## Materials Characterization in the Semiconductor Industry Focus Topic
## Room: 313 - Session MC+AP+AS-MoM

### Characterization of 3D Structures, 2D films and Interconnects

**Moderator:** Paul Ronsheim, CTO, PAR Technical Consulting, previously with IBM, Paul van der Heide, GLOBALFOUNDRIES, NY, USA

8:20am **MC+AP+AS-MoM1 Dopant/Carrier and Compositional Profiling for 3D-Structures and Confined Volumes.**, ***Wilfried Vandervorst***, *A. Kumar, J. Demeulemeester, A. Franquet, P. Eyben, J. Bogdanowicz, M. Mannarino, A. Kambham, U. Celano*, IMEC, KU Leuven Belgium **INVITED**

The introduction of three-dimensional devices (FinFets, TFETs and nanowires), has created as new metrology challenges the characterization of dopant /carrier and impurity distributions in 3D-devices and confined volumes. Beyond these dimensional challenges, the use of alternative materials such SiGe, Ge, GeSn alloys as well as III-V materials, adds to the metrology requirements. Recent evolution towards growth (and strain relaxation) mediated by the confined volume (for instance relying on aspect ratio trapping) calls for metrology suited for very small volumes and more atomic scale observations. Metrology in 3D-structures and confined volumes has demonstrated that the changing surface/volume ratios in confined devices versus blanket films lead to phenomena (dopant deactivation, enhanced diffusion,..) which cannot be observed in blanket experiments. Hence more emphasis should be placed on the analysis of device and structures with relevant dimensions relative to the exploration of blanket experiments.

Atomprobe tomography is able to provide composition analysis within very small volumes (a few nm3) with high sensitivity and accuracy and excellent spatial resolution. Hence this enables to observe dopant atom migration in 3D-devices, and through some data mining analysis, even cluster formation as precursor to strain relaxation such as seen in metastable alloys like GeSn. Field Ion Microscopy, a complement to APT, can be used to image impurity atoms clustered around defects within the crystal. Routine application of APT is still hampered by localization problems, reconstruction artifacts due to inhomogeneous evaporation, local magnification effects, sensitivity due to the limited statistics, laser-tip interaction phenomena, etc.

Although scanning spreading resistance microscopy is inherently 2D, analysis of 3D-devices (FinFet, ReRam, Sonos..) is possible by novel approaches such as SPM scalping. The introduction of novel modes such as soft retrace, FFT-SSRM has led of improved resolution and eliminates series resistances resulting from the current confinement in these narrow devices, decoupling the actual "spreading resistance" from the total resistance. Finally SSRM-carrier distribution have been coupled to device simulators leading to an accurate prediction of device performance.

In addition to APT we also present here the concept of "self focusing SIMS" whereby we demonstrate that it is possible to determine, for instance, the SiGe(III-V) composition in trenches as small as 20 nm without having an ion beam with nm-resolution. This represents a significant step forward in terms of production control and statistical relevance.

9:00am **MC+AP+AS-MoM3 Characterization of the Periodicity (Pitch) and Stress of Transistor Fin Structures using X-Ray Diffraction Reciprocal Space Mapping**, ***Alain Diebold***, *M. Medikonda,* SUNY College of Nanoscale Science and Engineering, *M. Wormington*, Jordan Valley Semiconductors Inc

Cleanroom compatible, high resolution X-Ray diffraction systems are now capable of measuring the average pitch and critical dimensions of ordered arrays of fins and the stress state of high mobility layers at the top of the fins. Reciprocal Space Mapping (RSM) characterizes both the main Bragg diffraction peak and the satellite peaks associated with the fin periodicity. The periodicity of the fin arrays has decreased to the point where the fin array adds satellite diffraction peaks to the main Bragg diffraction peak from the semiconductor. The pitch can be calculated from the angular spacing of the satellite peaks. State of the art lithographic processing using the spacer patterning process often results in a different spacing between every other fin. This is known as pitch walking. Pitch walking is very difficult to observed, even using TEM cross-sectional images. The stress state of the high mobility epilayers such as Si$_{1-x}$Ge$_x$ on Si fins can also be characterized using RSMs. In addition, some of the higher order satellite peaks will split when the fins have a near rectangular shape. This presentation compares the capability of cleanroom and synchrotron based XRD systems for reciprocal space mapping of Si and Si$_{1-x}$Ge$_x$ / Si transistor fins arrays.[1]

[1] Measurement of Periodicity and Strain in Arrays of Single Crystal Silicon and Pseudomorphic Si$_{1-x}$Ge$_x$/Si Fin Structures using X-ray Reciprocal Space Maps, M. Medikonda, G. Muthinti, J. Fronheiser, V. Kamineni, M. Wormington, K. Matney, T. Adam, E. Karapetrovaand A.C. Diebold, J. Vac. Sci. Technol**. B32**, (2014), 021804.

