Applied Surface Science Division
Room 204 - Session AS+NS-ThA

Profiling, Imaging and Other Multidimensional Pursuits

Moderators: Ashley Ellsworth, Physical Electronics, Jordan Lerach, ImaBiotech Corp.

2:20pm AS+NS-ThA1 Surface Science Study of Au/Ni/Cr/n-SiC and Au/Cr/Ni/n-SiC Thin Film Ohmic Contact Material, *Martyn Kibel,* La Trobe University, Australia*; A.J. Barlow,* La Trobe University, Australia*; P.W. Leech,* RMIT University, Australia

Silicon carbide (SiC) has become a promising semiconductor material for use in elevated temperature and high power devices. Although ohmic contacts to n-SiC have been widely fabricated using a metallization of Ni/n-SiC annealed at ~1000 °C, the formation of nickel silicides at the interface has resulted in uneven roughening of the metal surface. We have examined for the first time the development of ohmic contact materials containing layers of both Ni and Cr (Au/Ni/Cr/n-SiC and Au/Cr/Ni/n-SiC). A detailed study of these layered structures, both as-deposited and subsequently annealed at 750-1000°C has been undertaken using a range of surface analysis techniques. Auger electron spectroscopy (AES) depth profiling, both static and using Zalar rotation, has been used to etch through the layers into the epitaxial SiC. AES elemental mapping, in conjunction with SEM imaging, has been used to record the nature of the surface before and after profiling. AES line scans have also been employed to characterize the subsequent crater walls. In addition, X - ray photoelectron spectroscopy (XPS) depth profiling has been used to characterise the interfaces with a focus on the chemical states of the constituent elements. The nature of the interfaces between individual layers is discussed as well as the methodologies for generating depth profiles from the acquired data. The analysis has shown a wide-scale interdiffusion of the layers after annealing of the Au/Ni/Cr/n-SiC structure with the formation of surface globules. In comparison, the Au/Cr/Ni/n-SiC contacts have shown a limited interdiffusion of the layers and relatively smooth surfaces, indicating that the intermediate layer of Cr has acted as a diffusion barrier for the Ni. The electrical characteristics of the as-deposited and annealed contacts have been measured using circular transmission line test patterns and the results correlated with the AES and XPS analyses.

2:40pm AS+NS-ThA2 3D Imaging of InGaN/GaN based Nanowires and Nanotubes using Time-of-flight Secondary Ion Mass Spectrometry, *Jean-Paul Barnes,* Univ. Grenoble Alpes, CEA, LETI, France*; A. Kapoor,* Univ. Grenoble Alpes, CEA, France*; C. Durand,* Univ. Grenoble Alpes, CEA, France*; C. Bougerol,* Univ. Grenoble Alpes, CNRS, France*; J. Eymery,* Univ. Grenoble Alpes, CEA, France

GaN based nanowire light-emitting diodes (LEDs) can be grown in ordered arrays on sapphire and large Si substrates. The growth of coaxial InGaN/GaN multiple quantum wells (MQWs) on the nonpolar m-plane sidewalls of the GaN wire increases the active region area, reduces the defect density and can increase efficiency in the case of thick QWs due to the absence of quantum confined Stark effect [1]. Variants on this approach include InAlN/GaN MQW tubes and the integration of such wires in flexible substrates [2].

An important parameter controlling the light emission is the indium concentration in the MQWs and their thickness, which may vary along the length of the wire. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) has been used to perform 3D mapping of the indium concentration in the coaxial MQWs for both GaN wire geometries and InAlN/GaN MQW tube geometries.

Experiments are performed using a dual beam approach with a finely focused (<200 nm spot size) Bi_3^{++} analysis beam at 60 keV and oxygen sputtering at 500 eV. The indium concentration is calibrated from a 2-D MQW structure on which the nanowires are deposited for analysis so that TOF-SIMS analysis can be performed on the sidewall perpendicular to the MQWs. The TOF-SIMS analysis on single nanowires has allowed the composition of InGaN quantum wells to be quantified and the fact that the MQW structure becomes thicker towards the end of the nanowire to be determined. The ability to target specific nanowires allows the composition determined by TOF-SIMS to be compared with photoluminescence and cathodoluminescence measurements to link the emission of the wires to the MQW composition and thickness. Using a similar approach it was possible to characterize the InAlN/GaN MQWs on nanotube structures and confirm that the MQW structure remains after selective etching of the GaN

core and annealing. Such high resolution TOF-SIMS 3D imaging can also be used for other semiconductor structures such as those grown by selective epitaxial growth of for visualising doping in microelectromechanical systems (MEMS) systems.

