Applied Surface Science Division
Room 320 - Session AS+2D+EM+MS+NS+SS+TF-ThA

Probing Defects at Surfaces and Interfaces
Moderators: Michaeleen Pacholski, The Dow Chemical Company, **Zachary Robinson**, SUNY Brockport

2:20pm AS+2D+EM+MS+NS+SS+TF-ThA-1 Controlling InP Quantum Dot Surface Defects Using ALD-inspired Surface Chemistry and Phosphorus Kα and Kβ X-ray Emission Spectroscopy, *Nayon Park*, University of Washington **INVITED**
Colloidal InP quantum dots are a leading heavy-metal-free semiconductor material for spectral downconversion in current generation display technologies and future generation energy efficient LEDs. Achieving the brightest and narrowest photoluminescence (PL) relies on the synthesis of structurally and electronically defect-free quantum dots. InP quantum dots' high propensity for oxidation and the inherent oxidative defects arising from commonly used synthesis methods therefore motivates a systematic approach to probe InP oxidation as a function of synthesis and surface treatments and correlation with the resultant optical properties. Phosphorus X-ray Emission Spectroscopy (XES) presents itself as an exceptional tool in this regard. In this talk, I will show recent results from computational modeling where we find that native InP surface oxides give rise to dark states near the band edge. Replacing the surface indium with zinc to form a monolayer ZnO shell results in the reduction of dark states. Using ALD-inspired successive ionic layer adsorption and reaction (SILAR), we developed the colloidal, layer-by-layer growth strategy of metal oxide shells (i.e. ZnO, CdO, GaO$_x$, AlO$_x$) on InP quantum dots at room temperature using common ALD precursors (*i.e.*, metal alkyls and water). Metal oxide-shelled InP QDs generally show enhanced PL and evidence of bulk and local structural perturbations arising from the metal oxide as determined by X-ray diffraction and X-ray absorption spectroscopy. Further, we explore the impact of these metal oxide interfaces on the PL QY and emission linewidth of InP/ZnSe core/shell QDs. Upon growing a thin ZnSe shell, we observe improved PL properties, which we hypothesize to be attributable to the inhibition of phosphorus migration to the shell due to the presence of the metal oxide interlayer, as supported by X-ray emission spectroscopy. Taken together, these results suggest a clear path forward in the control and design of complex QD interfaces with atomistic insight for optoelectronic technologies.

3:00pm AS+2D+EM+MS+NS+SS+TF-ThA-3 Characterization of MAX Phases using a Combination of Micro-spot XPS, HAXPES and C60 Cluster Depth Profiling, *Kateryna Artyushkova*, Physical Electronics USA*; M. Anayee, Y. Gogotsi,* Drexel University
Two-dimensional (2D) transition metal carbides, carbonitrides, and nitrides (MXenes) have seen significant increases in the number of research areas and publications. MXenes have a unique combination of properties that have led to many applications.[1] MXenes are usually synthesized by etching "A" layers that interleave "MX" layers in the bulk MAX precursors. MAX are represented by Mn+1AXn, where M denotes early transition-metals (Ti, V, Cr, Mo, etc.), X is N or C, and A is an A-group element such as Al, Si and others. During synthesis, impurities and defects may be introduced, which significantly impact the properties of the resulting materials. It is therefore critical to detect and quantify these defects and impurities.

X-ray Photoelectron Spectroscopy (XPS) has the advantages of being easily quantifiable and providing chemical information such as surface termination and oxidation. However, there are many challenges in using XPS for analyzing MAX and Mxene. The first is a very small size of MAX, less than a few tens of microns. With the development of focused scanning micro-probe X-rays, these limitations can be overcome. The other challenge is the extreme surface sensitivity of XPS. It is challenging to separate surface adventitious carbon and oxygen from possible oxygen incorporation in the carbon site. Depth profiling using a monatomic Ar ion beam is not suitable as it can introduce damage to the structure of MAX.

In this work, we are presenting two approaches to address this challenge. The first involves the application of Hard X-ray Photoelectron Spectroscopy (HAXPES), in which a monochromated Cr X-ray source is used to probe ~3 times deeper than a soft Al X-ray. The second utilizes a cluster ion gun source, such as C60, for damage-free depth profiling through individual MAX particles using ~8µm X-ray spot for probing if oxygen is present in the MAX structure.

3:20pm AS+2D+EM+MS+NS+SS+TF-ThA-4 Unusual Trend in Thermal Stability of Alanine Different Ni Surfaces, *J. Ontaneda,* Queen Mary University of London, UK*; R. Grau-Crespo,* University of Reading, UK*; **Georg Held**,* Diamond Light Source, UK
Chirally modified heterogeneous catalysts promise massive savings of cost and toxic waste in the production of enantiopure precursors for high-value chemicals such as pharmaceuticals, fertilizers, or fragrants [1]. A key aspect is the thermal stability of chiral modifiers, which generally are chiral organic molecules bound to a chemically active metal surface. The enantioselective hydrogenation of methylacteoacteate (MAA) is a topical reaction, which is catalysed by nickel modified with chiral carboxylic acids, such as alanine, tartaric acid, or aspartic acid [2]. The components of this catalytic system have been investigated using various surface sensitive techniques [3,4,5]. Here we present a study of the thermal stability of alanine on the three most common Ni surfaces, {111}, {100}, and {110}, using synchrotron-based temperature-programmed photoelectron spectroscopy and X-ray absorption spectroscopy. In contrast to common experience with smaller molecules, alanine is more stable on the more open {110} and {100} surfaces compared to {111}. Comparison with a detailed DFT study identifies structural and electronic effects that play a role in this unusual behaviour.

