

PCSI

Room Redondo - Session PCSI-MoA2

Organics, Semiconductors, and Molecules

Moderator: Nancy Haegel, National Renewable Energy Laboratory

3:40pm PCSI-MoA2-21 Single-Molecular Tunnel Junctions: The BN/CC Isosterism Effectiveness in PAH Models, *Sandra Rodriguez Gonzalez*, Universidad Autónoma de Madrid, Spain

Boron-Nitrogen (BN)/Carbon-Carbon (CC) isosterism constitutes one of the most versatile and efficient doping techniques to improve the Polycyclic Aromatic Hydrocarbons (PAHs) properties in organic optoelectronic devices.[1] The diatomic polar BN unit modifies the electronic structure, and hence the aromaticity, simply by swapping its orientation; but maintains the good co-planarity and rigidity of the backbone. Motivated by the scarcely employ of this type of isoelectronic substitution to modulate the electronic transport properties in single-molecule devices, we report the BN/CC isosterism effect on the aromaticity and single molecule conductance in a series of 1,4 azaborine acene derivatives, as PAHs models.

Studied molecules were strategically designed and synthesized, to reveal a first, the unequivocal and utmost effect of BN doping on the conductance. Scanning tunneling microscope break-junction (STM-BJ) measurements, in combination with the nonequilibrium Green's function (NEGF) formalism coupled to self-energy corrected Density Functional Theory (DFT+ Σ) method,[2] within the Landauer framework, were employed.[3] A comprehensive study was possible considering different molecular polarization orientations in the [Au-molecule-Au] theoretical model junctions, and conformational changes related to the BN-substitution.

[1]. (a) C. Chen, C-Z. Du, X-Y, Wang, *Adv. Sci.*, 2022, 2200707; (b) X-Y. Wang, et. al., *Angew. Chem. Int. Ed.*, 2013, 52, 3117; (c) J. S. A. Ishibashi, et. al., *Dalton Trans.*, 2019, 48, 2807; (d) J. Huang, Yi Li, *Frontiers in Chemistry*, 2018, 341,1. [2]. (a) J. G. Fallaque, S. Rodríguez-González, F. Martín, C. Díaz, *J. Phys.:Condens.Matter.*, 2022, 34, 435901; (b) J. G. Fallaque, S. Rodríguez-González, C. Díaz, F. Martín, *Nanoscale*, 2022, 14, 464. [3]. L. Palomino Ruiz, S. Rodríguez González, I. R. Márquez, A. G. Campaña, J. M. Cuerva, F. Martín, C. Díaz, A. Millán, M. T. González, *Angew. Chem. Int. Ed.* 2021, 60, 6609.

3:45pm PCSI-MoA2-22 Surface Resonant Raman Scattering: Analysis of Vibrations at Clean Surfaces and Monolayer Films, *Norbert Esser*, TU Berlin and Leibniz-Institut für Analytische Wissenschaften-ISAS-e.V., Germany

INVITED

Raman spectroscopy is a standard analytical method to study organic and inorganic material structures. For analysing ultrathin films, plasmonic surface enhancement (SERS) or tip enhancement (TERS) is common nowadays. However, even without such plasmonic field enhancement, Raman spectroscopy can be sensitive enough to record surface phonons, surface resonances or adsorbate vibrations. This is strongly favoured by surface resonant Raman scattering, i.e. resonance enhancement involving surface electronic transitions. By choosing an appropriate energy of the exciting laser line, a surface specific resonance enhancement may be achieved.

On clean surfaces, confined phonons and phonon resonances have been detected using surface resonant excitation on Si, Ge, III-Vs and Cu. The termination of surfaces by adsorbates has been analysed with sub-monolayer precision, e.g. for Sb on III-V(110) substrates, Pb and Au on Si(111), H on Si(111) and O on Cu(110).

In collaboration with theory groups, DFT-based calculations of the structure and electronic bands have revealed the mechanism of surface resonant Raman Scattering. Moreover, comparison of theory and experiment allows one to conclude on particular surface/adsorbate structures. In particular, I will discuss the interplay between atomic and electronic structure, metal-semiconductor transition and the effect of strong electron-phonon-coupling in quasi 1D-nanowires (In and Au on Si(111) and Si(553)).

On conductive samples, Raman scattering by the charge transfer mechanism may play an important role, in addition to deformation potential scattering. Please note that charge transfer is an important part of SERS and TERS, called chemical enhancement effect. The free carrier concentration in the scattering volume may lead to a notable difference for Raman spectroscopy on surfaces as well, e.g. for conductive nanowire structures and for metals.

