

PCSI

Room Redondo - Session PCSI-WeA1

Photoemission Spectroscopy and high-k Dielectrics

Moderator: Igor Zutic, University at Buffalo-SUNY

2:00pm **PCSI-WeA1-1 Optical Field-Driven Ultrafast Electron Control Inside of Graphene and at the Surface of Metal Needle Tips**, Peter Hommelhoff, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany **INVITED**

With femtosecond laser pulses, electrons can be driven on ultrafast timescales. If these laser pulses are just two optical cycles long (roughly 5 fs pulse duration at 800 nm center wavelength, $1 \text{ fs} = 10^{-15} \text{ sec}$), it matters how the exact optical field looks like within the laser pulse envelope – but this optical field can be well controlled these days in so-called phase-stable laser pulses.

This talk will give an overview of our work circling around controlling electrons on sub-femtosecond time scales with phase-controlled laser pulses. After a brief introduction to these laser pulses, the first part of the talk will focus on strongly driven electrons inside of graphene. We could show that electrons undergo coherent coupled intraband motion and interband transitions. More specifically, we could demonstrate subsequent coherent Landau-Zener transitions, allowing us to realize Landau-Zener-Stückelberg-Majorana interferometry with electrons inside of graphene. Based on this physics, we could demonstrate a record-fast current switch, with a turn-on time of around 1fs, leading to real charge carrier generation [1]. Just recently, we also gained deep insights into how the graphene-gold interface can be used to read out virtual charge carriers. Based on these insight, we could demonstrate a logic gate potentially providing petahertz bandwidths [2].

The focus of the second part of the talk will be on strongfield physics at the surface of metal needle tips. Here we could demonstrate that we can control photo-emitted electrons with the help of phase-controlled laser pulses fully coherently. We observe all hallmarks of strongfield physics, now at the surface of a solid [3]. With more complex two-color laser fields, we could fully reconstruct the attosecond-fast emission dynamics ($1 \text{ as} = 10^{-18} \text{ sec}$). In particular, we find a tunneling time of $710 \pm 30 \text{ attosec}$, i.e., we can now trace electron emission dynamics from solids with attosecond time resolution [4].

[1] Higuchi et al., Nature **550**, 224 (2017); Heide et al., PRL **121**, 207401 (2018); Heide et al., Nat. Phot. **14**,

219 (2019); Heide et al. NanoLett. **21**, 9403 (2021); Heide et al., PRA **104**, 023103 (2021)

[2] Boolakee et al., Nature **605**, 251 (2022);

[3] Krüger et al., Nature **475**, 78 (2011); Krüger et al., J. Phys. B **51**, 172001 (2018);

[4] Dienstbier et al., manuscript submitted

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2:40pm **PCSI-WeA1-9 The Diamond (111) Surface Reconstruction and Epitaxial Graphene Interface**, Simon Cooil, University of Oslo, Norway

A rejuvenated interest in diamond as a state-of-the-art electronic material has occurred over the last couple of decades as its potential for use in emerging quantum information and sensing technologies becomes apparent. The growing demand for miniaturisation has also led to increased interest in the nanoscale properties of diamond and the production of diamond-graphene (sp³ – sp²) interfaces. However, fundamental studies of the diamond (111) surface electronic structure remain incomplete and controversy surrounding the metallic[1] or semiconducting[2] nature of the (2×1) surface reconstruction remains unresolved. We therefore follow the evolution of the diamond (111) surface electronic and physical structure as it undergoes reconstruction and subsequent graphene formation with angle-resolved photoemission spectroscopy, low energy electron diffraction, and compare to complementary density functional theory calculations.

