown how scavenger metals can be used to vary the O chemical potential and thus vary the O vacancy formation energy. The high stability of amorphous phase of Ta₂O₅ is relevant to the high endurance of its RRAM.

4:20pm **EM+NS+PS-MoA7 Lower Temperature Silicon Nitride ALD on Si_{0.5}Ge_{0.5}(110) with No Solid By-product Formation**, Steven Wolf, M. Edmonds, T. Kent, University of California at San Diego, D. Alvarez, RASIRC, R. Droopad, Texas State University, A.C. Kummel, University of California at San Diego

A silicon nitride passivation layer on semiconductor surfaces can serve several practical uses, such as acting as a diffusion barrier or channel passivation layer prior to dielectric deposition in FinFets or MOSFETs. When employed as a channel passivation layer, further reaction with an oxidant, such as anhydrous peroxide, can leave Si-N-OH termination, which is reactive with all metal ALD precursors thereby providing high nucleation density. Previous studies show stoichiometric ALD Si₃N₄ growth on Si(100) by hydrazine and Si₂Cl₆ at temperatures in excess of 350°C with solid ammonium chloride by-product formation¹. The first half reaction of N₂H₄ leaves N-H_x surface termination, and the second reaction with Si₂Cl₆ adds silicon to the surface and creates a gaseous HCl by-product. An ammonium chloride by-product is usually caused by wall reactions of unreacted precursors. This study focuses on developing a low temperature silicon nitride ALD process with no unwanted solid by-product formation. STM/STS and XPS are employed to characterize SiN_x film growth on Si_{0.5}Ge_{0.5}(110).

A test chamber consisting of a reactor chamber, dosing lines, and a dry pump was created and heated to 125°C for 12 hours to allow for sufficient heating of all stainless steel components. In excess of 100 ALD cycles were ran in the test chamber with no visible evidence of powder formation on any walls, and it was concluded that this lengthy heating process prior to SiN_x ALD is necessary to eliminate the unwanted powder by-product formation. Next, at a substrate temperature of 275°C and wall temperature of 20°C, the silicon nitride ALD procedure was performed on a p-type Si_{0.5}Ge_{0.5}(110) surface that underwent an ex-situ wet organic clean followed by a dip into a 2% HF/water solution with a toluene layer on top. The sample was pulled through toluene and loaded into UHV as quickly as possible to minimize native oxide formation. After a 315 MegaLangmuir anhydrous hydrazine dose, XPS shows N-H_x surface termination, and removal of half of the initial carbon contamination. A subsequent 21 MegaLangmuir Si₂Cl₆ dose followed by 17 cycles of 3 MegaLangmuir hydrazine and 3 MegaLangmuir Si₂Cl₆ leads to increased silicon nitride growth as shown by a large increase in XPS Si 2p and N 1s peaks, as well as a decrease in the Ge 3d substrate peak. After the ALD cycling with room temperature walls, a white powder, presumed to be ammonium chloride, was seen in the reactor, but will now be avoided using the 125°C wall temperature.

1. S. Morishita *et al.*, Appl. Surf. Sci., **112**, p:198-204 (1997).

4:40pm **EM+NS+PS-MoA8 Novel Delivery of Unstable Precursors for Atomic Layer Deposition**, Daniel Alvarez, J. Spiegelman, E. Heinlein, R. Holmes, C. Ramos, S. Webb, K. Johnson, RASIRC

A considerable amount of effort has gone into the development of novel metal precursors for Atomic Layer Deposition (ALD). This is primarily driven by the need for new high *K* materials and metals films. Largely ignored has been the need for novel oxidants and sources of nitrogen. This paper focuses on the delivery of anhydrous hydrogen peroxide and anhydrous hydrazine for ALD applications.

Hydrogen Peroxide (H₂O₂) in aqueous form is commonly used in semiconductor manufacturing for cleaning and surface preparation operations. Thirty percent and fifty percent two-component mixtures have been investigated in a few ALD studies with moderate success. Especially noteworthy are Kummel's findings that the use of hydrogen peroxide leads to a 3x increase in nucleation density on Ge versus water. However, H₂O₂ has limited general utility in aqueous form due to the volatility of water. At 30°C, Raoult's law predicts a headspace concentration of 294ppm H₂O₂ and 32373ppm for water, where the H₂O/H₂O₂ ratio is over 100. Clearly these are not optimal conditions for hydrogen peroxide ALD. However, in its pure state, hydrogen peroxide is highly unstable and has a propensity to decompose, forming water and oxygen. Our approach entails the use of a membrane delivery system where 99.6% hydrogen peroxide is dissolved in an organic solvent. Hydrogen peroxide permeates the membrane and is delivered to the ALD chamber, while the solvent does not permeate and remains in the liquid state. In this way, concentrations much higher than predicted by Raoult's law for aqueous mixtures are delivered to the process chamber in the absence of water.

Next generation devices have low thermal budgets and high aspect ratio structures that create new challenges for ALD grown nitride films. The use of ammonia is limited due to temperature constraints. Known Plasma methods cannot uniformly coat the side walls of the device structures and create surface damage. Hydrazine (H₂NNH₂) has been proposed as a thermal ALD low temperature nitride source. Hydrazine is highly flammable and its flash point decreases with reduced water content. In an analogous approach, we have developed a new method and formulation for the delivery of anhydrous Hydrazine by the use of an inert organic solvent and

membrane delivery system. Precursor vapor pressure is maintained at levels viable for ALD. Moreover, the addition of a high boiling solvent lowers the risk of explosion by raising the solution flash point.

