Paint-On OPTO

Artist’s rendition of a 1.54 μm-emitting laser made by solution-processing a colloidal quantum dot active layer onto the inner surface of a glass capillary.
Over the past few decades, researchers, and now companies, have begun spin-coating optoelectronic materials as a lower-cost alternative to epitaxially grown devices. But whether solution-processed optoelectronic devices can perform as well as their traditional grown-crystal counterparts has remained unclear. Now, a group of researchers at the University of Toronto have demonstrated that a “wet” semiconductor device with a painted-on layer of nanoparticles outperforms standard chips.
Semiconductors form the foundation of the information age. Computers run on silicon, with Moore’s Law clocking advances in chip density, power and cost-effectiveness. Internet data are carried over guided beams of light generated in lasers made of InGaAsP—a quaternary compound semiconductor. Digital cameras register images in silicon sensors, which are focal plane arrays exquisitely sensitive to visible light. Still other cameras used in military night-vision and security applications rely on InGaAs photodetector arrays read by a silicon electronic circuit.

Semiconductor technology today

Pure, perfect crystals are the basis of much of today’s semiconductor technology. Applications that require efficient electronic transport rely on a high electron or hole mobility. Perfect periodic regularity in the arrangement of atoms—crystallinity—enables the delocalization of charge carriers over large distances, a phenomenon that leads to high mobility.

Further, irregularities and interfaces in crystals work against the efficient production of light from a semiconductor. The creation of near-perfect crystals is generally viewed as a requirement for optoelectronics and electronics alike. The process of growing one perfect crystal on top of another is known as epitaxy. Building heterostructures—layers of different semiconductors—has been critical to producing high-speed electronic devices, sensitive light detectors and semiconductor lasers over a wide range of wavelengths.

Epitaxy, for all its tremendous benefits, comes at a cost. First, the equipment to grow such heterostructures is expensive, as is its operation, especially in view of the dangerous reagents that are often required. Second—and even more important—epitaxy typically requires a matching, or near-matching, of the atomic spacing (lattice constant) of the crystal substrate and its overlayers.

The lattice-matching constraints mean that direct bandgap optoelectronic materials tend to be very challenging to grow, especially with high quality, on top of silicon, the platform for electronics. Thus, instead of monolithically integrating the materials used in computation and communication, we have been constrained to co-packaging these classes of devices. This is costly and scales poorly. For example, while monolithic multi-megapixel silicon focal plane arrays have led to $100 digital cameras, InGaAs cameras for night vision cost upwards of $30,000.

Paint-on optoelectronics

Over the past few decades, researchers and companies have begun spin-coating optoelectronic materials from solution on top of chips. They’ve made transistors, photodetectors, solar cells and even lasers.

An important question in paint-on optoelectronics has remained: Can the performance of solution-processed optoelectronic devices compete with that of their epitaxially grown counterparts? If so, the low cost and ease of integration of spin-on sensors, sources and photovoltaic elements could revolutionize communications, computing, imaging and energy conversion.

An ultrasensitive solution-cast photodetector

This central question—of whether performance and ease of processing represent a fundamental trade-off—now has an answer: Not only can spin-cast infrared optical sensors compete with their perfectly single crystal counterparts; they can outperform them.

In the July 2006 issue of Nature, we reported a spin-cast photodetector, working out to 1.3 µm wavelength, that outperformed its InGaAs counterpart by nearly an order of magnitude. The figure of merit that accounts for the sensitivity of a photodetector is known as normalized detectivity, represented by the symbol D*.

Epitaxially grown InGaAs devices on an InP substrate achieve a matching, or near-matching, of the atomic spacing (lattice constant) of the crystal substrate and its overlayers.

The figure on the right illustrates the simplicity with which the device was built. Our substrate was a glass slide pre-patterned with identical gold electrodes laterally spaced by 5 µm. In a room ambient, we placed a droplet of PbS (lead sulfide) crystals atop the substrate.

We spun our substrate on a plate just the way photoresist is induced to spread out and form a thin, uniform film prior to photolithography.

Following another simple solution-phase
chemical treatment, the device was complete. Fabrication was done at room temperature and, with the nanoparticles already in hand, took about five minutes.

How could the device work so well without being made of a single, perfect crystal?

In photodetectors based on photoconduction—a reduction in resistance upon illumination—two things matter. The first is responsivity, or how much more current flows under constant bias when the device is illuminated. This responsivity can exhibit photoconductive gain, whereby multiple electrons’ worth of current are collected for every photon incident. Gain depends on having a large ratio of carrier excited-state lifetime to the transit time across the device. We sought to extend carriers’ lifetimes into the millisecond range, through control of interface states on the nanoparticles, while minimizing transit time by maximizing mobility.

Sensitivity also depends on minimizing noise. Fundamental processes such as the room-temperature generation and recombination of carriers at equilibrium put a bound on the extent to which noise can be minimized. We exploited quantum size-effect tunability in our material’s effective bandgap to tailor its absorption of light to that required in a specific application; excess noise due to the absorption of low-energy photons was thereby eliminated. In addition, photoconductive detectors have in the past often suffered from worse performance than fundamental thermodynamics dictate, a fact that has been attributed to multiplicative noise.

