Fundamentals
Room Great Lakes C - Session FM+SS-TuM3
Microelectronics

Moderators: Marinus Hopstaken, IBM T.J. Watson Research Center, **Paul van der Heide**, IMEC, Belgium

10:00am **FM+SS-TuM3-1 Keynote Industrial Talk: SIMS Quantification: Do You Remember When a Factor of Two was Good Enough?***, Charles Magee,* 314 Pennington-Rocky Hill Road **INVITED**

Well, do you remember when a factor of two was good enough? Probably not. You would have to have been around SIMS in the early 1970's like I was to remember those days. I will give many references back to the early days when a local thermal equilibrium (LTE) model was used to obtain the first results that were accurate to within a factor of two...but only 60% of the time. And it only worked for bulk silicate matrixes!

People were not using SIMS on semiconductors in those days. I will give several early references showing profiles of ion implants in Si, but it was not until 1980 that the first paper was published that explicitly showed how to use ion implants as SIMS standards. (People were using ion implants as standards before 1980, (I was one of them!) but only in limited cases, and with no formal published equations specifying how to use them.)

But the samples for which ion implants were used as standards were for dilute concentrations in a single matrix which was uniform in depth. The rest of the talk will show how we at Eurofins EAG Laboratories tackled the problem of quantification of both major and minor elements in non-uniform, multi-element samples with abrupt or continuously graded composition changes using Point-by-point CORrected-SIMS (PCOR-SIMS). These include:SiGe, AlGaAs, B in SiO2/Si, arsenide/phosphide heterostructures, PLAD B in poly-gates, As in SiO2/Si, and GaN/AlGaN structures.

10:40am **FM+SS-TuM3-5 ToF-SIMS Characterization of Chitosan as Water Developable 193 nm Photolithography Resist for Green Micro-Nanopatterning**, *P. Durin,* Univ Lyon, Ecole Centrale de Lyon, CNRS, France*; O. Sysova,* Université de Haute-Alsace, CNRS, Université de Strasbourg, France*; Y. Guan, C. Gablin,* Univ Lyon, CNRS, Université Claude Bernard Lyon 1, France*; A. Benamrouche,* Univ Lyon, Ecole Centrale de Lyon, CNRS, INSA Lyon, Université Claude Bernard Lyon 1, France*; S. Hajjar-Garreau,* Université de Haute-Alsace, CNRS, Université de Strasbourg, France*; A. Teolis, S. Trombotto,* Univ Lyon, CNRS, Université Claude Bernard Lyon 1, Université Jean Monnet, France*; T. Delair,* Univ Lyon, CNRS, , Université Claude Bernard Lyon 1, Université Jean Monnet, France*; I. Servin, R. Tiron, A. Bazin,* Univ. Grenoble Alpes, CEA, LETI, France*; D. Berling, O. Soppera,* Université de Haute-Alsace, CNRS, Université de Strasbourg, France*; T. Géhin,* Univ Lyon, Ecole Centrale de Lyon, CNRS, Université Claude Bernard Lyon 1, France*; E. Laurenceau,* Univ Lyon, Ecole Centrale de Lyon, Université Claude Bernard Lyon 1, France*; J. Leclercq, Y. Chevolot,* Univ Lyon, Ecole Centrale de Lyon, CNRS, Université Claude Bernard Lyon 1, France*; **Didier Léonard**,* Univ Lyon, CNRS, Université Claude Bernard Lyon 1, France

Lithography is one of the key steps in micro/nanofabrication. In this process, structures are written in a resist (film sensitive to electron beam or UV irradiation) that can subsequently be transferred to the substrate material (typically SiO_2 on silicon), often by etching. However, the use of toxic resists and solvents, as well as of harmful developing solutions, raises questions in terms of health, safety and environmental issues. In this context, there is a growing interest in using bio-sourced resists such as polysaccharides[1] that are water-soluble and can be processed as films with good adherence to substrates. Most of them still need to be chemically modified[1], which is outside the scope of a green resist. Chitosan appears then as an ideal candidate for replacing commercial synthetic resists, since it does not need any additional modification, and development of patterns is achievable with water or a slightly acidified solution[2].

