PCSI

Room Canyon/Sugarloaf - Session PCSI-1MoA

Catalysis/Nanowires

Moderators: Charles R. Eddy, Jr., U.S. Naval Research Laboratory, Hongping Zhao, The Ohio State University

2:00pm **PCSI-1MoA-1 Engineering Active and Stable Semiconductor Photoelectrodes by Atomic Layer Deposition***, Ian Sharp,* Walter Schottky Institut/Technische Universität München, Germany **INVITED**

The capture of solar energy and its direct conversion to chemical fuel in artificial photosystems provides a promising route to sustainably meet global energy demands and to overcome our current reliance on fossil fuels. However, development of practical photosystems has been impeded by a lack of semiconductor light absorbers that are simultaneously efficient and stable under the reactive conditions required for driving desired chemical transformations. To address this issue, new strategies based on atomic layer deposition (ALD) of conformal corrosion protection layers onto photoelectrode surfaces have recently been developed and yield highly robust systems. Here, we provide an overview of such approaches, discuss outstanding challenges that must be addressed, and highlight a multi-functional water splitting catalyst that is specifically engineered to be interfaced with semiconductor light absorbers. In particular, plasma-enhanced ALD is used to create biphasic cobalt oxide composites that strike a careful balance of necessary chemical, optical, and electrical properties [1]. This coating consists of nanocrystalline Co_3O_4 spinel that is physically robust and provides a stable interface with the chemically sensitive light absorber. This is combined with a chemically labile and disordered $Co(OH)_2$ surface layer that can be easily activated to provide high catalytic activity (Fig. 1). Functional characteristics of the working interface are probed by advanced *in situ* electrochemical X-ray photoelectron spectroscopy, which reveals how the interface transforms from the resting to the active state [2]. Application of the protective catalyst to Si photoanodes results in long-term stable operation with high photochemical activity. These results demonstrate that PE-ALD is a powerful method for synthesizing multi-functional catalysts that support desired chemical transformations, permit efficient interfacial charge transport, and minimize parasitic light absorption due to their conformal nature even at very low thicknesses.

2:40pm **PCSI-1MoA-9 Surface States Induced Catalyst-free CO Sensing at GaN and AlGaN/GaN Heterostructures***, Monu Mishra,* Indian Institute of Technology Delhi*; G Gupta,* National Physical Laboratory, India

III-Nitride semiconductors owing unique material properties have proven their potential in the detection of light, chemical, biomolecules and toxic/explosive gases. Despite of numerous advantages *viz*. biocompatibility, high temperature/frequency tolerance and harsh/adverse environmental condition sustainability, the use of expensive catalysts (e.g. platinum) and higher operation temperature for gas sensing (>250^{o}C) has plagued the development of GaN based cost-effective sensor technology. Upto the best of our knowledge, literature lacks research articles on the development of catalyst-free CO sensors operating at room-temperature using GaN or AlGaN/GaN structures which indicates the necessity of dedicated scientific attention in this area. Therefore, we report the fabrication of nanoflowers-decorated GaN and AlGaN/GaN heterostructure based catalyst-free CO sensors operating at lower (including room) temperature. A set of planar as well as nanostructured GaN & AlGaN/GaN thin films were employed for sensors fabrication which exhibited significant CO sensing associated with its superior surface and interface properties. For in-depth understanding, the obtained results were thoroughly analyzed and correlated to investigate the underlying science/phenomenon which revealed that CO sensing on GaN (and AlGaN/GaN) is governed by the chemical nature of ambient-oxidation induced amorphous oxide (O_2^-, O^{2-} orOH^- species) layer grown on the surface. These surface state act as donor/acceptor states and perturbed the CO adsorption and charge transfer mechanism significantly. Besides, electron accumulation at AlGaN/GaN interface also influenced the critical parameters like schottky barrier height, ideality factor etc. which govern the effective carrier transport and ultimately the device performance. In conclusion, we have observed that the surface and interface states has a strong impact on the efficiency of GaN and AlGaN/GaN based fabricated CO sensors. However, being a first study of its kind, further research is required to explore to uncover the scientific phenomenon and optimization of device performance.

