Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic
Room 103C - Session SA+2D+AC+AS+TF-TuM

Applications of Synchrotron-based Techniques to 2D Materials (8:00-10:00 am)/Complex Functional Materials and Heterostructures (11:00 am-12:20 pm)

Moderators: Nicholas Barrett, CEA Saclay, Giacomo Ceccone, European Commission, Joint Research Centre, IHCP, Italy

8:20am **SA+2D+AC+AS+TF-TuM2 A Versatile Method for the Fabrication of 2D-electron Systems at Functional Oxide Surfaces***, T.C. Rödel,* Université Paris-Sud - SOLEIL, France*; **Patrick Le Fèvre,*** Synchrotron SOLEIL, France*; F. Fortuna, E. Frantzeskakis,* Université Paris-Sud - IN2P3, France*; F. Bertran,* Synchrotron SOLEIL, France*; T. Maroutian, P. Lecoeur,* Université Paris-Sud - CNRS, France*; B. Mersey,* Université de Caen, France*; A.F. Santander-Syro,* Université Paris-Sud - IN2P3, France

A critical challenge of modern materials science is to tailor novel states of matter suitable for future applications beyond semiconductor technology. In this prospect, 2D electron systems (2DESs), analogous to those created in semiconductors heterostructures, have been observed at the LaAlO$_3$/SrTiO$_3$ interface [1] and show amazing physical properties like metal-to-insulator transitions, superconductivity or magnetism. It was then demonstrated that 2DES could also be stabilized at the surface of SrTiO$_3$ [2] or other oxides [3], although it requires the use of intense UV or X-ray synchrotron radiation to desorb oxygen from the surface and dope it with electrons. This opened the way for the use of surface sensitive techniques, like Angle-Resolved PhotoEmission spectroscopy (ARPES) which provided a clear description of the microscopic electronic structure of the quantum well states. However, 2DESs at oxygen-deficient surfaces can be only manipulated and studied in ultra-high vacuum (to preserve the O-vacancies from re-oxidation) and thus, are not suited for experiments or applications at ambient conditions. Here we demonstrate a new, versatile and cost-effective method to generate passivated 2DESs on large areas of UHV-prepared functional oxide surfaces. It consists in a simple evaporation at room temperature of an aluminum film onto the oxide surface. Aluminum acts as a reducing agent and pumps oxygen from the substrate. It oxidizes into an insulating AlO$_x$ layer, protecting an underlying homogeneous 2DES confined in the first atomic planes of the oxide substrate. 2 Å of Al are sufficient to create a saturated 2DES on differently oriented surfaces of SrTiO$_3$, anatase-TiO$_2$, or BaTiO$_3$, which were all studied by ARPES to determine the band structure (effective mass, orbital order and charge carrier densities) [4].

[1] A. Ohtomo, H. Y. Hwang, Nature **427**, 423 (2004).

[2] A. F. Santander-Syro, O. Copie, T. Kondo, F. Fortuna, S. Pailhes, R. Weht, X. G. Qiu, F. Bertran, A. Nicolaou, A. Taleb-Ibrahimi, P. Le Fèvre, G. Herranz, M. Bibes, N. Reyren, Y. Apertet, P. Lecoeur, A. Barthélémy, M. J. Rozenberg, Nature **469**, 189 (2011).

[3] T. C. Rödel, F. Fortuna, F. Bertran, M. Gabay, M. J. Rozenberg, A. F. Santander-Syro, and P. Le Fèvre, Phys. Rev. B **92**, 041106 (2015).

[4] T. C. Rödel, F. Fortuna, S. Sengupta, E. Frantzeskakis, P. Le Fèvre, F. Bertran, B. Mercey, S. Matzen, G. Agnus, T. Maroutian, P. Lecœur, and A. F. Santander-Syro, Adv. Mater. **28**, 1976 (2016).

