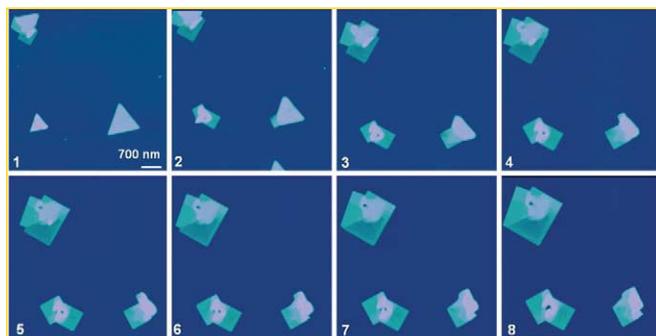


Controlling crystal evolution on the nanoscale

POLYMERS



Images taken at 256 s intervals while scanning an AFM tip coated with PLH molecules on mica, showing phase transformation of triangular prisms into cubes. (© 2005 AAAS.)

The study of most crystallization processes using X-ray diffraction or spectroscopic tools is limited until the crystal reaches a critical size of many microns – too late to determine the relationship between crystal growth and environmental parameters. Scanning probe microscopy allows *in situ* visualization, but typically of structures growing randomly on a surface from a bulk solution.

Now, Chad A. Mirkin and coworkers at Northwestern University have developed a method for initiating site-specific crystal nucleation of a polymer, controlling growth in a serial manner, and monitoring progress from nanoscopic seeds to macroscopic crystals as a function of environmental conditions [Liu *et al.*, *Science* (2005) **307**, 1763].

They use dip-pen nanolithography (DPN), which uses a coated atomic force microscope (AFM) tip to transport adsorbate to a surface in a controlled manner.

A Si AFM tip, coated with poly-D,L-lysine hydrobromide (PLH),

forms triangular prisms of PLH when raster-scanned in tapping mode over an 8 μm x 8 μm region of a freshly cleaved mica substrate at room temperature. There are just two orientations, differing by 180°, independent of scan direction. This indicates oriented epitaxial growth with respect to the pseudo-hexagonal lattice of the mica surface. More scans or a longer tip-substrate contact time increases crystal thickness and edge length. Edge length grows at a faster rate than thickness, partly because of the strong electrostatic interaction between the PLH molecule and substrate, which accelerates crystal growth along its edges. Small changes in environment (i.e. temperature, humidity, or pressure) can have enormous effects on the propensity to crystallize and the ultimate crystal morphology. In subsequent scans at 35°C, cubic-shaped features emerge at the corners or edges of the prisms. The morphological change is very reproducible. Mirkin says that they can determine why a crystal forms a particular shape as a function of environmental conditions.

Lower humidities favor the formation of smaller crystals, down to five orders of magnitude smaller than those observable by single-crystal X-ray diffraction, allowing observation of otherwise undetectable morphological changes. This may allow systematic determination of the optimum growth conditions for crystals that are normally difficult, or impossible, to grow. Since DPN can be a massively parallel tool, combinatorial approaches could identify conditions for initiating a particular type of crystal growth for a given set of target molecules. Obvious candidates are proteins and organic macromolecules.

Mark Telford

New dielectrics open gate for *n*-type organic field-effect transistors

POLYMERS

Organic semiconductors have applications in light-emitting displays and printable electronic circuits. However, they exhibit strong trapping of electrons but not holes. Organic field-effect transistors (FETs), therefore, typically show *p*-type but not *n*-type conduction (other than for special high-electron-affinity and narrow-band-gap organic semiconductors, which are susceptible to quasi-irreversible doping).

A team led by Richard H. Friend of the University of Cambridge, together with researchers from the National University of Singapore and Singapore's Institute of Materials Research and

Engineering, has shown that the electron trapping occurs at hydroxyl groups at the interface with the FET gate dielectric (e.g. silanol, SiOH, for commonly used SiO₂) [Chua *et al.*, *Nature* (2005) **434**, 194].

The researchers demonstrate that the use of alternative gate dielectrics, including polyethylene, parylene, and poly(methyl methacrylate), allows *n*-FET conduction. But the team also shows that a preferred choice is a crosslinkable divinyltetramethylsiloxane-bis(benzocyclobutene) derivative (BCB), since it can provide a high-quality, completely hydroxyl-free interface.