The studies begin on the hydrogen terminated H:C(111)-(1×1) surface, proceeding to the C(111)-(2×1) surface reconstruction that occurs following detachment of the surface adatoms at 920 °C. We then continue through to the liberation of the reconstructed surface atoms into a free-standing monolayer of epitaxial graphene at temperatures above 1000 °C. Our results show that the C(111)-(2×1) surface is metallic as it has electronic states that intersect the Fermi-level. This is in strong agreement with a

symmetrically π-bonded chain model and should contribute to resolving the controversies that exist in the literature surrounding the electronic nature of this surface. The graphene formed at higher temperatures exists above a newly formed C(111)-(2×1) surface and appears to have little substrate interaction as the Dirac-point is observed at the Fermi-level. Finally, we demonstrate that it is possible to hydrogen terminate the underlying diamond surface by means of plasma processing without removing the graphene layer, allowing for tuneable substrate interactions at the graphene-semiconductor interface[3].

1. Bechstedt, F., et al., *Origin of the Different Reconstructions of Diamond, Si, and Ge(111) Surfaces*. Physical Review Letters, 2001. **87**(1): p. 016103.
2. Graupner, R., et al., *Dispersions of surface states on diamond (100) and (111)*. Physical Review B, 1997. **55**(16): p. 10841.
3. Reed, B.P., et al., *Diamond (111) surface reconstruction and epitaxial graphene interface*. Physical Review B, 2022. **105**(20): p. 205304.

2:45pm **PCSI-WeA1-10 Hard X-Ray Photoelectron Spectroscopy for Material Science Applications**, P. Amann, Scienta Omicron, Germany; Takahiro Hashimoto, Scienta Omicron

Investigating buried interfaces, device electronics or batteries by chemically sensitive instrumentation is highly desired in materials science applications. X-ray photoelectron spectroscopy (XPS) is a powerful method to investigate the chemical nature of surfaces. However, investigations of buried interfaces occurring in, e.g., device electronics are difficult as the energies of the created photoelectrons are not high enough and scattering inside the material's bulk limit the detected signal intensity.

During the past decade, increased attention has been shown to hard X-rays in the photoelectron spectroscopy field [1]. This is primarily due to the increased information depth enabled by the higher photon energies.

Using Scienta Omicron's HAXPES Lab, featuring a monochromatic Ga Ka X-ray source in combination with a hemispherical electron analyzer that includes a +/- 30 degree acceptance angle [2], we were able to investigate buried interfaces, in-operando devices and real world samples (Fig.1 A). [3] In this presentation we will give an overview of applications with a focus on bias-applied measurements from device electronics. Si-based materials are widely used in the semiconductor industry and are subject to chemical changes upon voltage application. Investigating a layered structure of 4 nm thick ZrO₂ on 20 nm TiN on p-doped Si, the binding energy shift could be characterized upon applied voltage in-operando without sample destruction. These changes can be assigned to trapped carriers in the defect level at the Ti-N/p-Si interface. (Fig. 1 B, C).

2:50pm **PCSI-WeA1-11 Advanced Semiconductor-Oxide Interfaces of Ferroelectric and RRAM Devices**, Rainer Timm, Lund University, Sweden **INVITED**

Ferroelectric field effect transistors (FeFET) with ultrathin (below 5 nm) ferroelectric Hf_{1-x}Zr_xO₂ (HZO) layers or resistive random access memory (RRAM) stacks based on oxygen vacancy HfO₂ layers are currently in the focus of research towards steep-slope transistors, neuromorphic networks, and computation-in-memory application. Especially promising is their combination with III-V semiconductor substrates such as InAs, which offers superior charge carrier mobility compared to Si. Our collaborators at the Nanoelectronics group of Lund University are pioneering in developing InAs nanowire-based FeFET gate-all-around [1,2] and RRAM [3,4] devices including 1 transistor 1 resistor structures integrated in a single nanowire [4]. These novel devices have in common that their performance critically relies on the quality and structure of the semiconductor-oxide interface. Here, I will present in-depth studies of such interfaces using *operando* soft- and hard X-ray photoemission spectroscopy (XPS/HAXPES), complemented by other synchrotron-based methods, which are resulting in a paradigm change in the understanding of MOS structures.