References:

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[3] Keane, M. A., Langmuir 1994, 10, 4560–4565.
[4] P. Tsaousis, et al., J. Phys. Chem. C 122 (11) (2018) 6186 – 6194.
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3:40pm AS+2D+EM+MS+NS+SS+TF-ThA-5 Correlative Theoretical and Experimental Study of the PC | X Interfacial Bond Formation (X = TiN, AlN, TiAlN) During DC Magnetron Sputtering, *Lena Patterer, P. Ondračka, D. Bogdanovski, S. Karimi Aghda, J. Schneider,* Materials Chemistry, RWTH Aachen University, Germany
Due to their outstanding oxidation and wear resistance, cubic (Ti,Al)N is widely used as protective coatings on forming and cutting tools. These characteristics make (Ti,Al)N also an attractive candidate for the protection of polymer components. The composition-induced changes in the interfacial bond formation of DC magnetron sputtered TiN, AlN, and Ti$_{0.25}$Al$_{0.25}$N$_{0.5}$ onto polycarbonate (PC) substrates are systematically investigated by correlating theory and experiment. In order to simulate the sputtering condition by *ab initio* molecular dynamics, a periodic structural model of bulk PC consisting of 394 atoms was bombarded by several Ti, Al, and N atoms with a kinetic energy of 1 eV. While both Ti and N atoms show high reactivity towards all functional groups of the polymer during the surface bombardment, Al atoms selectively react only with the carbonate group of PC or other reactive functional groups that have formed during previous bombardment events (e.g. C-N groups). At the PC | TiN and PC | TiAlN interfaces, Ti and N contribute equally to the interfacial bond formation, whereas the PC | AlN interface is defined mostly by C–N groups with Al-rich clusters forming on top of these groups. X–ray photoelectron spectroscopy data of the PC | X interfaces (X = TiN, AlN, TiAlN) show a very good agreement with the above-discussed predictions as the formation of C-N, C-(Ti,Al), and (C–O)–(Ti,Al) bonds is experimentally verified. This shows that the here employed computational strategy enables predictions of the interfacial bond formation between polycarbonate and metal nitrides, and it is reasonable to assume that the here proposed research strategy can be readily adapted to other polymer | inorganic material interfaces.

4:00pm AS+2D+EM+MS+NS+SS+TF-ThA-6 Using Resonant Photoemission Spectroscopy to Probe the Electronic Structure of Complex Oxides with Elemental and Orbital Specificity, *Jessica McChesney, D. Fong, H. Hong,* Argonne National Laboratory, USA
Understanding the role of defects and interfaces is necessary in order to realize many of the promising novel properties of complex oxide heterostructure devices. To this aim, we employ resonant angle-resolved photoemission spectroscopy to probe the electronic structure with elemental and orbital specificity of complex oxide heterostructure LaTiO$_3$/SrTiO$_3$ (LTO/STO).Combining these spectroscopy measurements with in-situ growth characterization we are able to determine the minimum thickness required to achieve high quality heterostructures with abrupt interfaces and to correlate the formation with the 2DEG with the

interface termination LTO/STO vs STO/LTO.In addition, we explore the role of oxygen vacancies in formation of the 2DEG on the bare substrate and reveal that contrary to expectations, the 2DEG is Ti^{4+} in character while the oxygen defects are Ti^{3+} in character.

Author Index

Bold page numbers indicate presenter

— A —

Anayee, M.: AS+2D+EM+MS+NS+SS+TF-ThA-3, 1

Artyushkova, K.: AS+2D+EM+MS+NS+SS+TF-ThA-3, **1**

— B —

Bogdanovski, D.: AS+2D+EM+MS+NS+SS+TF-ThA-5, 1

— F —

Fong, D.: AS+2D+EM+MS+NS+SS+TF-ThA-6, 1

— G —

Gogotsi, Y.: AS+2D+EM+MS+NS+SS+TF-ThA-3, 1

Grau-Crespo, R.: AS+2D+EM+MS+NS+SS+TF-ThA-4, 1

— H —

Held, G.: AS+2D+EM+MS+NS+SS+TF-ThA-4, **1**

Hong, H.: AS+2D+EM+MS+NS+SS+TF-ThA-6, 1

— K —

Karimi Aghda, S.: AS+2D+EM+MS+NS+SS+TF-ThA-5, 1

— M —

McChesney, J.: AS+2D+EM+MS+NS+SS+TF-ThA-6, **1**

— O —

Ondračka, P.: AS+2D+EM+MS+NS+SS+TF-ThA-5, 1

Ontaneda, J.: AS+2D+EM+MS+NS+SS+TF-ThA-4, 1

— P —

Park, N.: AS+2D+EM+MS+NS+SS+TF-ThA-1, **1**

Patterer, L.: AS+2D+EM+MS+NS+SS+TF-ThA-5, **1**

— S —

Schneider, J.: AS+2D+EM+MS+NS+SS+TF-ThA-5, 1