Here, we focus on the ToF-SIMS spectra interpretation combined with multiple characterization techniques (XPS, IR,…) to understand (1) the mechanism making possible to write structures in chitosan films using UV irradiation at 193 nm; (2) the key parameters driving the plasma selectivity of the chitosan resist defined as the ratio of the resist etching rate over the substrate etching rate under given SiO_2 etching plasma conditions (selected parameters were SF_6/Ar vs CHF_3 etching plasmas as well as chitosan vs alginate films).

[1] S. Takei *et al.*, Microelectron. Eng., Volume 122, pp. 70–76, 2014

[2] M. Caillau *et al.*, Proc. SPIE - Volume 10587, pp. 105870S, 2018

11:00am **FM+SS-TuM3-7 NP-SIMS for Evaluating the Molecular Homogeneity of Photoresists***, **Michael Eller**, J. Cruz,* California State University Northridge*; D. Verkhoturov, S. Verkhoturov, E. Schweikert,* Texas A&M University

There is an urgent need to develop new semiconductor devices with critical dimensions below 20 nm. The semiconductor industry has identified extreme ultraviolet, EUV, lithography as a the most likely method to produce sub 20 nm features at scale. Chemically amplified resists, CAR, are well established materials for deep ultra-violet lithography and consist of a multi-component mixture including polymeric species, photoacid generator and base quencher. A key factor in the performance of CARs as EUV resists is local variation in resist sensitivity, due to a combination of factors including homogeneity of the resist components. Thus, there is a critical need for analytical methods capable of molecular analysis at the nanoscale to understand and optimize the performance of CARs as EUV photoresists. Here we describe a new methodology which allows for tests on molecular homogeneity at the nanoscale, with the ability to examine rare sites which deviate from the average composition. The technique uses Nano-Projectile Secondary Ion Mass Spectrometry, NP-SIMS, operating in the event-by-event bombardment detection mode. NP-SIMS has three innovative features (1) the nature of the projectile (2) the mode of data acquisition (3) the method of data analysis. Briefly, samples are analyzed with a suite of nano-projectiles (e.g. Au_{400}^{4+})separated in time and space. Each projectile generates abundant emission of analyte-specific ions. The ions emitted from each of these impacts are mass analyzed and stored as an individual mass spectrum prior to the arrival of the next projectile. Nanoscale analysis is possible because each projectile samples a nano-volume (10-15 nm in diameter). The homogeneity of a component(s) can be evaluated by examining these individual mass spectra for the co-emission of analyte-specific species. We applied this method to study how homogeneity of each component in the resist was affected by resist composition. Further, we identified rare sites which deviated significantly from the mean composition, based on the number of detected analyte molecules. These are likely due to ionic aggregations or domains with higher concentration within the top 10 nm of the film. Identifying and characterizing these rare sites is critical for understanding the fundamental and material processes occurring in these materials. This work is supported in part by the Semiconductor Research Corporation (Task ID 3032.001).

11:20am **FM+SS-TuM3-9 Dynamic SIMS Analytical Methods for Optimized Detection Limits of Atmospheric Species***, **Seoyoun Choi**, L. Créon, P. Peres,* CAMECA, France*; S. Miwa,* CAMECA, Japan*; J. Ren, R. Liu,* CAMECA, France

Information on hydrogen, carbon and oxygen impurities (atmospheric gas elements) introduced during processing and/or aging is of major importance to better understand the lifetime and failure modes of semiconductor devices.

Dynamic SIMS plays an important role in evaluating the concentration of impurities (H, C, O) in semiconductor materials because of its high sensitivity, ability for depth profiling at high throughput, and good detection limits. Dynamic SIMS imaging capabilities can also be used to investigate local non-uniformity of light elements at sub-micrometer scale. Based on a magnetic sector mass spectrometer, the CAMECA IMS 7f-Auto is a versatile magnetic sector SIMS that offers unequalled depth profiling performance.

This talk will present and discuss different analytical protocols for optimizing the detection limits of atmospheric elements.

Data obtained on the IMS 7f-Auto show that the detection limits of H, C, O in silicon can be significantly improved using a specific protocol including sample outgassing and pre-sputtering prior to analysis.

For bulk analysis, the "raster change" method is a powerful analytical method to obtain the bulk concentration of light elements. This method, based on the signals intensity variation when reducing the raster, allows to separate the net content in the sample from the instrumental background contribution, and thus provides the bulk impurity concentration.