An advantage of BCB is that it has a high dielectric breakdown strength of >3 MV cm⁻¹. Furthermore, it can be solution-cast to form the ultrathin films needed for practical low-gate-voltage plastic transistors.

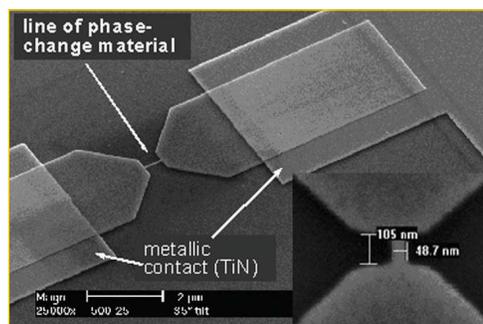
Unexpectedly, it was discovered that the use of BCB can yield ambipolar (i.e. both *p*-channel and *n*-channel) FET conduction in most conjugated polymers. Specifically, *n*-FETs show low threshold voltages ($V_T < 10$ V) and high on-off ratios (>10⁵). High electron field-effect mobilities of 10⁻³-10⁻² cm² V⁻¹ s⁻¹ – at least as high as hole mobilities – have been measured in polymers based on poly(fluorene) and dialkyl-substituted

poly(*p*-phenylenevinylene), all in the unaligned state. Proper chain alignment (e.g. in the liquid-crystalline phase) could yield electron mobility values approaching those for hole mobility in these materials with a SiO₂ dielectric. The researchers say that ambipolar behavior should greatly extend the range of suitable materials for organic complementary metal-oxide semiconductor (CMOS) circuits. The findings should also be relevant to cases where molecular semiconductors are in contact with inorganic oxide surfaces, e.g. in photovoltaic applications and single-molecule devices.

Mark Telford

In line for phase-change memory cell

NANOTECHNOLOGY



Micrograph of a phase-change memory cell. Inset: a cell of length ~100 nm and width ~50 nm.

Philips Research Labs' new 'line-cell' Si chip memory has an ultrathin line of phase-change material. An electric current is used to heat the material to its phase-change temperature, where it switches reversibly between crystalline and amorphous phases, and to detect the change in resistance [Lankhorst *et al.*, *Nat. Mater.* (2005) 4 (4), 347]. In phase-change ovonic unified memory, a high voltage is needed in the high-resistance amorphous state to drive enough current to heat it – impractical for future complementary metal-oxide semiconductor (CMOS) Si chips.

So, Philips developed a doped Sb/Te material that shows threshold switching, where highly conductive filaments form and Joule heating occurs at a low electric field (~14 V/μm for lines shorter than 200 nm). Unlike other nonvolatile memories, performance improves at the nanoscale, since crystallization occurs from the edge of the amorphous volume inwards. As chip sizes shrink, reducing the line length (e.g. to 50 nm) reduces the voltage for threshold switching (to 0.7 V). The Sb/Te line is surrounded by dielectric (SiO₂), which has low thermal conductivity and dissipates little power and current. This allows smaller cells and faster operation. In test devices, a 30 ns phase change and use of symmetrical pulses makes programming 100-200 times faster than flash memory, making it a feasible replacement for dynamic random access memory (DRAM). Further current reduction is possible by using better thermal insulation material or by shrinking the line's cross section.

Also, device fabrication needs just a few extra lithography steps for integration into CMOS logic processes, suiting low-cost production.

Mark Telford

Chemical control of magnetic semiconductors

MAGNETIC MATERIALS

Scientists at the University of Washington have provided the first evidence that ferromagnetism in Mn-doped ZnO relies critically on factors other than the magnetic dopants themselves [Kittilstved and Gamelin, *J. Am. Chem. Soc.* (2005), doi:10.1021/ja050723o], and demonstrated the controlled chemical manipulation of high-Curie-temperature (T_c) ferromagnetism in a diluted magnetic semiconductor (DMS) [Kittilstved *et al.*, *Phys. Rev. Lett.*, in press]. Targeted chemical perturbations were used to manipulate 300 K magnetic ordering in ZnO DMSs in controllable ways: *p*-type perturbation by amine binding then calcination induced ferromagnetic ordering in Mn²⁺:ZnO but quenched ordering in Co²⁺:ZnO; *n*-type perturbation by Zn interstitial vapor diffusion quenched ferromagnetism in Mn²⁺:ZnO but induced it in Co²⁺:ZnO. This is consistent with theoretical models in which ZnO DMS ferromagnetism is mediated by itinerant carriers. Control over physical properties also enables testing of proposed microscopic mechanisms for long-range magnetic exchange

interactions in oxide DMSs, says Kevin R. Kittilstved. The availability of DMSs with reliable magnetic properties should now focus attention on elucidating their magnetotransport properties. In particular, the electronic structure of Mn²⁺:ZnO is most analogous to those of ferromagnetic DMSs used in prototype spintronic devices (which process information by manipulating electron spins). These currently operate only at cryogenic temperatures.