4:25pm PCSI-MoA2-30 Ordered Monolayer Growth of N-Heterocyclic Carbenes on Silicon Surfaces, *M. Franz*, Technische Universität Berlin, Germany; *S. Chandola*, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Germany; *M. Koy*, Westfälische Wilhelms-Universität Münster, Germany; *Robert Zielinski*, Technische Universität Berlin, Germany; *H. Aldahhak*, Universität Paderborn, Germany; *M. Das*, *M. Freitag*, Westfälische Wilhelms-Universität Münster, Germany; *U. Gerstmann*, Universität Paderborn, Germany; *D. Liebig*, *A. Hoffmann*, *C. Kosbab*, *M. Rosin*, Technische Universität Berlin, Germany; *W. Schmidt*, Universität Paderborn, Germany; *C. Hogan*, Università di Roma 'Tor Vergata', Italy; *F. Glorius*, Westfälische Wilhelms-Universität Münster, Germany; *N. Esser*, Leibniz-Institut für Analytische Wissenschaften – ISAS e.V., Germany; *M. Dähne*, Technische Universität Berlin, Germany

N-Heterocyclic carbenes (NHCs) have been shown to be excellent modifiers and anchors for the functionalization of surfaces, but the investigation has been limited to metals. Thus a controlled functionalization of silicon surfaces by ordered NHC layers is particularly interesting. Here, we present an extensive scanning tunneling microscopy (STM), density functional theory, and X-ray photoemission spectroscopy study of the growth of NHCs on Si(111) and demonstrate a binding to the surface via a single Si-C bond. We varied the molecule-substrate interaction by using different model NHCs on a Si(111) $\sqrt{3}\times\sqrt{3}R30^\circ$ -B surface. This substrate is deactivated by the subsurface incorporation of B atoms and thus particularly suited for the ordered growth of organic films. We find that the NHC molecules bind via a single covalent C-Si bond in an upright adsorption geometry and demonstrate the formation of highly ordered monolayers that are thermally stable and show strong work function reductions. The degree of ordering in the monolayers as well as their periodicity depends on the NHC molecule, in particular on the nature of its sidegroups, as well as on the defect density of the substrate.

4:30pm PCSI-MoA2-31 Arrangement and Electronic Properties of Cobalt Phthalocyanine Molecules on B-Si(111)- $\sqrt{3}\times\sqrt{3}R30^\circ$, *Susi Lindner-Franz*, *M. Kubicki*, Technische Universität Berlin, Germany; *H. Eisele*, Otto-von-Guericke-Universität Magdeburg, Germany; *M. Dähne*, *M. Franz*, Technische Universität Berlin, Germany

In this contribution, we investigate the molecular arrangement and electronic properties of cobalt phthalocyanine CoPc on the passivated B-Si(111)- $\sqrt{3}\times\sqrt{3}R30^\circ$ (Si:B) surface in detail by means of scanning tunneling microscopy (STM) as well as tunneling (STS) and photoemission spectroscopy (PES). The STM images clearly show that submonolayers of CoPc lie flat on the surface, with either a four-leaf cloverlike or a circular appearance, depending on the presence of neighboring molecules or surface defects, which affect the molecular rotation, and that a selective orbital hybridization occurs. Furthermore, PES data explain that the spectral changes are mostly related to the chemical interactions, while the previously discussed changes of the band bending only play a minor role. For high CoPc coverages, in contrast, the molecules are tilted with respect to the Si:B surface, establishing exceedingly ordered molecular arrangements. The STS data in show that several monolayer thick films of CoPc exhibit identical electronic properties as compared with pure CoPc.

4:35pm PCSI-MoA2-32 Bio-Resorbable Memristor with Alginate as an Active Layer for Transient Electronics, *Hojung Jeon*, *Y. Rim*, Department of Intelligent Mechatronics Engineering, and Convergence Engineering for Intelligent Drone, Sejong University, Republic of Korea

Bio-resorbable and transient electronics that imply chemically or physically dissolution after a certain period operation have drawn considerable attention due to the demand of biocompatibility for eco-friendly applications [1]. This work presents alginate-based resistive random-access memory (RRAM) to establish bio-resorbable memristive system. Alginate is assumed as the switching layer by using solution process and prove its bipolar switching behavior, which refers we can apply set/reset operations in small ranges (-2V~3V) of voltage to enhance power consumption efficiency. High stability was also verified by endurance and retention time due to tolerance and long-term maintenance. Bio-resorbable properties of RRAMs, which were fabricated with water-soluble Mg electrodes was investigated by fully dissolving in DI water and dissolving time controllability was also demonstrated by modulating the thickness of Al₂O₃ capping layer, which was deposited using atomic layer deposition (ALD). With this approach, it is expected that biocompatible RRAMs can apply to a neuromorphic system by fitting two terminal devices which have closely characterized structures with artificial synapses [2]. Controlling the dissolving time, we can also consider of the hardware-security.

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Furthermore, the devices have implantable characteristics in human-body so it can be used in the area of medical surgery or health-care problems.

Fig. Set and reset of bio-resorbable alginate memristor devices

Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. 2020R1A2C1013693), Korea Institute for Advancement of Technology (KIAT) grant funded by By the Ministry of Trade, Industry & Energy (MOTIE, Korea) (P0012451, The Competency Development Program for Industry Specialist) and the Technology Innovation Program - (20016102, Development of 1.2kV Gallium oxide power semiconductor devices technology, RS-2022-00144027, Development of 1.2kV-class low-loss gallium oxide transistor) funded by MOTIE.

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