We will show applications of the "pre-sputtering" and "raster change" dynamic SIMS methods for measuring the impurities concentration in silicon.

11:40am **FM+SS-TuM3-11 Co-Sputtering EXLIE SIMS to Achieve Non-Fully Oxidizing Conditions***, **Alexandre Merkulov**, C. Noel, A. Franquet, V. Spampinato, P. van der Heide,* IMEC, Belgium

The SIMS technique can be used to monitor in-depth distributions of dopants within the first few nanometers of the surface, provided that SIMS profiles can be measured with depth resolution better than 1 nm/decade. The application of ultra-low impact energy sputtering with Oxygen at high incidence angle in the range of 40-60 degrees is limited. Several artifacts/effects inherent to ultra-low energy sputtering within the transient were encountered:1) exponential sputter rate variation through the native oxide, empirically explaining the so-called 'surface shift' of depth profiles toward the surface; 2) high Boron surface peak presence on the depth profile, correlating with sputter rate variation, however, not fully cancelling the surface peak if only sputter rate variation is applied; 3) surface roughening during the sputtering through the transient and roughness development. These effects do not allow to use quantification formalism established for steady state sputtering condition in SIMS experiments. In this work, the sputter rate variation through transient until the steady state sputtering is established was studied using direct physical method such as atomic force microscopy (AFM). The part of the signal enhancement in the transient (surface peak) after taking into account the sputter rate variation can be associated with surface oxidation, thus responsible for ion yield variation through the transient. Moreover, the oxidation related to the oxygen flow in the sputtering beam can be varied using the diluted oxygen beam obtained from a certain gas mixture. Several gases were studied to form a stable plasma and to produce a high-density beam, notably N_2, Ar, Xe and O_2. The advantage of N_2 is a molecular mass close to O_2 allowing to study the sputtering cascade and surface oxidation through the native oxide. Ar and Xe have lower backscattering compared to O_2, so, higher sputter yield can be achieved. The Cameca SC-Ultra SIMS tool ion column with Wien filtering allows to sputter with pure gas species (N_2^+, Ar+, Xe^+, O_2^+) or diluted flow to study the oxidation ramp according to the oxygen percentage in the sputtering beam.A special interest will be paid to the roughness development through the transient. The AFM measurements, used for sputter yield variation study provide the surface correlation function to observe the seeding and regular surface structures formation dynamics. The main accent of this research is to provide easy data interpretation layout, produce a much-needed information on partially oxidized surface chemistry in the early state of Silicon sputtering, with the aim to improve the very shallow implants quantification.

12:00pm **FM+SS-TuM3-13 AKONIS: Automation for Easier Use of SIMS***,* ***Anne-Sophie Robbes****, O. Dulac, K. Soulard, S. Choi, R. Liu, B. Salle,* CAMECA, France*; M. Pietrucha,* CAMECA Instruments Inc.

The new CAMECA AKONIS SIMS tool has been developped to fill a critical gap in semiconductor fabrication processes by providing high throughput, high precision detection for implant profiles, composition analysis and interfacial data directly in the semiconductor manufacturing line. AKONIS provides a very high level of automation to ensure repeatability across tools for fab level process control and tool-to-tool matching. Building upon fifty years of experience in ion instrumentation and over thirty years of close partnerships with leading semiconductor manufacturers worldwide, AKONIS is a leap forward in high precision characterization of implants, interfaces and compositional analysis along with high repeatability metrology for the most demanding semiconductor process development and control applications. AKONIS benefits from recent development in Ultra Low Impact Energy ionic column technology (< 150 eV), coupled with a full wafer handling system including a high-resolution stage enabling measurements on pads down to 30 µm.

AKONIS implements sophisticated automation routines on the primary ion column. These allow it to run an analysis at the target current setpoint with a tightly focused beam over a broad range of energies - from 150 eV to 7 keV - for applications from ultra-thin films to deep implants. Moreover, the instrument enables running automated chain analyses, switching between different applications that may require differing instrument conditions - such as mass resolution, analysis current, or impact energy - without any need for human intervention. In addition, fitted with optical carrier enhancement (OCE) capability, the instrument is reliably and easily used for charge compensation while analyzing thin insulating films (<30nm).

We'll demonstrate how the automation, especially of the primary column, developped for AKONIS can be useful and beneficial in SIMS in general.

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