This work was carried out on the nanocharacterisation platform (PFNC) of the CEA Grenoble.

References:

R. Koester et al. "M-plane core-shell InGaN/GaN multiple-quantum-wells on GaN wires for electroluminescent devices," Nano Letters **11** (11), 4839-4845 (2011).

[2] C. Durand et al. "Thin-Wall GaN/InAlN Multiple Quantum Well Tubes," Nano Letters **17** (6), 3347-3355 (2017).

3:00pm AS+NS-ThA3 Atom Probe Tomography: Applications and Prospects for Surface and Interface Science, *Austin Akey, D.C.. Bell,* Harvard University **INVITED**

Atom Probe Tomography (APT) is a three-dimensional, individual-atom composition mapping technique. Specimens are disintegrated atom-by-atom using a combination of high electric fields and voltage or laser pulses, causing individual ions to be ejected towards a position-sensitive detector with high time resolution. The resulting hit position, combined with the ion's time of flight, allows single-Angstrom, single-atom time-of-flight mass spectroscopy to be performed over volumes containing hundreds of millions to billions of atoms. Recent advances in instrument design and automation have greatly expanded the field of materials systems and scientific questions that the technique can address, and it is particularly well suited to analysis of surface and interface composition.

Datasets can be processed and analyzed as highly-localized 1D composition measurements, 2D surface mapping over an arbitrary surface in three-dimensions, or full volumetric composition maps, allowing a wide variety of questions to be asked of a material. We present applications including: bulk composition fluctuation and clustering measurements; full 3D composition mapping of electronic devices; interface composition and roughness determination; composition mapping of nanowire and other quasi-one-dimensional structures; and surface and bulk composition of catalytic materials. We also discuss the importance of correlating other microanalysis techniques with APT and give examples of one-to-one correlative work. The development of correlative electron microscopy and APT specimen geometries have allowed otherwise unresolvable questions to be answered, and new work extends this into the realm of combined in-situ and ex-situ measurement of the structural and compositional evolution of materials. Finally, we will discuss future prospects for the technique and its application to surface science.

4:20pm AS+NS-ThA7 Industrial Applications of Surface Analysis in Chemical Mechanical Planarization, *Hong Piao, Y.N. Liang, J. McDonough, C. Ballesteros,* FUJIFILM Planar Solutions, LLC, FUJIFILM Electronic materials USA., Inc.*; E. Turner,* FUJIFILM Planar Solutions, LLC, FUJIFILM Electronic materials USA., Inc*; A. Mishra, R. Wen,* FUJIFILM Planar Solutions, LLC, FUJIFILM Electronic materials USA., Inc.

Chemical mechanical planarization/polishing (CMP) is a chemical reaction assisted mechanical polishing process in the semiconductor manufacturing industry to remove overburden material or specific layers in the film stacking and to planarize the topography at the patterned wafer surface. Although the basic principles of CMP are understood, thorough understanding of surface chemical processes which occur during polishing is still lacking, especially the chemistry at the interface of the wafer/slurry/pad. Investigations aimed at understanding fundamental mechanisms usually employ electrochemical techniques. Surface analysis methods remain rather under-utilized in this field, especially when taking into account the explosive growth of these surface techniques for the analysis of "nano-structured" films in other research fields.

FUJIFILM Planar Solutions (PLNR) is a market leader for metals and dielectric CMP slurries. Our in-house XPS and ToF-SIMS surface analysis tools have greatly enhanced our capabilities in analyzing and understanding surface reactions, their mechanism, and fundamental science and engineering behind the slurry wafer interaction at the interface during CMP.