9:20am **MC+AP+AS-MoM4 MBE Grading Techniques for the Growth of InAsSb Films with Inherent Properties Unaffected by Strain**, ***Wendy Sarney****, S.P. Svensson,* US Army Research Laboratory*, Y. Lin, D. Wang, L. Shterengas, D. Donetsky, G. Belenky*, Stony Brook University

By using compositionally graded buffer layers, InAsSb can be grown by molecular beam epitaxy with its inherent lattice properties across the entire composition range. This direct bandgap, III-V alloy is of great interest for infrared detector applications, as it can cover both the mid (3-5 µm) and long wavelength (8-12 µm) bands. The direct bandgap provides the high quantum efficiency that allows it to directly compete with HgCdTe but at potentially much reduced fabrication costs. InAsSb was sidelined for decades, because conventional wisdom indicated its bandgap bowing parameter would not allow it to reach the needed 10-12 µm benchmark. The material was further maligned because it was thought to exhibit CuPt ordering, which affects the bandgap. By revisiting the growth techniques we have determined that the bandgap bowing parameter of InAsSb is more than sufficient for LWIR applications and it can be grown free of ordering, provided that the material is grown with its inherent, undistorted lattice constant.

As there is no perfect substrate available for the InAsSb compositions of interest (typically containing ~40-50% Sb), we grow the films on compositionally graded buffer layers on GaSb substrates. The buffer layers consist of AlGaInSb, GaInSb, or InAsSb grades based on the theories described by J. Tersoff.[1] In this paper we provide experimental verification of Tersoff's theories applied to ternary and quaternary grades, and for both tensile and compressive grades. Furthermore, the specific parameters calculated by Tersoff, such as the boundary for the dislocation-free region (Zc) is exactly verified by transmission electron microscopy (TEM).

Reciprocal space maps show that the InAsSb layers grown on compositional graded buffer layers have their native lattice constant. The films are free from strain-relieving dislocations within the field of view allowed by TEM. Furthermore, we see no evidence of group V ordering for films grown in this manner. Although ordering is known to further reduce the bandgap, it is a difficult property to control, and it would be very undesirable to rely on it to induce the needed longer wavelengths. We have observed that a finite amount of residual strain that is small enough not to cause dislocation formation can induce CuPt ordering, but this can be completely avoided by using appropriate grading techniques. We also see no evidence of phase segregation or miscibility gaps.

Photoluminescence wavelengths have been measured for numerous InAsSb films, with a maximum wavelength to date of 12.4 µm. This may be the ideal material for direct bandgap infrared device applications.

J. Tersoff, Appl. Phys. Lett. 62, 693 (1993);

9:40am **MC+AP+AS-MoM5 Quantitative 3-D Imaging of Filaments in Hybrid Resistive Memory Devices by Combined XPS and ToF-SIMS Spectroscopies**, *Y. Busby,* ***Jean-Jacques Pireaux***, University of Namur, Belgium

Resistive switching has been observed in a multitude of inorganic (oxides, chalcogenides...) and hybrid (organic or polymers plus metal nanoparticles) thin films simply sandwiched between two metal electrodes. Organic memory devices are particularly promising candidates for developing large scale, high density, cost efficient, non-volatile resistive memories. Their switching mechanism has been for a long time suggested to depend on the formation/rupture of localized conducting paths (filaments). Using electrical characterization by impedance spectroscopy, filament formation has been experimentally demonstrated to be the dominant switching mechanism in many organic memories, only very recently (2014). Otherwise, despite of very dedicated efforts, few experimental techniques have so far succeeded in characterizing and providing information on filament(s).

The present work combines for the first time High Resolution X-Ray induced Photoelectron Spectroscopy (for its quantitative information capability) and Time-of-Flight Secondary Ion Mass Spectrometry (for its very high atomic sensitivity and 3D imaging capabilities) to quantitatively study both lateral and in depth elements distribution in a complete and operative organic memory device: what happens to be top electrode metal diffusion and filament formation is evidenced and quantitatively evaluated in memory devices which are based on a highly insulating and *cross-linked polystyrene layer*, processed by plasma polymerization, sandwiched between silver and indium tin oxide electrodes. Depth profiles evidence the metal diffusion in pristine and electrically addressed memory elements through the whole organic layer where the silver concentration can reach value as high as 5.10$^{19}$ at/cm$^{3}$. Filament formation is shown to be initiated during the top electrode evaporation, and is then successively enhanced by field induced diffusion during the electrical addressing. The 3-D ToF-SIMS images evidenced the formation of metallic paths extending through the entire device depth, electrically bridging the two electrodes when the element is in its low resistance state. Filaments with different characteristics have also been studied in organic memories based on a semiconducting polymer (Polyera N1400 ActiveInk) or on semiconducting small molecules (Tris-(8-hydroxyquinoline)aluminum, AlQ$_3$). It appears therefore that metallic filaments are indeed at the origin of switching in organic memory devices.