References:

1. M. Mishra, N. K. Bhalla, A. Dash and G. Gupta, Nanostructure GaN and AlGaN/GaN heterostructure for catalyst-free low-temperature CO sensing, Appl. Surf. Sci. 481, 379 (2019).

2:45pm **PCSI-1MoA-10 Cu_2O Nanoparticles for Ennhancing Gas Phase Photocatalysis over Metal Oxide Semiconductor Nanostructures***, Hikaru Masegi,* Keio University, Japan

【 **Background and Purpose** 】Gas phase photocatalysis over metal oxide (widegap) semiconductor materials has been attracting attention as one of the environmentally friendly technologies such as air purification and clean and renewable energy conversion. In addition, monitoring gas phase photocatalysis is of great use for discussing the basic reaction mechanisms [1]. Since a large part of the metal oxide semiconductor materials are n-type, the development and utilization of p-type materials are quite promising in order to facilitate charge separation and enhance photocatalytic activities via pn-heterojunctions. In this work, we focused on p-type Cu_2O nanoparticles (CNPs) and performed electrochemical fabrication of composites of CNPs and anodized n-type nanotubular arrays such as hematite (α-Fe_2O_3) and TiO_2. Then, the gas phase photocatalysis over the prepared nanocomposites was examined to understand roles of CNPs for the enhanced photocatalytic functions.

【 **Experimental** 】As an example, hematite nanotubular arrays (FNTs) were fabricated by anodizing pure iron foils in ethylene glycol containing NH_4F, and crystallized by annealing in oxygen atmosphere. After that, CNPs were deposited onto the anodized samples by pulse electrodeposition in a deposition bath containing $CuSO_4$ and lactic acid. The CNPs were deposited by applying a potential of -0.6 $V_{Ag/AgCl}$ for 0.5 s (on pulse) and 0 $V_{Ag/AgCl}$ for 5 s (off pulse). Then, the H_2 amount from decomposition of gas phase water/methanol mixture was evaluated by gas chromatography.

【**Result and Discussion**】CNPs with an average diameter of 200 nm were deposited on the FNT surface with a pore diameter of 20 nm (See Fig.1). As for their photocatalytic properties, the H_2 amount produced with the CNP/FNT sample increased monotonically with longer time of the visible light irradiation (380-800 nm), and the maximal H_2 yield was 0.08 μmol/cm^2 after 6 hours of visible light irradiation (See Fig.2). In addition, H_2 was not detected either with only FNT or only CNP. H_2 production with the FNT/CNP sample may be attributed to Z-scheme mechanism. Besides, we also confirmed that CNPs can work as cocatalysts for photocatalytic TiO_2 nanotubular arrays.

2:50pm **PCSI-1MoA-11 UPGRADED: Self-Selective Formation of 1D and 2D GaBi Structures on GaAs***, Y Liu,* Lund University, Sweden*; S Benter, J Knutsson, S Lehmann,* Lund University*; E Young, N Wilson, C Palmstrom,* University of California, Santa Barbara*; A Mikkelsen, **Rainer Timm**,* Lund University, Sweden

Bismuth (Bi) incorporation and alloying in III-V semiconductors such as InAsBi and GaAsBi has become a popular topic during recent years, due to a number of promising properties including band gap engineering, a large spin-orbit splitting, and predicted band inversion and topological behavior in the case of high Bi concentrations [1,2]. However, the realization of alloys with high Bi content by epitaxial growth has remained challenging [3].

We follow a different approach and deposit Bi onto the surfaces of GaAs and InAs planar substrates and nanowires (NWs), aiming for a surface layer of high Bi content. We use scanning tunneling microscopy and spectroscopy (STM/S) for systematically studying Bi adsorption and incorporation for different Bi deposition temperatures and post-deposition annealing parameters. Nanowires give us an extra degree of freedom, since they can be grown containing both segments of cubic zincblende (Zb) and of hexagonal wurtzite (Wz) crystal phase, resulting in a variety of surface facets. Previously, we studied the deposition of Sb on GaAs NWs with STM/S and observed a preferential incorporation of Sb atoms into Zb {110} surface facets as compared to {11-20} Wz facets [4].