The goal of this presentation is to review selected results provided by advanced surface analysis tools combined with other complementary testing methods. Examples describing CMP characterization are given in two technological areas that are growing in importance: (1) Cu and Co CMP and (2) Defectivity in front end of line polishing involving dielectrics. We also pay particular attention to show how the recent improvements in

instrumentation could open new opportunities and fundamental understanding of how surface analyses can enable improvements in slurry design for CMP, thus leading to the development of next-generation advanced CMP slurries and processes.

4:40pm AS+NS-ThA8 Correlative Images of Microscopy Spectroscopy: Beyond the 3D Characterization in Surface Analysis, *Tanguy Terlier,* Korea Institute of Science and Technology, Republic of Korea*; R. Verduzco,* Shared Equipment Authority, Rice University*; Y. Lee,* Korea Institute of Science and Technology, Republic of Korea

Technological progress has spurred the development of increasingly sophisticated analytical devices. The full characterization of structures in terms of sample volume and composition is now highly complex. Traditionally, the surface spectroscopic techniques such as AES or ToF-SIMS provide the chemical distribution of sample surfaces. Nevertheless, an important issue in surface analysis is to perform 3D chemical mapping of structured samples with a complex architecture, conserving as well high spatial resolution (lateral and in-depth) as high mass resolution. During the surface analysis, only a projection into 2D surface mapping is achieved which reverse the topographic render after the in-depth analysis. Moreover, the use of ion beam sputtering induces preferential sputtering and damage accumulation due to the sputter beam. So, the surface roughness generated by the sputtering affects the depth profiling of chemical signals. In consequence, the authentic 3D chemical distribution as a function of the depth is completely distorted or lost.

Alternative approaches to resolve the artifacts of 3D chemical images exist. Among these solutions, the use of Scanning Probe Microscopy (SPM) in combination with a surface spectroscopic analysis permits to correct the depth scale of the data and to reduce the artifacts due to the depth profiling. In addition to the data correction, correlative approach using SPM and surface spectroscopy offers the unique possibility to couple topography with 3D chemical information for having access to the accurate volume render. Merging other measurable signals such as electrostatic force microscopy with 3D chemical analysis can also enhanced the understanding of the surface properties and structure characteristics.

After a brief introduction to the data fusion, different methods of 3D reconstruction used in surface analysis will be discussed. In particular, we will show a recent method, the dynamic-model-based volume correction. This method has been applied on a patterned sample using two combination of techniques, SPM/ToF-SIMS and SPM/AES. Then, we have compared the performances of *ex situ* SPM/ToF-SIMS with a new instrument, an *in situ* SPM/ToF-SIMS. To illustrate the new potentials of the correlative imaging method, we have characterized two different samples, a cryo-freezing prepared cell sample and a self-assembled block copolymer film. Finally, we will explore the applications of the correlative microscopy and spectroscopy analyzing a standard SRAM sample that is composed of patterned structures integrating concentration-controlled doping. This sample has provided multi-signal mappings and a quantitative analysis.

5:00pm AS+NS-ThA9 3D Structure of Atomically Dispersed Metal Species on an Oxide Single Crystal Surface Studied by Polarization-dependent Total Reflection Fluorescence (PTRF)-XAFS, *Satoru Takakusagi,* K. Asakukra, Hokkaido University, Japan

Precise size control of metal species on an oxide surface, especially in the range of <1 nm, is now highly important to develop the next-generation catalysts, sensors, and electronic devices. However this is not easy since metal atoms are easily aggregated to form large particles on an oxide surface. This is due to the small stabilization energy and/or the small activation energy for the metal diffusion. If one can obtain a monatomic metal species on an oxide surface, it can be a building block for synthesis of the metal cluster and helps us to control the cluster size in one-atom precision. Our group has developed the "premodified surface method" to obtain a highly dispersed metal species on an oxide single crystal surface. In the premodified surface method, the oxide surface is precovered with a functional organic molecule possessing a substituent atom which can strongly coordinate to a metal atom before metal deposition. We have determined the precise 3D structures of such metal species by polarization-dependent total reflection fluorescence (PTRF)-XAFS technique.

In this study, various metals such as Cu, Au, Ni and Pt were vacuum-deposited on a $TiO_2(110)$ surface premodified with *o*-mercaptobenzoic acid (*o*-MBA) and their 3D structures were determined by the PTRF-XAFS technique. We have found that Cu, Au and Ni were atomically dispersed by bond formation with sulfur of *o*-MBA and oxygen in the TiO_2 lattice, but Pt was aggregated to form clusters. We will discuss the factors that govern

single metal dispersion based on the energy difference between sulfur–metal–oxygen and metal–metal bond formations.