Preliminary ALD data will be presented showing unique properties of these new precursors along with theoretical data on precursor delivery under variable ALD conditions.

5:00pm **EM+NS+PS-MoA9 Passivation and Functionalization of SiGe(001) and (110) for ALD Nucleation in FinFET Structure**, SangWook Park, H. Kim, University of California at San Diego, B. Sahu, S. Siddiqui, GLOBALFOUNDRIES U.S. Inc., N. Yoshida, A. Brandt, Applied Materials, Inc., E. Chagarov, A.C. Kummel, University of California at San Diego

Silicon Germanium (SiGe) is a promising candidate for FinFET channels, sources, and drains due to its high mobility and utility in strain engineering. Since FinFETs are composed of three-dimensional structures utilizing multiple crystalline planes, the cleaning and passivation must provide uniform and clean surfaces in each plane to combine high mobility with low interface trap density (Dit). In this study, passivation and functionalization of SiGe(001) and (110) surfaces are discussed, using scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and x-ray photoelectron spectroscopy (XPS).

The SiGe(001) is dimer terminated while the SiGe(110) is dimer-free leading to differences in surface stoichiometry and order. STM and XPS measurements indicate that clean (001) is mostly terminated with Ge atoms with a uniform and well-ordered structure while (110) is terminated with adatoms of both Si and Ge atoms and lower surface order. STS measurements indicate the clean (001) surface is unpinned while the clean (110) surface is pinned mid gap between the valence and conduction band edge due to adatom dangling bonds. The sputter cleaned SiGe(110) surface was dosed at 300°C with 3,600L dose of atomic H to passivate the dangling bonds of the adatoms. STS measurements demonstrate the atomic H dosed (110) surface is unpinned with a Fermi level near the valence band due to Si-H and Ge-H bonds on adatoms. The unpinned SiGe (001) and (110) surfaces were dosed at room temperature with a saturation dose of H₂O₂(g) leaving the SiGe surface terminated with an ordered monolayer of only Ge-OH sites on (001) and both of Ge-OH and Si-OH sites on (110). STS shows that on the HOOH dosed SiGe(001) and (110), the Fermi level is shifted to near the valence band edge due to the large surface dipole from the hydroxyl bonds. TMA was subsequently dosed on the HOOH/SiGe(001) and HOOH/atomic H/SiGe(110) surfaces forming an ordered monolayer of Al-O-Si bonds. In order to understand the thermal stability of the TMA dosed SiGe surfaces, the surface was annealed to 300°C and XPS measurements verify that Al-O bonds are totally transferred from Ge atoms to Si atoms forming Al-O-Si bonds on both (001) and (110) indicating that the strong affinity between Si and oxygen is pulling Si atoms toward the surface to bond with oxygen or hydroxyls while pushing Ge atoms into the subsurface during the annealing. STS indicates this unpins the Fermi level on both surfaces, leaving an electrically passive ordered layer which serves as an ideal template for further high-k ALD.

5:20pm **EM+NS+PS-MoA10 Band Structure and Critical Points of Pseudomorphic Ge_{1-y}Sn_y Alloys on Ge**, Nalin Fernando, T.N. Nunley, S. Zollner, New Mexico State University, D. Zhang, R. Hickey, J. Kolodzey, University of Delaware

We calculate the dependence on composition and strain of the band structure of Ge_{1-y}Sn_y alloys grown pseudomorphically on Ge and compare with spectroscopic ellipsometry measurements. Germanium is an indirect band gap material with limited optoelectronic applications. Because the band structure of Ge is a strong function of strain, a transition from an indirect to a direct band gap has been found for Ge under a tensile strain, which constrains the layer thickness and the composition of the substrate for heterostructure growth. Indirect to direct band gap crossover of unstrained Ge_{1-y}Sn_y has been reported for y~6-10% indicating the possibility of widespread applications of Ge-based photonic devices and paving the way for the design of Ge_{1-y}Sn_y lasers. Hence it is important to study the compositional dependence of the Ge_{1-y}Sn_y band structure through measurements of the optical properties of Ge_{1-y}Sn_y alloys. The complex pseudodielectric functions of pseudomorphic Ge_{1-y}Sn_y alloys grown on Ge by MBE were measured using spectroscopic ellipsometry at 300 K in the 0.76-6.6 eV energy range for Sn contents up to 11%. Dielectric functions of Ge_{1-y}Sn_y alloys were obtained to investigate the compositional dependence of the E₁ and E₁+Δ₁ critical point (CP) energies. CP energies and related parameters were obtained by analyzing the second-derivative of the dielectric function. Our experimental results are in good agreement with the theoretically predicted E₁ and E₁+Δ₁ CP energies of compressively strained Ge_{1-y}Sn_y on Ge based on deformation potential theory. We will discuss the compositional and strain dependence of the direct and indirect band gaps as well as E₁ and E₁+Δ₁ CP energies and related parameters of Ge_{1-y}Sn_y alloys. We will present the nature of the band gap of pseudomorphic Ge_{1-y}Sn_y on

Ge and will discuss the effects of strain which critically depend on the bowing parameter of the lattice constant.

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