Here, we observe the incorporation of Bi atoms in the topmost layer of the GaAs surface through group-V exchange, replacing As atoms, upon Bi deposition on GaAs NWs at a temperature of 250°C. The NWs had been cleaned before by annealing in atomic hydrogen, which has been shown previously to remove the native oxide layer [4]. On the NW Zb segments, Bi atoms are scattered at random positions (though generally on As lattice sites), with an increase in density towards step edges of the surface terraces. On the Wz segments, however, the incorporated Bi tends to form one-dimensional GaBi chains and extended two-dimensional GaBi islands along the <0001> edges of surface terraces. A model for the incorporation of Bi through the step edges will be discussed, including differences

observed between {11-20} and {10-10} Wz facets and for different densities of surface steps. Importantly, the ordered 1D and 2D GaBi structures are exclusively found on the Wz segments, which can be tailored in size through NW growth conditions, forming atomically sharp interfaces to Zb segments [5]. This lays the path towards the formation of ordered GaBi structures with atomic-scale precision.

[1] M. Ferhat, A. Zaoui, Phys. Rev. B **73**, 1 (2006).

[2] F.-C. Chuang et al., Nano Lett. **14**, 2505 (2014).

[3] L. Wang et al., Crystals **7**, 63 (2017).

[4] M. Hjort et al.,Nano Lett. **17**, 3634 (2017).

[5] J.V. Knutsson et al., ACS Nano **11**, 10519 (2017)

3:10pm **PCSI-1MoA-15 Iuliacumite: A Novel Two-Dimensional Chemical Short Range Order in a Wurtzite Single Monolayer $InAs_{1-x}Sb_x$ Shell on InAs Nanowires**, ***Michael Schnedler,*** Forschungszentrum Jülich, Germany*; T Xu, I Lefebvre, J Nys,* Université Lille, CNRS, Centrale Lille, ISEN, Université Valenciennes, France*; S Plissard,* Université Lille, CNRS, Centrale Lille, ISEN, Université Valenciennes, Germany*; M Berthe,* Université Lille, CNRS, Centrale Lille, ISEN, Université Valenciennes, France*; H Eisele,* Technische Universität Berlin, Germany*; R Dunin-Borkowski, P Ebert,* Forschungszentrum Jülich, Germany*; B Grandidier,* Université Lille, CNRS, Centrale Lille, ISEN, Université Valenciennes, France

The reduced dimensionality of semiconductor nanowires (NWs) offers the unique opportunity to grow materials with crystal structures, which are otherwise unstable. One of the most prominent example is the growth of wurtzite (WZ) structure InAs NWs, although stable InAs bulk material prefers the zincblende (ZB) structure. In contrast, other III-V materials, notably $InAs_{1-x}Sb_x$, prefer to keep their ZB bulk structure even in NWs or nanostructures with reduced dimensionality. However, lateral overgrowth of these ternary III-V semiconductor alloys on sidewall facets of WZ structure III-V nanowires offers the prospect to nevertheless obtain reliably a WZ structure shell, despite being unstable. Thereby new polytype structures of ternary III-V semiconductor alloys can be achieved, offering additional degrees of freedom for adjusting the band structure in, e.g., core-shell nanowires. Therefore, we designed a two-dimensional single monolayer $InAs_{1-x}Sb_x$ WZ structure shell on sidewall facets of InAs nanowires and investigated the chemical ordering using atomically resolved scanning tunneling microscopy. We identify the existence of a short-range chemical ordering in this WZ structure single monolayer shell. The new type of two-dimensional ordering, called Iuliacumite, is characterized by an ordering vector in [0001] and an anti-ordering vector in <11-20> direction. The ordering is driven by a strong repulsive interaction of neighboring Sb atoms along the <11-20>-oriented atomic chains on the *m* plane sidewall facets.

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