Synchrotron Analysis Focus Topic
Room: 203 C - Session SA+AS+MI+SS-WeM

Synchrotron and Imagery: PEEM, Nano-ARPES and Others (8:00-9:40 am)/Synchrotron TXRF and Related Techniques (10:40 am-12:00 pm)

Moderator: M.C. Asensio, Synchrotron SOLEIL, France, J. Kawai, Kyoto University, Japan

8:00am **SA+AS+MI+SS-WeM1 LEEM, PEEM and ARPES Studies of Epitaxial Graphene on SiC(0001)**, ***U. Starke***, Max Planck Institute for Solid State Research, Germany **INVITED**

Large area epitaxial graphene (EG) can be grown on SiC(0001) by heating in Ar atmosphere [1]. However, such graphene layers are *n*-doped due to the influence of a covalently bonded carbon interface layer. This influence can be completely eliminated and the graphene layers be decoupled from the substrate by atomic intercalation. The electronic structure can be tuned in various ways for these decoupled graphene layers. Detailed investigations of the π-band structure, the spatial arrangement, chemical bonding and local surface order are shown based on angle-resolved photoemission spectroscopy (ARPES), low-energy electron microscopy (LEEM), photoemission microscopy (PEEM) combined with microscopic X-ray photoelectron spectroscopy (μ-XPS) and low-energy electron diffraction (μ-LEED), as well as scanning tunneling microscopy (STM) experiments.

By annealing the EG samples in atmospheric H_2, atomic hydrogen reacts under the interface layer, so that the underlying SiC layer becomes passivated [2]. The interface layer alone transforms into a quasi-free standing monolayer while monolayers and bilayers turn into decoupled bilayers and trilayers [3,4]. As a result, charge neutral quasi-free standing graphene layers can be obtained. By intercalation of Germanium the graphene layers can also be decoupled. In this process both *p*- and *n*-doping can be produced, depending on the amount of Ge material intercalated. By preparing both phases in coexistence on the surface, lateral *p-n* junctions can be generated on a mesoscopic scale [5]. Intercalation of Cu induces a coincidence superstructure on top of the SiC surface, which originates from periodic regions of different bond configuration for the carbon atoms in the graphene layer. As a result, a long range periodic potential is imposed onto the graphene layer, which leads to a profound modification of its electronic spectrum. A surprisingly strong doping and the development of mini-Dirac cones are observed [6].

References:

[1] K.V. Emtsev, et al., Nat. Mater. 8, 203 (2009).

[2] C. Riedl, C. Coletti, T. Iwasaki, A.A. Zakharov, and U. Starke, Phys. Rev. Lett. 103, 246804 (2009).

[3] S. Forti, K.V. Emtsev, C. Coletti, A.A. Zakharov, C. Riedl, and U. Starke, Phys. Rev. B 84, 125449 (2011).

[4] C. Coletti, K.V. Emtsev, A.A. Zakharov, T. Ouisse, D. Chaussende, and U. Starke, Appl. Phys. Lett. 99, 081904 (2011).

[5] K.V. Emtsev, A.A. Zakharov, C. Coletti, S. Forti, and U. Starke, Phys. Rev. B 84, 125423 (2011).

[6] K.V. Emtsev, S. Forti, A.A. Zakharov, C. Coletti, and U. Starke, in preparation.

8:40am **SA+AS+MI+SS-WeM3 An Imaging NEXAFS Detector for Compositional and Structural Analysis**, ***C. Weiland***, Synchrotron Research, Inc., *Z. Fu, C. Jaye, D. Fischer,* National Institute of Standards and Technology (NIST), *K. Scammon,* University of Central Florida, *P. Scobol, E. Principe*, Synchrotron Research, Inc.

We present the development of the second generation Large Area Rapid Imaging Analytical Tool (LARIAT MKII) for near edge x-ray absorption fine structure (NEXAFS) surface chemical and structural analysis. This analyzer utilizes magnetostatic electron optical elements to maintain the lateral distribution of electrons into a 16 mega channel detector, while providing a near 180° collection angle for high collection efficiency enabling rapid parallel imaging. A series of electrostatic lenses can be used to tune the energy and depth sensitivity of the imaged electrons allowing for 3D analysis of the near surface region (<7nm). The first LARIAT MKII will be installed on the NIST SST beamline at NSLS II; initial testing is currently being performed at NSLS beamline U8B.

The first generation LARIAT has demonstrated capabilities in determining simultaneously the concentration and orientation of single-strand DNA micro array sensors, organic electronic combinantorial device arrays, and semifluorinated molecular gradients. Additionally, LARIAT MKI was used to identify cancerous versus non-cancerous dermal tissue through spectroscopic analysis. LARIAT MKII advances these capabilities by improving the lateral resolution of the analyzer to below 7 μm and improving collection efficiency through a series of gridless electrostatic lenses. Here we will present an overview of LARIAT MKII and its capabilities, as well as some of the initial data recorded from the system.

