Charting routes to zinc oxide applications

A wide bandgap and piezoelectric properties make zinc oxide an interesting material for research into producing and detecting light (up to ultraviolet) and for electromechanical systems. Dr Mike Cooke looks at progress in producing p-type doping, allowing light emission from p–n junctions, and new ideas for mechanical coupling and photodetection from nanowires.

Research into semiconductor materials that are not in the mainstream often comes in spurts. The beginning of a spurt is marked by an old problem overcome or a new idea. Zinc oxide has recently seen something of a renaissance [1], with some progress on the long-term problem of finding techniques to create p-type doping [2]. Also, further new ideas have arisen in application areas in terms of using the piezoelectric properties of the material. Device opportunities include optoelectronics (particularly UV), high power, transparent thin-film transistors and even spintronics. ZnO is often in the frame when nanowires need to be constructed.

Zinc oxide is already used as an electronic material for producing varistors (voltage dependent resistors). Such devices use zinc oxide grains in a metal (e.g. cobalt, bismuth, manganese) oxide matrix. Diode junctions are formed between the grains such that only small currents flow for moderate voltages, but avalanche breakdown at high voltage produces a large current. Such devices are used to divert surges away from delicate circuits.

Polycrystalline ZnO is also used in phosphors, piezoelectric transducers, optical waveguides, acousto-optic media, conductive gas sensors and transparent electrodes (e.g. in photovoltaics). Properties such as piezoelectricity could be further developed to produce surface acoustic wave (SAW) filters for RF devices, such as in mobile wireless electronics.

The material could also be useful for applications needing radiation hardness (e.g. space, defense). Indeed, it is even better than gallium nitride in this respect. For thin-film transistors, it can be deposited in amorphous or crystalline forms on flexible substrates, with the resulting (transparent) material having higher mobility than organic semiconductors. Doping with manganese (Mn) or other 3d transition metals produces spintronic opportunities.

More recently, ZnO substrates have been produced with a view to providing substrates for nitride-based optoelectronic devices. For example, Cermet of Atlanta, GA, USA produces ZnO (n-type) bulk substrates up to 50mm in diameter. The wurtzite crystal structure matches much more closely that of GaN and related AlInGaN compound semiconductors compared with traditional sapphire (Al_2O_3) substrates. Indeed, a perfect match is achieved between ZnO and $In_{0.22}Ga_{0.78}N$, and the ZnO–GaN mismatch is of the order of 2% rather than the about 16% for sapphire. This situation is also used in reverse, where a ZnO thin film is grown on a GaN buffer layer on sapphire. However, a general problem arising from the strongly increased ionic character of II–VI bonds in ZnO compared with GaN is that stacking defects can easily occur within a short distance of a perfect interface between the slightly mismatched materials.

Another alloy system that can be used with ZnO is MgCdZnO. Non-equilibrium techniques enable the inclusion of magnesium beyond its normal solubility limit of 10% up to 50%, allowing the band gap to be varied over the range 3.0–4.5eV. Using Cd enables one to slightly lower the bandgap range to 2.8eV. By comparison, the band gap of pure ZnO is about 3.4eV.

Another interesting property of ZnO is its high exciton binding energy of 60meV (bound states of electrons and holes) compared with 21–25meV for GaN and the 26meV k_BT equivalent of of room temperature (300K). Superlattice structures of $ZnO/Mg_xZn_{1-x}O$ have enabled exciton binding energies to reach 115meV. Excitons are seen as a route to lasers with low threshold currents [3].