Implementation requires an understanding of the relationships between compositional, structural, and physical properties. So, future work will probe the identities and properties of lattice defects that can be introduced chemically, and the dependence of magnetic properties on such chemical parameters. The results also suggest new possibilities for the development of hierarchical magnetoelectronic device structures by integrating ferromagnetic oxide nanostructures with organic conducting polymers using soft-chemical methods, says coauthor and lead researcher Daniel R. Gamelin.

Mark Telford

Molecular spintronics a reality?

MAGNETIC MATERIALS

Theoretical work from Trinity College Dublin, Ireland, along with coworkers in the UK and Spain, has demonstrated the potential for highly tunable, self-assembling molecular spintronics. This chemical approach toward spintronics may have great potential for the multibillion-dollar industry of magnetostorage devices. [Rocha *et al.*, *Nat. Mater.* (2005) 4 (4), 335]. Spintronic devices use the spin of an electron as well as its charge. The team, led by Stefano Sanvito, shows that organic spin valves can achieve high magnetoresistance values and so could overcome previous efficiency and performance pitfalls of spintronic devices using conventional inorganic materials.

"We demonstrate that it is possible to inject spins into a molecule with very high efficiency," says Sanvito. "The lack of hyperfine and spin-orbit interactions in organic molecules means spin coherence can be maintained over longer times and distances than conventional metals and semiconductors," he explains.

The group show that an organic molecule sandwiched between Ni contacts can display magnetoresistance ratios of up to 600%. The effect can be tuned by engineering the side and end groups of the molecules.

The team used a combination of density functional theory and a nonequilibrium Green's function method to obtain current-voltage characteristics of the spin values. The algorithm is incorporated in a code created to compute magnetotransport properties at the atomic level. The 'SMEAGOL' code is freely available at www.smeagol.tcd.ie.

Patrick Cain

Setting your teeth on edge

BIOMATERIALS

Researchers in Japan have devised a dental paste of synthetic enamel that rapidly repairs early caries lesions in teeth via nanocrystalline growth, with minimal wastage of natural enamel (Yamagishi *et al.*, *Nature* (2005) **433**, 819). This avoids normal treatment involving filling with resin or alloy, which removes a disproportionate amount of healthy tooth to make the filling stick. Acid-forming bacteria create cavities <50 μm deep in the 1-2 mm thick hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) enamel. These cannot be repaired by simple setting of restorative materials, since differences in chemical composition and crystal structure prevent perfect adhesion.

So, the scientists prepared a white crystalline hydroxyapatite paste that chemically and structurally resembles natural enamel, and repaired an early caries lesion before sealing off the affected site within 15 mins.

Transmission electron microscopy shows no gap between the enamel and the regrown layer, which contains elongated crystals (100-400 nm long and 20-80 nm wide) that grow across the interface and are regularly oriented to the surface.

Time-lapse atomic-force microscopy shows that the crystals of the original tooth enamel initially dissolve slightly then quickly grow again, with the paste acting as a source of hydroxyapatite crystals. This creates a continuous, nanoscale structure that extends from the enamel to the regrown layer. The crystals cover the whole surface in a densely packed array after 3 min, and are stacked three-dimensionally after 15 min. Strong acidity ($\text{pH} < 2$) of the mother solution and paste probably contributes to fast growth by dissociating the calcium and phosphate ions.

Mark Telford

Same scaffold, different cells

BIOMATERIALS

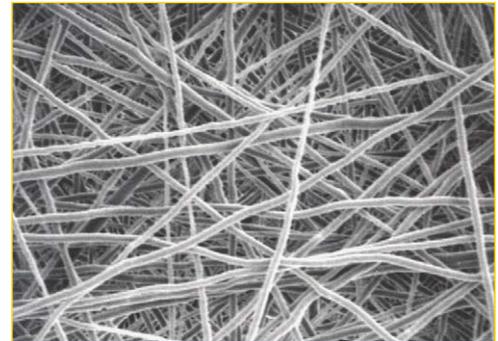
Researchers at the US National Institutes of Health and Thomas Jefferson University have generated adipose, cartilage, and bone cells *in vitro* on a polymer nanofiber scaffold seeded with stem cells [Li *et al.*, *Biomaterials* (2005) **26 (25), 5158].**

Cells grown on a biodegradable scaffold can be used to help repair damaged tissues in the body. Stem cells could prove useful because they can differentiate into a variety of specialized cell types. Ideally, a single biomaterial scaffold should support multiple cell types, so mimicking natural tissues.

