

Nanometer-scale Science and Technology

Room: 203 B - Session NS+AS+EM-MoA

Nanowires and Nanotubes

Moderator: C. Mattevi, Imperial College, London

2:00pm **NS+AS+EM-MoA1 Fe-doped Titania Nanotubes: Iron Role in Structural Modification**, *P.M. Hosseinpour*, Northeastern University, *J. Liu*, Northeastern University and Brookhaven National Laboratory, *I. McDonald*, Northeastern University, *D. Arena*, Brookhaven National Laboratory, *D. Heiman*, *L. Menon*, *L.H. Lewis*, Northeastern University

Ordered arrays of Fe-doped TiO₂ nanotubes are semiconductors with potential enhanced catalytic properties and have prospective applications in photocatalytic devices, sensors and dye-sensitized solar cells. Unified understanding of the interrelations between the band structure, crystal structure and response in presence of dopants is fundamental for tailoring functionality. In this study, Fe (1.8 at%)-doped TiO₂ nanotubes are synthesized via electrochemical anodization followed by annealing in an oxygen-rich environment at 450 °C to induce crystallization. The morphology, crystal structure and electronic structure of nominally-pure and Fe-doped titania nanotubes are investigated in the as-anodized and annealed states. Regardless of precise composition, scanning electron micrographs show that the nanotubes are 50 microns in length with 100-nm pore size, arranged in a closed-packed architecture. In the as-anodized state the nanostructures are amorphous; upon annealing in oxygen the anatase structure forms, with a slight expansion (~0.3% increase) in the unit cell volume and larger calculated crystallite size in presence of iron. Near-edge x-ray absorption fine structure spectroscopy (NEXAFS) carried out at the U7A beamline of the National Synchrotron Light Source at Brookhaven National Laboratory clarifies the electronic structure and chemical environment in pure and Fe-doped titania nanotubes. Preliminary results obtained from the oxygen K-edge and the Ti and Fe L-edge data of the nanotube surface confirm formation of the anatase structure upon annealing, with a lower oxidation state of titanium (lower than Ti⁴⁺) noted in presence of iron. Furthermore, the surface anatase formation was more significant (higher surface crystallinity) in the pure nanotubes versus the iron-doped nanotubes. Annealing the nanotubes in an oxygen-rich environment changes the oxidation state of iron. Correlations between the surface and bulk characteristics of the pure and Fe-doped titania nanotubes confirm incorporation of the iron into the lattice structure which modifies the electronic structure by changing the bonding and oxidation state of titanium. These results highlight potential pathways towards further optimization of these nanostructures in order to enhance catalytic functionality.

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2:20pm **NS+AS+EM-MoA2 Impact of Crystallinity, Chemical Environment and Electronic Structure of TiO₂ Nanotube Arrays for Photocatalysis**, *J. Liu*, *P.M. Hosseinpour*, Northeastern University, *S. Luo*, Brookhaven National Laboratory and SUNY Stony Brook, *D. Arena*, Brookhaven National Laboratory, *L.H. Lewis*, Northeastern University

The photocatalytic ability of TiO₂ nanostructures to remove organic pollutants in wastewater has attracted considerable attention [1]. Understanding the influence of crystallinity, chemical environment and electronic structure of TiO₂ nanotubes on the photocatalytic activity is very important in optimizing this functionality. In this work, TiO₂ nanotube arrays with an average tube length of 25 μm were prepared by the electrochemical anodization of Ti foil, followed by thermal treatment in O₂ (oxidizing), Ar (inert), and H₂ (reducing) environments at 350 °C to induce crystallization. The nanotube structure-property correlations were examined with x-ray diffraction (XRD), scanning electron microscopy (SEM) and x-ray absorption spectroscopy (XAS). The photocatalytic properties of the TiO₂ nanotubes (as-anodized and annealed) were evaluated using degradation of methyl orange (a model dye compound of water pollution) in an aqueous solution under UV-visible light irradiation. The Ti L_{3,2}-edge and O K-edge x-ray absorption spectra provide the information concerning the near-surface (~5 nm) local bonding environment and electronic structure of the nanotubes. The XAS results show that while the as-anodized amorphous TiO₂ nanotubes were partially transformed to anatase phase via thermal treatment, variations in crystallinity and surface defects were observed to depend on the type of annealing atmospheres. Characteristics of anatase