8:40am **SA+2D+AC+AS+TF-TuM3 Advanced Spectro-microscopy of Ion Irradiated Graphene-metal Interfaces: From Substitutional Implantation to Nanobubble Formation***, **Andrea Locatelli,** A. Sala, T.-O. Menteş,* Elettra - Sincrotrone Trieste, Italy*; G. Zamborlini,* Peter Grünberg Institute (PGI-6) Jülich*; L. Patera, C. Africh,* IOM-CNR Laboratorio TASC, Italy*; M. Imam, N. Stojić, N. Binggeli,* Abdus Salam International Centre for Theoretical Physics, Italy **INVITED**

The exploitation of graphene in the next generation electronics depends on our ability of preserving and tailoring its unique electronic and transport properties. Whereas the preservation of the free-standing characteristics of graphene demands to decouple the film from its support, their modification requires functionalization and thus chemical doping. Varied methods have been devised to implant exospecies into and under the C lattice mesh. Among them, irradiation of nitrogen ions has emerged as one of the most powerful approaches, producing enhanced physical and chemical properties rather than detrimental effects. At variance with other methods, ion irradiation enables implementation of lithographic approaches for doping graphene, a feature which is most desirable for creating arrays of devices.

The characterization of complex and laterally-heterogeneous interfaces, such as that of ion-irradiated graphene, demands advanced microscopy tools. Here, we will demonstrate the present capabilities of cathode lens spectro-microscopy. As a first example, we report a proof of principle experiment demonstrating that low energy ion irradiation through an aperture can be used to achieve local control on doping in graphene. Our study tackles the fabrication of a 2-dimensional heterojunction between *n*-doped and almost neutral single-layer graphene on Ir(111). Here, XPEEM is employed to characterize the transition region between areas with metallic and semimetal-like density of states and its thermal stability [1].

Then, we will focus on the irradiation of graphene with low energy Ar and Ne ions, reporting on the formation of nanobubbles upon annealing. The morphology and local stoichiometry of the Ar-ion irradiated interface were characterized by LEEM, XPEEM and STM, specifically addressing the thermal stability of noble gas nanobubbles. These structures display a lateral size up to tens of nanometers and height of several atomic layers. Remarkably, the Ar clusters remain trapped under graphene up to temperatures nearing 1100°C, suffering no material loss through the mesh or its edges. Ab-initio calculations demonstrate that intercalated Ar undergoes extreme pressures, up to few tens GPa. The nanobubble ripening process turns out to be driven by the minimization of the energy cost of film distortion and loss of adhesion [2]. The electronic properties of the ion irradiated interface will be also discussed.

[1] A. Sala, G. Zamborlini, T.O. Menteş, A. Locatelli; Small **11**(44), 5927–5931(2016).

[2] G. Zamborlini, M. Imam , L.L. Patera , T.O. Menteş , N. Stojić , C.Africh , A. Sala , N. Binggeli , G. Comelli and A.Locatelli; Nano Lett. **15**(9), 6162–6169 (2015).

9:20am **SA+2D+AC+AS+TF-TuM5 Gas-source MBE Growth of 2D Materials Examined using X-ray Synchrotron Radiation***, **Hugh Bullen,** R.K. Nahm, S. Vishwanath, H.G. Xing, J.R. Engstrom,* Cornell University