For InAs/HfO₂ RRAM devices, we found that the existence of a sufficiently thick As-oxide interface layer, obtained through extended oxygen plasma pulses, below the HfO₂ film is crucial for enabling resistive switching [4]. This is contrary to the case of conventional InAs-based MOSFETs where we previously were aiming for the perfect self-cleaning and observed complete As-oxide removal during HfO₂ deposition [5]. Furthermore, also the structure of the HfO₂/TiN top metal interface of RRAM devices is relevant, where substantial band-bending can result in strong Schottky barriers [3].

Wednesday Afternoon, January 18, 2023

From initial *operando* HAXPES studies of FeFET devices, with applied dc bias or upon positive-up-negative-down (PUND) switching pulses, we derived the unexpected result that the applied bias does not drop across the ferroelectric HZO oxide layer, but instead only across a very thin interfacial InAs-oxide layer. Simulations explain this behavior by the defect density in the interfacial oxide. Nevertheless, the FeFETs show high polarization values and good endurance.

The close connection between state-of-the-art device development and detailed characterization of the involved materials science aspects are the key to an improved understanding of the device functionality.

- [1] A. E. Persson et al., Appl. Phys. Lett. **116**, 062902 (2020).
- [2] R. Atle et al., Adv. Mater. Interfaces **2022**, 2201038 (2022).
- [3] Z. Yong et al., Appl. Surf. Sci. **551**, 149386 (2021).
- [4] M. S. Ram et al., Nature Electronics **4**, 914 (2021).
- [5] R. Timm et al., Nature Communications **9**, 1412 (2018).

3:30pm **PCSI-WeA1-19 Stoichiometric Control and Optical Properties of BaTiO₃ Thin Films Grown by Hybrid MBE**, *Benazir Fazlioglu Yalcin, A. Suceava, T. Kuznetsova, Z. Wang, I. Dabo, V. Gopalan*, Penn State University; *R. Engel-Herbert*, Paul Drude Institute, Germany

BaTiO₃ is a technologically tremendously relevant material in the perovskite oxide class with above room temperature ferroelectricity and a very large electro-optical coefficient, making it highly suitable for emerging electronic and photonic devices. [1,2] An easy, robust, straightforward, and scalable growth method is required to synthesize epitaxial BaTiO₃ thin films with reproducible thin film properties allowing sufficient control over the film's stoichiometry. Here, we report on the growth of BaTiO₃ thin films by hybrid molecular beam epitaxy. A self-regulated growth window was identified using complementing information (Fig. 1a, b), the evolution of reflection high energy electron diffraction images during film growth, the deviation of the intrinsic lattice parameter, and film surface morphology. Subsequent optical characterization of the BaTiO₃ films by spectroscopic ellipsometry revealed refractive index and extinction coefficient values closely resembling stoichiometric bulk BaTiO₃ (Fig. 1c, 1d). In addition to the expected degradation of optical properties with increasing deviation from the self-regulated growth window, an optical absorption peak emerged at 700 nm even in the absence of a detectable lattice parameter expansion of BaTiO₃ thin films. This feature was identified by first-principles calculation as Ba vacant lattice site. In addition, optical second harmonic generation analysis was performed to determine the polar symmetry of the films which revealed bulk-like SHG coefficients. In this talk, we will discuss how the optical properties of BaTiO₃ can be utilized as a much finer probe than intrinsic lattice parameter expansion to determine the stoichiometry level present in BaTiO₃ films. This work is supported by the US Department of Energy, Basic Energy Sciences, under Award Number DE-SC0020145 as part of the Computational Materials Sciences.

Figure 1. (a) A RHEED image taken along the [100] direction (b) an AFM micrograph of a BaTiO₃ film grown at 58 mTorr (c) Ordinary refractive indices, n_o , and (d) ordinary extinction coefficients, k_o , of BaTiO₃ thin films plotted together with bulk BaTiO₃

- [1] S. Abel et al., Nat. Mater. **18**, 42 (2019)

- [2] L. Mazet, et al., Sci. Technol. Adv. Mater. **16**, 36005 (2015)

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