5:20pm AS+NS-ThA10 XPS Imaging and Spectromiscroscopy Investigation of Extended Release Pharmaceutical Tablets, *Jonathan Counsell,* S.J. Coultas, C.J. Blomfield, Kratos Analytical Ltd, UK*; D.J. Scurr,* The University of Nottingham, UK*; L. Mason,* University of Nottingham, UK*; V. Ciarnelli, J.M. Garfitt, S. Rigby-Singleton,* Juniper Pharma Services Ltd, UK*; M.R. Alexander,* The University of Nottingham, UK*; M.C. Davies,* University of Nottingham, UK*; C. Moffitt,* Kratos Analytical Inc.*; S.J. Hutton,* Kratos Analytical Ltd, UK

The effects of formulation methodology on the performance of tablets have been studied for decades. Typically tablets consist of the active drug and excipients which influence stability, release rate and binding. HPMC (Hydroxypropyl Methylcellulose) is a hydrophilic polymer commonly used in extended-release tablets as it shows rapid hydration and uniform gel formation. The microstructure of HPMC particles in matrices influences the ability of HPMC to form gel layers after contact with water, thereby affecting release characteristics. While previous studies described the use of Raman spectroscopy as a benchmark method for chemically imaging solid pharmaceutical formulations[1], there are relatively few contributions reporting the application of XPS (X-ray Photoelectron Spectroscopy) in this field. New insight into tablet component distribution could be employed in the successful formulation design and development process.

Herein we investigate the novel application of XPS to elucidate the distribution of both drug and excipients species. Parallel XP imaging capabilities will be illustrated and demonstrated for several tablet systems yielding information on particle size, distribution and shape. The use of small-spot XPS provides quantitative and chemical-state information on imaging features. The novel use of argon cluster ion bombardment will be discussed for both cleaning and depth profiling. Peak-fitting, pitfalls and limitations will be explored and compared with other complementary techniques such as ToF-SIMS.

Strachan *et al*. Journal of Pharmacy and Pharmacology. 2007. 179-192.

5:40pm AS+NS-ThA11 An experimental Guide to Conversion of Tof-SIMS Spectrum to BIG DATA: Application in Analysis of Ultrathin Coatings, *Kevin Abbasi,* A.A. Avishai, Swagelok Center for Surface Analysis of Materials, Case school of Engineering, Case Western Reserve University

Thin films are traditionally being characterized using cross sectional analysis with scanning or transmission electron microscopes. Although accuracy of these technique are very high, it's hard to analyze a large number of samples this way. Surface analysis instruments such as X-ray photoelectron spectroscopy (XPS), Auger Electron Spectroscopy (AES) and Time-of-flight secondary ion mass spectrometry (Tof-SIMS) can be used to analyze the top surface and erode it with focused ions. Alternating the analysis and ion etching cycles, concentration profiles can be achieved.

In specific conditions where the element of interest has very low concentration or the thickness of the coating is less than the analysis volume (ultrathin films), Tof-SIMS becomes a very powerful tool as it provides the best detection limit and smallest analysis depth. Extracting useful and specific information from the mass spectra and reducing the dimensionality of very large datasets, is a challenge, that has not been fully resolved. Multivariate analysis has been widely deployed to assist in the interpretation of the Tof-SIMS data. Principal component analysis is a popular approach that can help ease the task of analyzing spectrums acquired at different locations from the top surface, compare it against different samples and help extract trends.

The purpose of this talk is to provide experimental guide for the characterization of ultrathin coatings (both flat and in form of particles). Two set of samples will be described: Inter-diffusion will be characterized in a flat coating obtained from Atomic layer deposition (ALD) process and contamination analysis will be then discussed on micron size particles with ultrathin coating. Different strategies will be then discussed to obtain concentration profiles using Time-of-flight secondary ion mass spectrometry. Principal component analysis will then be used to successfully convert mass spectrums into big data and extracting similarities between spectrums and samples.

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