A large photoconductive gain with near-minimal noise gave us an ultrasensitive photodetector—one that worked in the short-wavelength infrared range used in communications, as well as new biomedical procedures.
We designed our process sequence so as to keep noise to within 3 dB of its fundamental lower bound for our chosen bandgap.

Taken together, a large photoconductive gain with near-minimal noise gave us an ultrasensitive photodetector—one that worked in the short-wavelength infrared range used in communications, as well as new biomedical procedures.

A laser painted on a chip

Electronics also hold the potential to be augmented by convenient integration with optoelectronic devices. The term “copper bottleneck” refers to the limits on chip speed imposed by the slow-down introduced in electronic interconnects. Higher data transfer rates could be achieved by using optical interconnects instead. Thus, scientists are interested in pursuing a source of infrared light (not absorbed by silicon) that can be directly integrated on a silicon chip.

Research teams have recently shown that silicon itself can be made to lase. Another approach is to spin-coat a different, gain-providing material onto a silicon substrate. We reported in the April 2006 Optics Express that we could make such a paint-on infrared laser.

We began by demonstrating the presence of optical gain in a solution containing semiconductor nanocrystals by means of ultrafast pump-probe experiments. We obtained a gain value of about 7 percent of the linear absorption at the photoluminescence peak, corresponding to a few tens of inverse centimeters of optical gain in a solid thin film. Such numbers for optical gain require low propagation losses in a waveguide in order to establish lasing operation.

By changing the ligands that passivate the surface of nanocrystals and the solvents from which the solid thin films were cast, we were able to produce 1-µm-thick films with waveguide propagation losses less than 10 cm⁻¹. The corresponding ligands have an additional benefit in that they create densely packed films with fill-factors of about 30 percent. This results in very fast stimulated emission buildup times, compared to ultrafast non-radiative parasitic processes such as Auger recombination.

These findings provided the right ingredients to realize the first infrared colloidal quantum dot laser. For this, we dipped the end of a glass microcapillary tube in a PbS nanocrystal solution, and forced the solvent to evaporate, to leave a thin nanocrystal film on the inner wall of the capillary. We subsequently mounted the capillary into a liquid nitrogen cryostat, cooled it to 80 K, and optically pumped the structure using a regeneratively amplified Ti:Sapphire laser with 2-ps pulses.

The 1530-nm emitted light clearly shows a threshold behavior as a function of pump power. Above threshold the spectrum exhibits a narrow lasing peak. (See the figure on the left.) The feedback system in this laser relied on total internal reflection at the nanocrystal-glass interface. From the mode-spacing, we determined that the laser mode was highly confined inside the nanocrystal thin film.

Much work remains to be done to make on-chip sources for interconnects.
One of the many challenges to overcome in making solution-processible solar cells efficient is figuring out how to make the best use of the sun’s spectrum. The sun’s power is nearly half in the infrared. Visible-absorbing polymers therefore access only a limited portion of the sun’s power.

However, infrared solution-processible solar cells have recently emerged and shown rapid improvement. A year and a half after the first report, these devices are now a factor of 20 to 40 from tapping the sun’s infrared rays with sufficient efficiency to augment significantly the overall (AM1.5) performance of polymer solar cells.

A path forward for flexible optoelectronics

We now know that, in one critical area of semiconductor optoelectronics, namely optical sensing, paint-on optoelectronic devices can demonstrate spectacular performance. Whether this conclusion can be broadened to encompass not just signal, but also energy conversion—from light to electricity and from electricity to light—remains an open question that urgently invites resolution. If the answer is yes, optoelectronics could become even more ubiquitous.

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Harnessing the sun’s power

One thousand times more sunlight reaches the earth’s landmass each day than we consume across all our energy habits. If we could cover 1 percent of the earth with 10 percent-power-conversion-efficiency solar cells, we could then harness this powerful, clean source of energy to considerable effect.

Crystal growth on few-inch substrates is unlikely to allow us to build thousands-of-square-kilometer photovoltaic devices. New techniques, such as those based on roll-to-roll processing of multicrystalline and amorphous inorganic silicon, as well as solution-processed polymers and other organics, are thus under active investigation.

Whereas cost limits single-crystal devices’ applicability to our energy challenges, efficiency limits today’s solution-processible devices. The general belief is that these need to show about 10 percent power conversion efficiency to pay back their cost of fabrication and installation. However, today’s polymer and solution-processed nanocrystal solar cells recycle only a few percent of the sun’s energy as electricity.

One of the many challenges to overcome in making solution-processible solar cells efficient is figuring out how to make the best use of the sun’s spectrum. Peaking at about 550 nm, the practical. The devices need to be made on an actual silicon resonator; they need to operate at room temperature; and they should ideally work under electrical injection. Fortunately, silicon has in recent years emerged as an admirable basis for low-loss optical resonators. While electrically driven light sources based on solution-processed semiconductors show promise, the current densities needed for lasing still need to be mastered.