were more evident in both the Ti L_{3,2}-edge and the O K-edge XAS spectra of TiO₂ nanotubes annealed in O₂ than in those annealed in H₂ and Ar, which indicate relatively higher local order and less local defects in O₂ annealed nanotubes. Nanotubes annealed in H₂ exhibited a higher photodegradation rate of methyl orange than those annealed in Ar and O₂. These results can be correlated with the different electronic structures that reflect the different degrees of crystallinity and the varied nature of the surface defects (i.e., oxygen vacancies) of TiO₂ nanotubes that result from different processing conditions.

[1] Paramasivam, H. Jha, N. Liu and P. Schmuki, *Small* (2012), 8, 3073-3013.

Research supported by the National Science Foundation under Grants No. DMR-0906608 and DMR-0908767, and by the U.S. Department of Energy, Division of Materials Science, Office of Basic Energy Sciences under Contract No. DE-SC0005250. Use of the National Synchrotron Light Source, Brookhaven National Laboratory, was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886. This work was also financed by the U.S. Department of Energy, Office of Basic Energy Sciences under Contract DE-AC02-98CH10086.

2:40pm **NS+AS+EM-MoA3 Enhanced Field Emission from Oxygen-deficient TiO₂ Nanotube Arrays**, *C.W. Wang*, *J.-B. Chen*, *W.-D. Zhu*, Northwest Normal University, China

Due to their high aspect ratio, low work function, and excellent controllability of morphology, TiO₂ nanotube arrays (TNAs) are found to be promising candidate for field emitters. Further improvement on the field emission (FE) properties of TNAs requires more precise control of both the morphology and the electronic structure. Reduction treatment including hydrogenation, nitriding and carbonization to obtain oxygen-deficient TNAs, is known as a facile strategy to modify the morphology and electronic structure of TNAs [1-3]. In this study, TNAs obtained by anodization are treated by various reduction treatments. It is found that the morphology shows no significant change after hydrogenation at the temperature below 550 °C. But the electronic structure exhibits large variation, which is critically depended on the treatment temperature. When the temperatures of hydrogenation are 400, 450, 500, and 550 °C, the work functions are 3.68, 3.48, 3.03 and 2.20 eV. However, after the treatments of nitriding and carbonization, both the morphology and the electronic structure of TNAs are substantially modified. The nitriding treatment can reconstruct the amorphous TNAs to be nanoworm/nanotube hierarchical structures and implant nitrogen into them, which show lower work function, higher electrical conductivity, and larger field enhancement factor. Correspondingly, after the carbonization treatment, the as-anodized TNAs are successfully transformed to be simetal and a retained tubular morphology with rough surface can be obtained. With respect to FE, compared to as-anodized TNAs, oxygen-deficient TNAs prepared by hydrogenation, nitriding and carbonization show dramatically enhanced FE properties including a lower turn-on field of 1.75 V/μm, a higher FE current density of 4.0 mA/cm² at 4.50 V/μm, and a remarkable FE stability. These results indicated that oxygen-deficient TNAs can be promising candidates for FE.

Acknowledgements

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References

- [1] X. B. Chen, L. Liu, P. Y. Yu and S. S. Mao, *Science* 2011, 331, 746.
- [2] Y. M. Kang, C.W. Wang*, J. B. Chen, L. Q. Wang, D. S. Li, W. D. Zhu and F. Zhou, *J. Vac. Sci. Technol. B* 2012, 30, 041801.
- [3] W. D. Zhu, C. W. Wang*, J. B. Chen, D. S. Li, F. Zhou and H. L. Zhang, *Nanotechnology*, 2012, 23, 455204.

