# **TECH HIGHLIGHTS**

## Development of Hybrid Electro-Electroless Deposit (HEED) Coatings and Applications

Electrodeposition can be achieved via electroplating, whereby current is applied to the work piece serving as the cathode, or by using an electroless deposition process, wherein the reductant is a co-dissolved species in the plating solution. Researchers in Canada have developed a combined deposition process, termed hybrid electroelectroless deposition (HEED) to deposit two metals. The authors present a method in which the more noble metal is deposited by electroless plating, to prevent the disruption of the electroless process by the application of the electroplating potential. When the electroplating process is concurrently employed, thereby effecting HEED, multilayered structures as well as controlled alloys and composites may be deposited. The advantages and disadvantages of the two electrodeposition processes are both present in HEED as is the added complexity engendered by the presence of electroplating species in an electroless deposition solution. Nonetheless, the authors explored and demonstrated initial success in forming (i) a tri-layer deposit containing Co and Au and (ii) a bi-layer on a Mg alloy from a Ni-Zn-P electrolyte.

# From: J. Electrochem. Soc., 161, D470 (2014).

# "Time of Flight" Electrochemistry

Measurement of molecular diffusion coefficients is important in understanding and determining the kinetics of physical and chemical processes. Among the measurement techniques employed are those based on pulsed field gradient nuclear magnetic resonance spectroscopy, field flow fractionation, and electrochemistry. Electrochemical methods such as chronoamperometry (based on the Cottrell equation) and polarography (based on the Ilkovic equation) are two of the techniques used by electrochemists for these measurements. Researchers at the University of Wyoming, USA, recently reported the development of a simple and straightforward measurement method based on the use of interdigitated array (IDA) electrodes. In their article published in the JES Focus Issue in Recognition of Adam Heller and His Enduring Contributions to *Electrochemistry*, the authors measured the diffusion time between a generator electrode (where the electroactive species of interest is formed) and a collector electrode (where the electroactive species is measured), and used this value to calculate the diffusion coefficient based on digital simulations chronoamperometric of and cyclic voltammetric experiments. This "time of flight" approach uses the special structure of IDA electrodes and simple diffusion equations to provide good estimates of diffusion coefficients without the need for accurate knowledge of electroactive species concentration, electrode surface area, or

other parameters. The only requirement is accurate knowledge of the distance between the individual electrodes in the array.

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## Atomic Layer Deposition of High Quality HfO<sub>2</sub> Using *In-Situ* Formed Hydrophilic Oxide as an Interfacial Layer

High-quality HfO<sub>2</sub> is now the dominant high-k oxide in mainstream manufacturing processing in the semiconductor industry. Atomic-layer deposition (ALD) is the deposition method of choice for ultra-thin, controlled HfO2 growth. For uniform ALD of HfO<sub>2</sub> on silicon (Si), an interfacial oxide layer is always needed. This interfacial oxide is best formed on hydrophilic surfaces such as OH-terminated Si. Previous methods relied on ozonated water spraying to prepare the surface for ALD. However, in 3D silicon MOS device structures, such as FinFETs and related nanoscale architectures, it is difficult to allow uniform oxide formation on vertical fins and underneath nanowires due to limited access for reactive species. Researchers at the University of Kentucky have successfully demonstrated a method for highly hydrophilic SiO<sub>2</sub> interfacial layer growth formed in-situ in an ALD chamber using 1 cycle of ozone and water. Subsequent growth of HfO<sub>2</sub> on this interfacial layer showed promising growth linearity of 1 Å/ cycle, and stoichiometric composition. In test structures, capacitance-voltage analysis shows negligible frequency dispersion and hysteresis, confirming high dielectric quality comparable to traditional methods. The researchers state that the approach removes the need for chemical oxidation process in HfO<sub>2</sub> growth for advanced integrated circuits manufacturing processes. It certainly provides a useful manner for high-k oxide growth for more complex geometries in nanoscale CMOS devices.

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#### Evaluation of the SEI Using a Multilayer Spectroscopic Ellipsometry Model

The solid electrolyte interphase (SEI) plays a critical role in the performance and stability of Li-ion batteries. Formed at the anode by reduction of electrolyte solution components, the film is comprised of an inner layer (adjacent to the electrode) composed primarily of inorganic matter and an outer layer (adjacent to the electrolyte) composed of organic matter. Prior spectroscopic ellipsometry (SE) studies have simplified modeling of the SEI by treating it as a single layer. A researcher from Idaho National Laboratory in the U.S. has developed a model that incorporates two layers to characterize the SEI. The author identified four regions during the scanning of the potential of a Cu substrate to 0.02 V vs. Li and back to 1.7 V. The first region showed initial increase in thickness due to reduction of solvent. The second region exhibited an

increase in the inner layer thickness due to subsequent reduction of the initial products. Loss in thickness in both layers, attributed to dissolution of semi-soluble components, is revealed in the fourth region and corroborates quartz crystal microbalance data from other authors. Cycling revealed a slow growth of the SEI film arising from the inner layer growing during each cycle. This initial SE modeling work suggests more can be learned about the dynamic SEI layer.

From: ECS Electrochem. Lett., 3, A108 (2014).

## Acidic Buffer-Free Organic Solar Cells Using Vanadium-Doped Indium Oxide Anodes

Organic solar cells (OSCs) are comprised of thin layers of materials arranged to exploit their inherent properties that together enable the conversion of light into separated charge carriers and the flow of current. Conventional OSCs employ a poly(3,4-ethylene dioxylene thiophene):poly(styrene sulfonic acid) (PEDOT:PSS) buffer layer that enables increased hole extraction efficiency from the active layer, but owing to its acidity leads to eventual etching of the Sn-doped In<sub>2</sub>O<sub>3</sub> (ITO) anode. Some researchers have prepared ITO anodes protected by a V<sub>2</sub>O<sub>5</sub> coating. In this work, researchers from South Korea developed a V-doped In2O3 (IVO) film to address both the need for greater chemical stability of the transparent anode and for simplifying the manufacturing process. IVO films (200 nm thick) were prepared by cosputtering V<sub>2</sub>O<sub>5</sub> and In<sub>2</sub>O<sub>3</sub> followed by rapid thermal annealing (RTA). RTA at 600 °C yielded a film with lower resistivity, higher carrier concentration, and comparable carrier mobility and optical transmittance when compared to as-deposited and 500 °C-annealed films. OSCs containing the IVO anode or reference ITO anode were fabricated with and without the PEDOT:PSS buffer layer. Cells fabricated using annealed IVO films performed reasonably similar to the same initial level of the conventional OSC containing PEDOT:PSS on ITO. The authors demonstrated that the IVO film served well as a buffer- and anode-integrated electrode, eliminating the need for the extra layer.

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