TECH *Highlights*

Molecularly Interlaced Heterojunctions

More efficient conversion of photons into electrical energy in organic photovoltaic devices is the goal of some chemists at Northwestern University. These researchers hypothesized that shrinking the dimensions of the heterojunction donor-acceptor interface to the molecular scale would facilitate more electrons and holes, generated by dissociated excitons, contributing to photocell current rather than recombining. Interdigitated heterojunctions were assembled *via* layer-by-layer growth of zirconium phosphonate films composed of porous aligned donor structures, consisting of frameworks of either molecular square or monomeric forms of phosphonated porphyrin, that are subsequently in-filled with similarly aligned acceptor structures: diphosphonated perylenediimide. Photocells made of these interlaced heterojunctions performed better than those having a bilayer structure or a blended structure. Interdigitation results in a greater interfacial area and enhanced phase connectivity. However, the overall incident-photon-to-current-efficiency remains low, suggesting poor charge carrier collection efficiency. Charge collection could be improved by using an electron-blocking species grown at the indium tin oxide electrode to eliminate the electron shunting behavior set up by the perylene phase spanning the thickness of the cell. Additionally, other possibilities for further exploration are employing more highly conjugated layer interconnects than the zirconium phosphonate linkages used in this work and bundling more molecular strands together to provide fewer electron-hole encounters during charge migration.

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Direct Photoelectrochemical Water Splitting

Direct splitting of water into hydrogen and oxygen by solar light in photoelectrochemical cells has received much attention, since hydrogen is often considered the energy storage medium of the next generation. The main effort in recent studies on solar energy conversion is to reduce the fabrication cost while maintaining reasonable conversion efficiency, as demonstrated in a report by Park and Bard at the University of Texas at Austin. In this report, the authors achieved direct water electrolysis with a novel monolithic photoelectrochemical cell. Bipolar WO_3/Pt and dye-sensitized TiO_2/Pt semiconductor panels, capable of vectorial electron transfer, were used for water splitting to yield hydrogen and oxygen with light as the only energy input. The hydrogen production efficiency of this tandem cell, based on the short-circuit current, was ~1.9% and the maximum hydrogen production efficiency was ~2.5% when 0.2 V positive bias was applied. The maximum yielding efficiency of hydrogen and chlorine was ~1.8%. A distinctive feature of this device was its internal vectorial electron transfer that eliminated the need for external wiring between the photoelectrochemical cells. Moreover, the photocatalytic behavior of the WO_3 photoanode offered specificity in Cl_2 production for the first time when a concentrated LiCl aqueous solution was used as the electrolyte.

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A Difference-Imaging Technique Used to Study Streaking Corrosion of Aluminum Alloys

Optical evaluation of the early stages of corrosion on electrode surfaces is difficult, particularly for abraded or otherwise complex surfaces, as changes due to the corrosion process are often masked by the surface features of the sample. Recently, a difference-viewing methodology has been developed to evaluate surface changes in these situations. In this technique, an image of the surface taken previously is subtracted from the image at any given time following corrosion initiation. This allows only the changes in the surface—in this case the development of a corrosion site—to be seen, unencumbered by the visible noise created by the static surface features of the sample. Researchers at Xiamen University and Brookhaven National Laboratory used the difference-imaging technique to observe streaking corrosion on the surface of several aluminum alloys. By adding a broad range pH indicator to the electrolyte, local variations in solution chemistry were also captured. For both materials, corrosion took place in a thin susceptible surface layer, formed by either abrasion or thermomechanical treatments. Based upon the rate of streak growth and the accompanying decrease in the local pH at the advancing edge of a growing streak, it was postulated that the local corrosion rate was comparable to that of active pit growth, and that advance of the corrosion site was supported by depassivation of the regions in front of the advancing streak by the aggressive solution formed at the active corrosion site due to metal ion hydrolysis.

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Producing Shape-Controlled Metal Nanostructures

The unique chemical and physical behavior of nanostructures has spurred widespread interest in the field of nanotechnology in recent years. While typically, nanostructures are produced by vacuum or plasma processing, Fukunaka and coworkers at Kyoto University have illustrated the use of electrodeposition to synthesize nanowires and nanotubes of nickel. The technique involves sputtering a 30 nm layer of Pt-Pd on a polycarbonate template and depositing nickel on the layer through the pores of the template. The template thickness is 6 to 10 µm and the pore sizes range from 15 to 200 nm. Depending on the pH of the plating bath and the potential at which the plating is conducted, the authors show that both the thickness and the morphology can be controlled. While lower pH results in thinner wires, a more anodic potential results in the formation of tubes (*i.e.,* hollow interior), with the tube thickness increasing with pH. The authors speculate that the formation of tubes occurs due to H_2 evolution that results in a bubble that fills a portion of the cross-section of the pore. The presence of the bubble in the center of the pore results in deposition of nickel only on the pore walls, thereby producing a nanotube.

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Metrology Capabilities for Very Thin Dielectric Films

The continual drive to decrease metal-oxide semiconductor (MOS) transistor dimensions presents significant challenges with respect to fabrication process metrology. Particularly difficult are thickness measurements for gate dielectrics, the thinnest layer in MOS transistors. Here, equivalent oxide thicknesses of < 1 nm are being roadmapped for 2007, with precision requirements of < 0.01 nm on measurements designed to monitor oxide fabrication processes. Recently, a multi-institution collaboration (National Institute of Standards and Technology, North Carolina State University, International SEMATECH, Duke University, The Ohio State University, and Advanced Technology Development Facility, Inc.) reported the results of a comparative study of three dominant techniques used in the microelectronics industry for thickness measurements on ultra thin SiO_2 films: ellipsometry, capacitance-voltage (C-V) measurements, and transmission electron microscopy (TEM). The goal of the work was to evaluate metrology capabilities that would support the development of reference materials for thin dielectric films. The authors concluded that it should be possible to select an effective ellipsometry model for developing reference materials in good agreement with TEM and/or electrical thickness scales. However, it does not yet appear possible to develop a reference material that is traceable with respect to absolute thickness and that has a thickness uncertainty in the 0.02 nm range, which approaches the roadmap requirement.

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