3:00pm **NS+AS+EM-MoA4 Fabrication and Controlled In Situ Morphological Transformation of Highly Ordered Hollow Oxide Nanostructures based on Nanoscale Kirkendall Effect**, *A. El Mel*, Univ. of Mons, Belgium, *M. Buffière*, IMEC, KU Leuven, Belgium, *P.-Y. Tessier*, Inst. des Matériaux Jean Rouxel – Univ. de Nantes, Belgium, *K. Du*, *C.H. Choi*, Stevens Inst. of Technology, *L. Molina-Luna*, *S. Schildt*, *H.J. Kleebe*, Technische Univ. Darmstadt, Germany, *S. Konstantinidis*, *C. Bittencourt*, *R. Snyders*, Univ. of Mons, Belgium

Huge efforts are nowadays dedicated to the development of relevant methods to fabricate hollow nanostructures of a wide variety of materials. Among hollow nanostructures, oxide nanotubes appear to be an interesting building block for nanoelectronics. Until today, the oxide nanotubes suffer

of their short length and poor organization. In this contribution, we report on highly organized ultra-long metal oxide nanotube arrays (length-up to several centimeters) fabricated by thermal oxidation of metal nanowire arrays. The metal nanowires were grown on nano-grated surface by the plasma-assisted inverse-template method that we have developed recently. Based on the extensive structural study, performed by transmission electron microscopy, the fundamental mechanisms occurring during the formation of such oxide nanotubes will be discussed and explained according to the nanoscale Kirkendall effect. We further show that such method can be extended to the fabrication of periodic zero-dimensional hollow nano-objects.

In addition, we present an extensively structural study of the morphological transformation of oxide nanotubes upon *in situ* annealing in a transmission electron microscope. Based on this, the role of oxygen on the fundamental mechanisms occurring during the formation of such oxide nanotubes will be discussed. These results show the structural transformation and copper ions diffusion inside an oxide nanotube due to the effect of heating.

3:40pm **NS+AS+EM-MoA6 Carbon Nanotube Macroelectronics and Nanoelectronics**, *C. Zhou*, University of Southern California **INVITED**

Carbon nanotubes and graphene offer great promise but also face significant challenges for future beyond-silicon nanoelectronics. This talk will focus on our recent work on nanoelectronics based on aligned nanotubes, macroelectronics based on separated nanotubes, and wafer-scale CVD graphene. We have developed the synthesis of massively aligned single-walled carbon nanotubes atop sapphire and quartz substrates, and we will also present our recent progress toward type-controlled and chirality-controlled carbon nanotube synthesis. In addition, we will report macroelectronics based on separated nanotube thin film transistors, including key technology components such as assembly of separated nanotube networks, high-yield fabrication of devices, and applications for AMOLED displays and printed electronics. Furthermore, we will present scalable fabrication of self-aligned T-gate graphene transistors for RF applications.

4:20pm **NS+AS+EM-MoA8 Geometry-Dependent Formation of Multiple Twins in Si Nanowires**, *N. Shin*, Georgia Institute of Technology, *M. Chi*, Oak Ridge National Laboratory, *M.A. Filler*, Georgia Institute of Technology

Precise control of twin boundaries and stacking faults in semiconductor nanowires provides a number of exciting opportunities to fundamentally manipulate their optical, electrical, and thermal properties. Group IV nanowires, as opposed to their III-V counterparts, rarely exhibit planar defects perpendicular to the {111} orientation and rationally engineering their insertion remains challenging. Here we extend our recent demonstration of defect introduction in vapor-liquid-solid (VLS) synthesized, {111} oriented Si nanowires¹ and report on the appearance of consecutive, geometry-dependent twin boundaries for the first time. Si nanowires with double twins were grown with a Au catalyst by initiating growth at $T = 490\text{ }^{\circ}\text{C}$ and $P = 2 \times 10^{-4}\text{ Torr}$ for 10 min before changing to $T = 410\text{ }^{\circ}\text{C}$ and $P = 5 \times 10^{-4}\text{ Torr}$ for another 10 min. While the position of the first twin boundary (TB_1) corresponds to the point where growth conditions were changed, and was the same for all nanowires, the second twin boundary (TB_2) exhibits a diameter-dependent axial position. Detailed electron microscopy analysis shows that thin {111} sidewall facets, which elongate following TB_1 and deform the triple-phase line, are responsible for the formation of TB_2 . We hypothesize that an increased amount of surface hydrogen, present as a result of the condition change, favors the thin {111} facets. Our findings help to elucidate the mechanisms that underlie defect introduction in semiconductor nanowires and represent an important step toward the creation of complex defect superstructures in Si.