The team immersed human mesenchymal stem cells in an electrospun poly(ϵ -caprolactone), or PCL, scaffold and induced the cells to differentiate into different cell lineages. "The electrospun nanofibrous scaffold... can be considered as a candidate biomaterial scaffold for the fabrication of a single-unit-based, multicomponent tissue construct," says Wan-Ju Li.

The scaffold is effective because its 700 nm diameter fibers imitate the collagen fibrils that support cells in the body. The fine fibers also provide a desirable degradation rate.

"Unlike many other biomaterials that have



Scanning electron micrograph of electrospun PCL-based scaffold nanofibers of average diameter 700 nm. (© 2005 Elsevier.)

been tested as scaffolds, PCL dissolves slowly," explains lead author Rocky S. Tuan. "Some materials, like poly-D,L-lactic-co-glycolic acid, will disappear after only a few days." "We have begun testing [the tissue-engineered constructs] *in vivo* and have had preliminary success," he adds. "The goal is to create cartilage, but that is still about five years down the road." Tissue patches like these could alleviate pain, while more applications will be seen in the coming years, he believes.

Patrick Cain

Improved materials for bone grafts

BIOMATERIALS

The aging of populations in developed countries is increasing interest in improved materials for bone grafts. With increased life spans, such materials must last longer to avoid later surgery to reinforce grafts weakened through extended use. Inadequate long-term performance of grafts is frequently a result of a mismatch in the mechanical properties of the implanted material and the surrounding tissue, leading to implant failure and tissue damage.

Bone is a composite of collagen, a protein-based hydrogel template, and inorganic apatite (calcium phosphate) crystals. Bone biogenesis is thought to occur by templated mineralization of apatite crystals on an elastic protein scaffold. Researchers at the University of California, Berkeley and Lawrence Berkeley National Laboratory have modeled this process using synthetic, biomimetic hydrogel polymers [Song *et al.*, *J. Am. Chem. Soc.* (2005), **127** (10), 3366]. Carolyn R. Bertozzi and coworkers functionalized crosslinked

polymethacrylamide and polymethacrylate hydrogels with mineral-binding ligands to mimic bone matrix proteins. Hydrogels based on poly(2-hydroxyethyl methacrylate) were chosen for more extensive study, based on their excellent biocompatibility and ease of functionalization, and used as templates for hydroxyapatite formation. Functionalization with carboxylate or hydroxyl groups promoted strong adhesion between organic and inorganic materials. Slow heating of the hydrogel in an acidic solution of hydroxyapatite in the presence of urea was used to model the bone-grafting process. Circular calcium phosphate domains grew from individual binding sites and eventually merged to cover the entire hydrogel surface. X-ray diffraction suggests that the calcium phosphate domains were either amorphous or nanocrystalline. Deliberate fracturing of these domains did not lead to their delamination from the hydrogel surface, indicating good interfacial adhesion – a critical property in bone grafts.

John K. Borchardt

Swollen liquid crystals as nanoreactors

POLYMERS

Researchers from France's CNRS, Université Montpellier, and Université Paris, Delft University of Technology in the Netherlands, and Brasil's Instituto de Quimica, UNESP, report a new way of preparing nanomaterials by polymerization within cylinders of swollen liquid crystals [Surentran *et al.*, *Chem. Mater.* (2005) **17**, 1505]. Controlling synthesis and self-assembly (e.g. by confining the reaction to a specific geometry) is essential for electronics and other applications. Reverse micro- or miniemulsions can be used as 'nanoreactors', but need vigorous stirring. Control can be given by the topology of liquid crystals, but these are usually restricted to water/surfactant systems.