9:00am **SA+AS+MI+SS-WeM4 Recent Advances in High Resolution Real and Reciprocal Space Photoelectron Emission Microscopy**, ***K. Winkler***, *B. Kroemker,* Omicron NanoScience, Germany, *N.J. Weber, M. Escher,* FOCUS GmbH, Germany, *N. Barrett*, Cea Dsm Iramis Spcsi, France

Conventional electron spectroscopy methods are limited in providing simultaneous real and reciprocal or k-space information from small areas under laboratory conditions. Therefore, the characterization of materials with only micron scale sample homogeneity requires new instrumentation. Recent improvements in aberration compensated energy-filtered photoelectron emission microscopy (PEEM) can overcome the known limitations in both synchrotron and laboratory environments.

We present first results from real and reciprocal space photoelectron emission microscopy (PEEM) e.g. on Ag (111) showing high k and high energy resolution using a laboratory based He I and II radiation at room temperature and temperatures below 40K. The combination of a recently developed LHe cooled sample stage with an improved aberration compensated energy-filter allows 30 meV energy resolution while a new type of event counting detector improves the signal to noise ratio of the detector.

9:20am **SA+AS+MI+SS-WeM5 Quantum Material Spectroscopy Center at the Canadian Light Source**, ***S. Gorovikov***, *B. Yates,* Canadian Light Source, *A. Damascelli, H. Davis,* University of British Columbia, Canada, *R. Reininger,* Advanced Photon Source, *K.I. Blomqvist,* Consultant, *M. Sigrist, S. Chen, E. Hallin*, Canadian Light Source

We report on the concept and design features of the Quantum Material Spectroscopy Center (QMSC), a state-of-the art XUV and soft X-ray beamline facility currently under construction at the Canadian Light Source. The QMSC will operate within the photon energy from 15 to 1200 eV and is intended for spin- and angle-resolved photoemission spectroscopy (SARPES and ARPES).

A distinctive feature of the QMSC is the combination of two independent end stations dedicated to SARPES and ARPES experiments with a unique source consisting of a pair of 4 m long APPLE type undulators. The low- and high-energy undulators will be installed side by side in a switch yard arrangement and will provide the highest possible photon flux within this photon energy range. Complete polarization control in both linear and circular modes will be available. Moreover, the quasiperiodic magnetic structure of the low-energy undulator will result in optimized suppression of the higher order harmonics.

The optical design of the beamline is based on the Variable Line Spacing Plane Grating Monochromator (VLS PGM) design and will deliver 10^{12} - 10^{13} photons/second at the experimental stations with a resolving power higher than 10^4 over the full photon energy range.

The theoretical performance of the beamline will be presented. Research capabilities of the beamline will be illustrated.

9:40am **SA+AS+MI+SS-WeM6 Nano-ARPES Beamline at SOLEIL: A Powerful and Innovative Probe for Nanoscience**, ***M.C. Asensio***, Synchrotron SOLEIL, France

Over the last decades, we have witnessed exponential advances in a wide diversity of new nanotechnologies. These advances, seen particularly in nanoelectronics, nanomagnetism and nanochemistry, among others, affect almost every aspect of our lives. Following the fundamental step in the creation of nano-objects and even if these "building blocks" have shown remarkable properties, they would have remained unexploited if, at the same time, we had not developed new tools capable of analyzing, viewing and scrutinizing objects on a wide range of scales, from a few microns to a few tens of nanometers.

Recently, great progress has been made as a result of the rapid expansion in the range of modern microscopies. However, if they have achieved nanometer spatial resolution, the challenge still remains to provide powerful high-energy-resolution spectroscopic tools for probing nano- and micro-areas. The challenge then, is to quantify and analyze the electronic properties of advanced materials on a nano- and mesoscopic-scale. For such a result, analysis of the electronic structure must be comprehensive, not

only with regard to detection of core levels, but especially to study the structure of electronic states of the valence bands, directly responsible for chemical bonds, electrical transport and the thermal and mechanical properties.

In this presentation, the latest results of the ANTARES microscope beamline at the synchrotron SOLEIL will be disclosed. In particular, nano-ARPES findings describing the electronic band structure of mono-atomic thick graphene films grown on copper substrates by chemical vapor deposition will be presented[1]. This end-station, with a spatial resolution of several tens of nanometers, has already been able to carry out direct imaging of core levels, their chemical shifts and the band electronic structures of several ordered materials. High precise Chemical images and valence band information of nano-objects like exfoliated grapheme, granular materials and Nanowires will be reported.

1.- J. Avila et al., Sci. Rep. 2013, 14, August 3 : 2439 | DOI: 10.1038/srep02439

10:40am **SA+AS+MI+SS-WeM9 Grazing Incidence and Grazing Exit X-ray Spectroscopy of Ultra Shallow Arsenic Implants in Silicon**, ***F. Meirer***, Utrecht University, Netherlands **INVITED**

Grazing incidence (GI) and grazing exit (GE) geometries exhibit exotic geometries in x-ray fluorescence (XRF) spectroscopy and are mainly used to restrict the information depth of the analysis to the sample surface. For samples with sufficiently small surface roughness, variation of the angle of incidence within the range of the critical angle of total (external) reflection of x-rays allows obtaining information about the depth distribution of elements within the sample's surface. In total reflection x-ray fluorescence analysis (TXRF) the effect of total reflection is utilized adjusting the measurement angle below the critical angle. TXRF offers excellent detection limits and is routinely used for chemical trace analysis and surface contamination control.