(1) Shin, N.; Chi, M.; Howe, J. Y.; Filler, M. A. *Nano Lett.*, **2013**, *in press*

5:00pm **NS+AS+EM-MoA10 Plasma Modification of Chemically Vapor Deposited SnO₂ Nanowires and SnO₂ Nanoparticles for Enhanced Gas Sensing**, *E. Stuckert*, *E.R. Fisher*, Colorado State University

As toxic gases like NO_x, benzene, and formaldehyde continue to be emitted globally, their negative impacts on people's health persist. With gases capable of causing harm on the part per billion level, it is critical to accurately sense toxic gases in real time. This requires creating sensors that operate at lower temperatures, are more sensitive, and are more selective for sensing a desired gas than what is commercially available. SnO₂ is commonly used to create sensing materials because it has enhanced gas-surface interactions as a result of its variable oxidation states, namely Sn²⁺ and Sn⁴⁺. Plasma modification is one method of altering the SnO₂ surface to enhance sensitivity and selectivity. The plasma treatments create more surface oxygen vacancies in the SnO₂, which allows for increased sites for atmospheric oxygen to adsorb. The sorption of gases is highly dependent on

the predominant oxygen species on the sensor surface at a given plasma treatment and temperature. Our results demonstrate that SnO₂ nanowires grown by chemical vapor deposition (CVD) and commercial SnO₂ nanoparticles treated in Ar/O₂ plasmas have lattice oxygen removed from the surface. Removal of surface oxygen is corroborated through X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD). XPS data show that low plasma power treatments (10-60 W) alter the surface oxygen composition of SnO₂ nanowires and nanoparticles, with the maximum change in composition peaking at 30 W. More importantly, the oxygen vacancies in the treated nanowires are significantly higher than those observed for treated nanoparticles. In addition to surface analysis results, resistance of SnO₂ nanowire and nanoparticle sensors when exposed to a range of gases (i.e., methanol, ethanol, propanol, benzene, and formaldehyde) is used to explore specific gas-surface interactions. By relating plasma treatment conditions to the resulting surface composition and the sensor's response upon exposure to gases, insight into how surface modification affects gas-surface interactions in sensors will be presented.

Keywords:

Plasma modification, Gas sensor, Tin oxide, Nanowire, Nanoparticle

5:20pm **NS+AS+EM-MoA11 Vapor Transport Growth and Thermal Conductivity Measurement of Chalcogenide Nanowires with Axial Heterojunctions**, *C.J. Hawley*, *J.E. Spanier*, Drexel University

We report on the controlled vapor transport growth of bismuth chalcogenide nanowires by the vapor-liquid-solid (VLS) mechanism, both in the form of ternary alloys as well as axial variation of the binary compounds bismuth telluride and bismuth selenide. The nanowires exhibiting axial heterojunctions are of specific interest as they promise to reduce a device's effective thermal conductivity through the incorporation of boundary impedances at each junction. These nanowires are measured by suspending a single nanowire between contacts and joule heating the nanowires in a four-probe configuration. The change in resistivity due to the joule heating, in combination with numerical modeling of the axially varying nanowire system, allows for the calculation of the effective thermal conductivity of the nanowires, useful for their exploration as a more efficient low temperature thermoelectric nanostructured material.

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