Two-dimensional materials, in particular transition metal dichalcogenides, are attracting considerable interest from both fundamental and applied viewpoints. Here we report on the gas-source MBE growth of thin films of WSe$_2$ using W(CO)$_6$ and elemental Se, where we monitor the process *in situ* and in real time with X-ray synchrotron radiation. In this work, we have two independent means to introduce the thin film constituents: a (supersonic) gas-source of W(CO)$_6$ in a carrier gas of He, and an effusion cell containing elemental Se. We can collect both the scattered X-rays, and those emitted due to fluorescence. We have examined growth for a variety of conditions: growth with coincident fluxes of W(CO)$_6$ and Se, and growth in which one of the two reactant fluxes was gated. These experiments were conducted at several different substrate temperatures, on graphite (HOPG), and on so-called epitaxial graphene (graphene on SiC). First, for continuous exposure to W(CO)$_6$ and Se we observe, after an short incubation period, continuous growth of both the W and Se intensities. Analysis of this data indicates a stoichiometry consistent with WSe$_2$. We also find diffraction features consistent with the crystalline phase of WSe$_2$, where the basal plane is in the plane of the substrate. Particularly interesting is what we see when one of the reactants is gated: We have found that growth is halted by gating the incident flux of W(CO)$_6$, while the film is stable in the presence of a flux of Se$_n$. The physical properties of these thin films are essentially the same as those grown using continuous exposure to both reactants. We find a much different result when the flux of Se$_n$ is gated: the absence of Se, but the presence of W(CO)$_6$, leads to *loss* of Se, and an increase in the amount of W. Since the termination of both fluxes does not lead to the loss of either element, it must be that W(CO)$_6$ is providing the species that leads to the loss of Se. The most likely scenario is that a ligand exchange reaction occurs producing the gas phase species, SeCO(*g*). Perhaps our most exciting result involves the growth of WSe$_2$ on epitaxial graphene. In these experiments, in addition to measuring the X-ray fluorescence, we also measured *in situ* and in real time the intensity at the anti-Bragg condition, which we have shown to be are very effective way to monitor thin film crystal growth. We observe strong and sustained oscillations, indicating layer-by-layer growth of WSe$_2$ of up to at least 5 monolayers. This is a very exciting result, and it indicates the effective use of synchrotron radiation to examine the growth of TMD thin films.

9:40am **SA+2D+AC+AS+TF-TuM6 Nanostructured Surface of Multilayer Graphene on Cubic-SiC**, ***Victor Aristov,*** ISSP RAS, Chernogolovka, Russia, Russian Federation; *H.-C. Wu,* BIT, Beijing, China; *O.V. Molodtsova, S.V. Babenkov,* DESY, Hamburg, Germany; *A.N. Chaika,* ISSP RAS, Chernogolovka, Russia, Russian Federation

The results of atomically resolved scanning tunneling microscopy, low energy electron diffraction, low energy electron microscopy, micro-LEED and angle resolved photoelectron spectroscopy studies of graphene synthesized on cubic-SiC will be presented. Uniform few layer graphene was fabricated on SiC/Si wafers using Si-atom sublimation followed by SiC surface layer graphitization during high-temperature annealing in ultrahigh vacuum. Using the new dynamic-XPS end-station, based on the Argus spectrometer installed on the high-brilliance soft X-ray P04 beamline at PETRA III (DESY) one can control layer-by-layer graphene growth in real time following the evolution of the photoemission spectra with an acquisition time of ~ 0.1 sec/spectrum. Recording spectra during graphene growth on the SiC/Si(001) wafer, one can stop the process as soon as the desired number of graphene layers is reached. Angle-resolved photoemission measurements allowed us to extract the information about the electronic structure and the stacking order of the few-layer graphene on SiC(001). The preferential directions of the nanodomain boundaries coincide with the directions of carbon atomic chains on the SiC(001)-c(2x2) reconstruction, fabricated prior to graphene synthesis. Electrical measurements conducted on the vicinal SiC(001) samples demonstrate the opening of a transport gap in the nanostructured trilayer graphene. Our measurements demonstrate that the self-aligned periodic NBs can induce a charge transport gap up to 1.3 eV at low temperatures. The transport gap opening produces high current on-off ratio of 10^4. This development may lead to new tuneable electronic nanostructures made from graphene on cubic-SiC, opening up opportunities for a wide range of new applications.

This work was supported by the RAS, RFBR grants No 140200949 and 140201234, by the BMBF-Project No. 05K12GU2, PSP-Element No. U4606BMB1211, by a Marie Curie IIF grant No 12/IA/1264, by SPP 1459 of DFG.

11:00am **SA+2D+AC+AS+TF-TuM10 Full-field Photoelectron Spectromicroscopy of Ferroelectric Surfaces**, ***Nicholas Barrett,*** CEA Saclay, France **INVITED**

Advanced low energy electron optics combined with synchrotron radiation has transformed photoelectron emission microscopy (PEEM) into a powerful technique for the microscopic study of material surfaces. High lateral, wave-vector and energy resolution makes it possible to probe spatial variations in the chemical and electronic structure of nanoscale materials.