So, highly ordered liquid crystal media were prepared by combining salt water and nonpolar solvents with cationic, anionic, or nonionic surfactants and cosurfactants to form hexagonal phases – a network of parallel cylinders regularly spaced in a continuous aqueous salt solution whose diameters can be swollen with a nonpolar solvent. Very high optical transparency enables the photopolymerization of diacetylenes within the cylindrical nanoreactors. A mixture of sodium chloride, sodium dodecyl sulfate, cyclohexane, and 1,4-diphenylbutadiyne was structured by adding 1-pentanol and stirring under N_2 . After polymerization, adding equal amounts of water and ethanol led to separation of an organic layer containing the polymer. Evaporating the organic solvents gave polymer fibers floating on the surface.

The geometry and size of the liquid crystal composition can readily be adjusted via the solvent, salt, reagent precursor, pH, and swelling agent.

John K. Borchardt

Colloidal crystal wires for new materials

FABRICATION & PROCESSING

Colloidal crystals have potential applications in photonics and as biomaterials, catalytic supports, and lightweight structural materials. Improving control over the geometry and relative dimensions of silica spheres and the channels between them could yield materials with both chiral and achiral structures for photonic applications. John B. Wiley and coworkers at the University of New Orleans and Sweden's KTH Royal Institute of Technology have formed colloidal crystals within confined channels in porous silica templates (Li *et al.*, *J. Am. Chem. Soc.* (2005) **127 (10), 3268). Using confined cylindrical channels provides chiral and achiral sphere packing geometries not produced in open grooves. Subsequent fusion of the silica spheres forms colloidal crystal wires.**

The porous template is prepared via a two-step chemical-electrochemical etching method. SiO_2 spheres (1.3 μm) are then inserted into the $\sim 3 \mu m$ pores using vacuum filtration and annealed at high temperature to fuse them together. Repeating the annealing steps encases the colloidal wires within a thin silica sheath ~ 20 nm thick to give peapod structures.

The colloidal crystal wires are $\sim 60 \mu m$ long and the spheres are readily observable within



Colloidal crystals within silica tubes, coated with metal to reduce charging during imaging. (© 2005 American Chemical Society.)

the translucent sheaths. The silica pores are not perfectly uniform, so different sphere-packing geometries can be produced; most commonly wires with six helical strands result, but between four and seven strands can be observed.

Sputtering these structures produces metal-coated, silica-encased colloidal crystals, providing a stable support to the wires and reducing surface charging during imaging.

Applying this techniques to materials other than silica could provide a variety of other structures. In particular, the sphere and the sheath could be made from different materials, producing composite materials that could have interesting properties.

John K. Borchardt

Stable organic thin-film transistors

POLYMERS

Acene and thiophene oligomers have been studied extensively as organic semiconductors, with pentacene-based thin-film transistors showing promise for low-level logic circuits and displays. However, stability, especially the slow reaction of pentacene with oxygen, and poor pentacene solubility have raised concerns about its viability. Now, C. Daniel Frisbie and coworkers at the University of Minnesota, 3M Company, and Stanford Linear Accelerator Center report that materials based on anthracene and tetracene units combined with thiophene oligomers exhibit promising semiconductor properties [Merlo *et al.*, *J. Am. Chem. Soc.* (2005) **127** (11), 3997].

This new class of hybrid acene-thiophene organic semiconductors is thermally stable. High-melting-point solids readily sublime to form high-quality polycrystalline films. At sublimation temperatures below 260°C, continuous, highly crystalline films are

formed on silica and silica-polystyrene surfaces. Atomic force microscopy and X-ray diffraction results are consistent with a herringbone packing geometry.

The oligomers were: (1) 5,5'-bis(2-tetraceny)-2,2'-bithiophene and (2) 5,5'-bis(2-anthraceny)-2,2'-bithiophene. Both show excellent thermal stability and, according to scanning calorimetry, differential thermal, and thermal gravimetric analyses, are more air-stable than pentacene and other organic semiconductors.

Electrical characterization indicates excellent thin-film transistor performance (high mobility, large on/off current ratio, and increased air stability). After 500 hours of operation in air, (2) gives no loss in current while (1) loses 24% and pentacene 31%. So, compound 2 seems particularly promising as an air-stable *p*-channel organic semiconductor.

John K. Borchardt

Block copolymers for nanoscale devices

CONFERENCE REPORT



AFM image of a triblock copolymer thin film after removal of both the PMMA and PEO. (Courtesy of Craig J. Hawker.)