### 10:00am **MC+AP+AS-MoM6 High Throughput Electron Diffraction-Based Metrology of Nanocrystalline Materials**

*X. Liu,* Carnegie Mellon University*, D. Choi,* Korea Railroad Research Institute, Republic of Korea*, N.T. Nuhfer,* Carnegie Mellon University*, D.L. Yates, T. Sun,* University of Central Florida*, G.S. Rohrer,* Carnegie Mellon University*, K.R. Coffey,* University of Central Florida*,* ***Katayun Barmak***, Columbia University

The resistivity of Cu, the current interconnect material of choice, increases dramatically as the conductor's dimensions decrease towards and below the mean free path of electrons (39 nm at the room temperature). Two scattering mechanisms that contribute to this resistivity size effect are surface scattering, evidenced by thickness dependence of resistivity, and grain boundary scattering, evidenced by grain size dependence of resistivity. Quantification of microstructural parameters, such as grain size, at the scale of the resistivity size effect necessitates the use of transmission electron microscopy (TEM). In this work, an electron diffraction-based orientation mapping system installed on the TEM is used to characterize not only nanometric Cu films, but also new materials, W, Ni, Ru and Co, that are potential candidates to replace Cu as the next-generation interconnect material. In this characterization technique, spot diffraction patterns are collected as the nano-sized beam scans the area of interest. The crystallographic orientation of each scanned pixel is determined by cross-correlation with pre-calculated diffraction patterns (termed, templates). Precession is used to reduce the dynamical scattering effects, increasing the reliability of the orientation mapping. The raw orientation data is then processed to yield the microstructural data via a well-defined procedure developed to parallel that used to process electron backscatter orientation data taken in scanning electron microscopes. This characterization yields full range of microstructural parameters including grain size, grain size distribution, orientation distribution, misorientation distribution, grain boundary and interface character and plane distribution that are extracted from the crystal orientation maps in a nearly fully-automated manner. These microstructural parameters, along with sample thicknesses, are used to evaluate the validity of the semiclassical resistivity size models for Cu and the new materials, and, where applicable, to determine the relative contributions of surface and grain boundary scattering to the resistivity increase.

### 10:40am **MC+AP+AS-MoM8 LEIS Characterization of the Outer Surface, Ultra-Thin Layers and Contacts**

***Hidde Brongersma***, ION-TOF / Tascon / Calipso, Netherlands*, P. Bruener, T. Grehl,* ION-TOF GmbH, Germany*, H.R.J. ter Veen*, Tascon GmbH, Germany **INVITED**

Modern day technologies are increasingly based on high performance nanomaterials and novel preparation techniques for such materials are developed at a rapid pace. Advances in nanoscience and nanotechnology heavily rely on the availability of analytic techniques that can validate and support new nanomaterials synthesis procedures. With the introducing of the Qtac$^{100}$, a new high-sensitivity Low Energy Ion Scattering (HS-LEIS) instrument, one can quantitatively analyze the atomic composition of the surface of a wide range of materials with an unparalleled surface sensitivity.

The outermost atoms of a surface largely control processes such as growth, nucleation, poisoning, adhesion and electron emission. While analytic tools (such as XPS) probe an average of many atomic layers, LEIS can selectively analyze the outer atoms. In addition, non-destructive in-depth information, with high depth resolution, is obtained for the heavier elements (0 - 10 nm). HS-LEIS is just as well suited for the *quantitative analysis* of amorphous, insulating and extremely rough surfaces as for flat single crystals. Since HS-LEIS is a fast analysis technique, it can be used to follow diffusion processes in-situ.

The focus will be on applications where valuable information has been obtained that is impossible (or very difficult) to obtain with other analytical techniques. The unique possibilities will be illustrated with state-of-the-art applications for: ALD growth of ultra-thin layers, surface modification, interface diffusion, core/shell nanoparticles, graphene, self-assembled monolayers for sensors.

The findings will be compared and contrasted to those obtained by other analytic techniques such as XPS, Auger, SIMS, RBS and conventional LEIS.