The use of synchrotron radiation (SR) is highly beneficial for TXRF and for angle-dependent XRF in general, because its properties (e.g., high intensity, linear polarization, small source size, and natural collimation) make it ideally matched to the requirements of these techniques. Furthermore, when using SR as x-ray source these methods can be combined with x-ray absorption spectroscopy (XAS) analyzing the local coordinate structure of an element of interest in the sample. This extends XAS to the trace element level (ppb) in samples where only small amounts are available or where the sample is confined in or on the surface of a substrate material.

In this presentation I will review strengths and weaknesses of SR induced TXRF, GI-XRF and GE-XRF and their combination with XAS on the basis of the analysis of state-of-the-art ultra shallow arsenic implants in silicon produced by plasma immersion ion implantation and deposition (PIIID) and subsequent LASER annealing.

11:20am **SA+AS+MI+SS-WeM11 Basic Principles and Applications of Time Resolved Grazing Incidence EXAFS Experiments for Surface Studies in the 50 ms Range**, ***D. Lützenkirchen-Hecht***, *J. Stötzel, O. Müller, R. Frahm*, Bergische Universität Wuppertal, Germany

The surfaces of materials play a decisive role for many fundamental physico-chemical processes such as e.g. acqueous and gaseous corrosion, catalysis, or coating procedures. Many of those processes proceed in non-vacuum environments, so that classical surface analytical techniques like XPS or scanning electron microscopy are not suited for in-situ investigations. Furthermore, all of the above mentioned processes are strongly time dependent, so that fast surface sensitive in-situ probes are necessary to study the respective phenomena. EXAFS can be made surface sensitive by using the grazing incidence geometry: For incidence angles below the critical angle of total reflection, the penetration depth of the X-rays amounts to only some few nanometers, and the reflected X-ray beam only contains information about the near surface region of the studied samples. Here we have combined the grazing incidence geometry with the Quick-scanning EXAFS (QEXAFS) data collection. Recent experimental developments of QEXAFS have substantially improved the time resolution to about 50 ms for a single spectrum, thereby enabling completely new surface science experiments.

In this contribution, we will briefly discuss the experimental setup and present results obtained in-situ during the film deposition by sputtering. The growth of gold and copper thin films on float glass substrates and Si wafers were investigated as examples. We will show that the evolution of the film structure can be followed with a subsecond time resolution, and a detailed modelling of the experimental data using the distorted wave Born approximation yields e.g. the film composition, thickness and roughness as a function of time. First experiments showed the need for an automated analysis, and we will also introduce appropriate software solutions for the processing of huge amounts of data acquired in a typical time resolved experiment with several thousands of spectra. Furthermore, we will also discuss the oxidation of the Cu thin films by their exposure to ambient air at different temperatures. The results clearly show that the dynamics of the oxidation are strongly depending on the actual temperature of the samples.

11:40am **SA+AS+MI+SS-WeM12 Portable versus Synchrotron TXRF Analysis**, ***J. Kawai***, *Y. Liu, S. Imashuku*, Kyoto University, Japan

Total reflection X-ray fluorescence (TXRF) analysis is a micro (absolute amount is less than pg) and trace (relative concentration is less than ppb) analysis method. When synchrotron X-rays are used, the minimum detection limit becomes down to fg for transition metals. However the synchrotron radiation is an elemental selective method, and thus overall elements are not detectable. On the other hand, synchrotron radiation can eliminate the interference of elements whose analytical lines overlap, such as Ba and Ti, As and Pb. The TXRF spectrometers can be classified into three categories: (i) synchrotron radiation TXRF, (ii) high power X-ray tube (kW) TXRF, and (iii) low power (1-50 W) desk top TXRF. Type (i) achieves highest sensitivity, with WD-TXRF spectrometer (wavelength dispersive), down to fg, however ED (energy dispersive type) is also used, where polarization is additionally used to reduce the scattering of incident X-rays. Type (ii) is used for routine analysis of Si wafer analysis (ISO standard methods), but due to the recent progress of the semiconductor processing, the detection limit is not enough for the advanced semiconductor processing systems. Type (iii) is again classified into monochromatic and non-monochromatic types. Monochromatic type needs 50 W X-ray tube (cooling by fan), but non-mono type is possible only by 1 W X-ray tube. The sensitivity is comparable. Type (iii) is mainly used for environmental analysis, toxic elements analysis, and water quality analysis. We must also consider the sensitivity of elements for mass spectrometry such as SIMS and ICP-MS. These methods are sometimes more sensitive than synchrotron radiation TXRF. Most versatility method is the non-monochromatic X-ray tube (1 W) type portable TXRF spectrometer, by which we can analyze something toxic materials, whether it is truely toxic or not toxic. Several examples which show the ability of the low power TXRF, such as laboratory hazard analysis, will be presented.

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