Perovskite based ferroelectrics are one important family of oxide materials requiring such analysis. Their robust polarization, switchable by an external field, makes them extremely interesting candidates for post-CMOS electronics.

First, the principles of fully energy filtered PEEM will be presented. By a combination of both direct and reciprocal space imaging the surface charge, work function, topography, chemistry and band structure of ferroelectric materials can be studied. This will then be illustrated by several examples.

The surface charge and hence the ferroelectric polarization can be estimated from the the work function as measured in PEEM. There is a critical film thickness in $BiFeO_3$ below which the film polarization drops to zero despite constant tetragonality, suggesting the formation of stripe domains in ultra-thin films [1].

The band structure of ferroelectric domains in $BaTiO_3$(001) are studied using spatially resolved reciprocal space PEEM and synchrotron radiation. The dispersion relations can be correlated with domain chemistry and in- and out-of-plane ferrolectric polarization [2].

The ferroelectric stability as a function of temperature of piezo force microscopy written domains has been studied using threshold PEEM. A Curie temperature of 490°C is recorded which is also dependent on the poling voltage.

We will conclude with a brief demonstration of an operando PEEM experiment, opening up the perspective of studying the changes in functional oxide properties under electric stimulation.

[1] J. Rault, W. Ren, S. Prosandeev, S. Lisenkov, D. Sando, S. Fusil, M. Bibes, A. Barthélémy, L. Bellaiche and N. Barrett, Physical Review Letters 109, 267601 (2012)

[2] J. E. Rault, J. Dionot, C. Mathieu, V. Feyer, C. M. Schneider, G. Geneste, and N. Barrett, Physical Review Letters 111, 127602 (2013)

11:40am **SA+2D+AC+AS+TF-TuM12 Electron Confinement at Magnetic Oxide Interfaces: Insight from Photoemission Spectroscopy**, ***Martina Mueller,*** Forschungszentrum Juelich GmbH, Germany **INVITED**

Recent advances in the fabrication of oxide heterostructures with atomic-scale precision has enabled interface and size control of complex oxide materials, for which unique phenomena with no bulk analogues have been demonstrated. In designated heterostructures, two-dimensional electron systems can be confined at oxide interfaces -- typically along the growth direction – which offer possible alternatives to conventional semiconductors in terms of functional (e.g. spin-polarized) electronic transport properties. Using redox-controlled synthesis [1, 2], the electronic properties of oxide heterostructures and interfaces can be engineered -- in terms of quality that were thought to be unique to semiconductors.

The basic idea of electron confinement applies to complex oxides just as to conventional semiconductors, but the physics is much richer. In metal oxides, confined electrons are subject to strong electron-electron interactions leading to a variety of physical phenomena that can be accessed, modified and controlled. For example, using oxides with intrinsic magnetic order allows to explore spin-related phenomena in low dimensions.

We present how to create two-dimensional electronic systems (2DES) in all-oxide heterostructures using EuO, a ferromagnetic insulator [1]. By interfacing Eu metal to $SrTiO_3$, a non-magnetic insulator, a redox reaction takes place at the interface which involves the oxidation of Eu metal into ultrathin EuO [2], and the reduction of Ti cations. This redox process strongly suggests that mobile electrons are created at the resulting interface. Using synchrotron-based soft, hard and angle-resolved photoemission spectroscopy [3] we probe the electronic structure and chemical composition at the EuO/STO interface and give a direct indication of a redox-created 2DES. The observed electronic confinement in all-oxide heterostrctures provides a route for controlling spin functionality for emerging applications.

[1] G. Prinz, T. Gerber, A. Lorke, M. Müller, submitted (2016)

[2] T. Gerber, M. Müller *et al*, J. Mater. Chem. C, 4, 1813 (2016)

[3] M. Müller *et al*, J. Electron Spectrosc. Relat. Phenom. 208, 24 (2016)

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