### 11:20am **MC+AP+AS-MoM10 Backside versus Frontside Characterization of High-k/Metal Gate Stacks for CMOS sub-14 nm Technological Nodes**

***Eugenie Martinez***, CEA, LETI, MINATEC Campus, France*, B. Saidi, P. Caubet, F. Piallat,* STMicroelectronics, France*, H. Kim,* CEA, LETI, MINATEC Campus, France*, S. Schamm-Chardon,* CEMES-CNRS, France*, R. Gassilloud*, CEA, LETI, MINATEC Campus, France

Down-scaling of CMOS transistors beyond the 14 nm technological node requires the implementation of new architectures and materials. The gate last integration scheme is a promising solution to better control the threshold voltage of future MOSFETs, because of its low thermal budget [1]. Advanced characterization methods are needed to gain information about the chemical composition of such structures. The analysis of thin layers and interfaces buried under a thick metal electrode is particularly challenging. An effective approach based on backside sample preparation is proposed here.

To tune the work-function toward nMOS values, the technology currently investigated is based on HfO$_2$ for the dielectric and a thin TiN layer capped by a TiAl alloy for the gate [2]. For a better understanding of aluminium and other elements redistributions after a 400°C annealing, a specific methodology has been developed based on the removal of the Si substrate. It allows to achieve XPS and Auger analyses from the backside of the sample [3].

In particular, Auger depth profiling performed on HfO$_2$/TiN/TiAl/TiN/W gate stacks at low energy (500 eV Ar$^{+}$) brought the following main conclusions: a) no Al diffusion toward the HfO$_2$/TiN interface, b) nitrogen out diffusion in the upper TiAl film, c) significant oxygen scavenging. By comparison, these results evidenced that Auger frontside analyses suffer from sputter-induced artifacts.

In a further study, to understand the behavior of nitrogen out diffusion in the TiAl layer, we deposited TiAlN$_x$ thin films with various nitrogen flows by reactive sputtering deposition and performed backside XPS analyses. At low/medium nitrogen flows, which correspond to the TiAlN$_x$ film after TiN/TiAl bilayer anneal, the N1s core level spectra obviously shows that N is mainly bonded to Al rather than Ti. Results are compared with frontside XPS performed with a thinner TiN upper layer. The backside approach is shown to be more representative of the technological stack, in particular with respect to the TiN oxidation.

*Measurements were carried out at the NanoCharacterization Platform (PFNC) of MINATEC.*

[1] C. L. Hinkle et al., Appl. Phys. Let. 100, 153501 (2012).

[2] A. Veloso et al.., Symposium on VLSI Technology, Digest of Technical Papers (2011).

[3] M. Py et al., AIP conference proceedings 1395, 171 (2011).

### 11:40am **MC+AP+AS-MoM11 Charge Storage Properties of Al/(1-x)BaTiO$_{3-x}$Ba(Cu$_{1/3}$Nb$_{2/3}$)O$_3$ (x = 0.025) (BTBCN)/HfO$_2$/p-Si Metal/Ferroelectric/Insulator/Semiconductor Devices**

***Souvik Kundu****, M. Clavel, D. Maurya, M. Hudait, S. Priya*, Virginia Tech

Metal-ferroelectric-insulator-semiconductor (MFIS) devices with pulsed laser deposited 300 nm (1-x)BaTiO$_{3-x}$Ba(Cu$_{1/3}$Nb$_{2/3}$)O$_3$ (x = 0.025) (BTBCN) ferroelectric film and atomic layer deposited 10 nm HfO$_2$ insulating layer on silicon semiconductor substrate were developed for next generation ferroelectric non-volatile memory applications. For the first time, the structural, interfacial, and electrical properties of these Al/BTBCN/HfO$_2$/p-Si MFIS devices were studied, and the role of BTBCN as charge storing elements was also established. The X-ray diffraction and transmission electron micrograph with selected area diffraction pattern clearly demonstrate the single crystallization of BTBCN ferroelectric films. It was found that insertion of 10 nm HfO$_2$ in-between BTBCN and Si improves the interfacial properties and also prevents the interdiffusion of semiconductor into the ferroelectric layer. The optical bandgap of BTBCN was found to be 4.38 eV using transmission spectrum analysis. The MFIS structure showed capacitance-voltage hysteresis loops due to the ferroelectric polarization of BTBCN and the maximum memory window was found to be 1.65 V when the sweeping voltage was ±10 V. However, no memory window was found in metal-insulator-semiconductor devices, i.e., when there is no BTBCN layer in between metal and insulating layer. The leakage current of these devices was found to be $7\times10^{-9}$ A/cm$^{2}$ at an applied voltage of -1 V. The wide memory window and superior retention

properties were achieved due to the presence of BTBCN. The electronic band diagrams of these MFIS devices during program and erase operations were proposed.

*Keywords:* BTBCN; MFIS; Memory window; Leakage current; Band-diagram

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