Craig J. Hawker of the University of California, Santa Barbara was presented with the Applied Polymer Science Award at the 229th American Chemical Society National Meeting in San Diego. In receiving the prize, he reviewed his work on designing high-value polymeric materials for nanoscale commercial applications, particularly for energy storage devices and microelectronics. Fabrication of nanoscale devices requires precise control over material properties and function on the scale of about 5 nm to several microns. Hawker noted that advances in preparing nanoparticles, shape-persistent three-dimensional polymer molecules, and improved control over 'living'

free-radical polymerizations have increasingly enabled this to be achieved.

It is difficult and expensive to control polymer films on the 50-100 nm scale using lithography, he added. Alternative, low-cost chemistry is needed to assemble molecules at scales of <50 nm. He has developed an approach based on self-assembling block copolymers. The critical process steps are preparing a neutral surface, forming a poly(methyl methacrylate)-polystyrene (PMMA-PS) block copolymer in selected areas, achieving vertical alignment of PMMA cylinders, followed by their photochemical removal from the PS matrix. Initially, the targeted use is flash memory, and development work on these self-assembling block copolymers is underway at IBM. For other applications, long-range order can be provided by block copolymers of PS and poly(ethylene oxide), or PEO, but these have poor biodegradability. Hawker is developing nanostructured films based on terpolymers of PS, PEO end blocks (for long-range order), and short PMMA blocks (for biodegradability). Atomic force microscopy (AFM) indicates that the block terpolymers are defect-free over large areas.

John K. Borchardt

Building functional materials layer by layer

CONFERENCE REPORT

Electrostatic layer-by-layer deposition is a simple but elegant method for constructing polymer and organic-inorganic composite thin films from alternate layers of oppositely charged molecules. At the American Chemical Society National Meeting, Paula T. Hammond of Massachusetts Institute of Technology described how her group has used this approach to prepare ultrathin multilayer films with high ionic conductivity. Using conjugated polymers and inorganic nanoparticles yields materials that are potentially useful for electrochromic displays and proton exchange membranes in fuel cells. The gradual release of drugs and biomacromolecules from thin films under physiological conditions is desirable for therapeutic applications. David M. Lynn of the University of Wisconsin-Madison described films that provide sustained release of functional DNA and which could aid development of localized gene therapies. But attaining both spatial distribution and temporal

release of DNA at the surface of a device requires sophisticated biodegradable materials.

Lynn assembled multilayered polyelectrolyte films designed to incorporate and then release transcription-active plasmid DNA. For this to occur, design features must promote dissolution, disintegration, or erosion of the multilayered assemblies. Ways of initiating this deconstruction include changing the ionic strength or pH. Lynn's group prepared multilayer films up to 100 nm thick from a degradable cationic polyester and conventional polyanions. Both film thickness and absorbance exhibited a linear correlation with the number of polymer and DNA layers deposited. The conditions for film deconstruction were designed to model human physiology (pH 5.1 at 37°C). The researchers demonstrated that significant levels of the released DNA could be incorporated into mammalian cells.

John K. Borchardt

Nanocrystals in electronic devices

CONFERENCE REPORT

Richard H. Friend presented new results from his University of Cambridge group at the Materials Research Society Spring Meeting in San Francisco. The team has obtained efficient heterojunction photovoltaic devices by dispersing CdSe nanocrystals within a polymer brush. Polyacrylate chains with hole-accepting side groups are grown from the bottom electrode of the device. By controlling the density of initiator sites for the polymerization reaction, a brush showing substantial chain extension normal to the substrate can be synthesized. The strong organization of the polymer brush results in a high hole mobility. CdSe nanocrystals <2.8 nm in size are then added to the brush, where they form interactions with the hole-transporting group. These photovoltaic devices have surprisingly good internal quantum efficiencies of ~50%.

Other speakers at the meeting also showed how nanoparticles could enable cheap electronic devices. Nanocrystal inks can be printed and sintered at low temperature to form uniform thin films. Joerg Rockenburger described how Kovio, a start-up company in California, is developing commercially viable synthesis techniques for nanoparticle inks. Soluble Ag and Si nanocrystals are obtained simply, reproducibly, and in gram quantities. Yiliang Wu and coworkers at the Xerox Research Centre of Canada are exploring Ag and Au nanoparticle inks for printing electrodes for organic thin-film transistors. Low-temperature annealing of the inks is compatible with plastic electronics and gives films with metal-like conductivity. Device performance is equal to those with vacuum-deposited electrodes.

Jonathan Wood