The p-type problem

Since unintentionally doped ZnO tends to have n-type properties, p-type doping is difficult to achieve. Such an asymmetric doping limitation is common in wide-bandgap materials. The n-type property in ZnO can be enhanced using doping with Group III elements such as Al or Ga. One factor creating the n-type bias is a shallow donor level that is thought to be associated with hydrogen. In addition to the desire to create

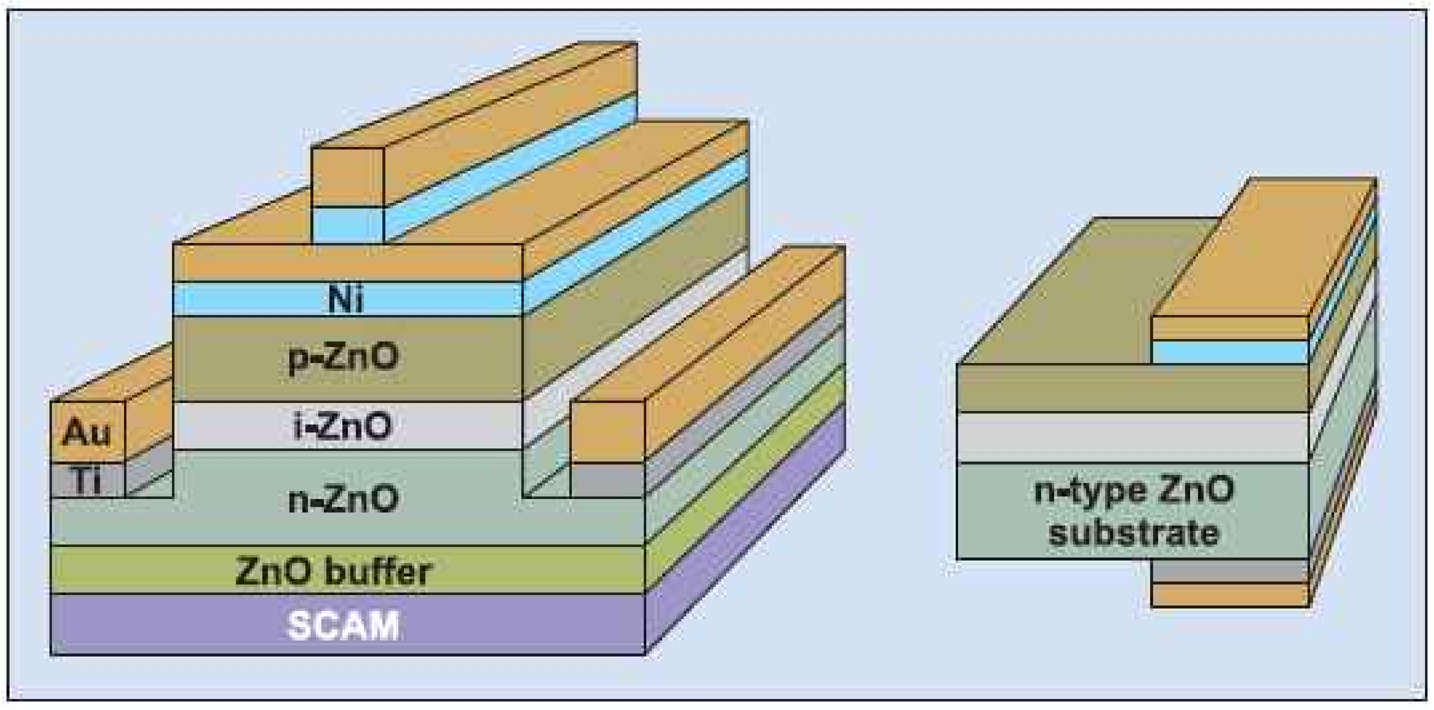

Figure 1. ZnO LED structures on $ScAlMgO_4$ substrate (left, from [5]) and on pure ZnO substrate (right, as developed by Cermet [6]).

p–n junctions, p-type doping is also seen as being important for creating dilute magnetic semiconductor devices with Curie transitions above room temperature, since theoretical predictions indicate that p-type (but not n-type) Mn-doped ZnO has a ferromagnetic transition [4].

For p-type properties, one looks for acceptor levels, and here Group I or Group III elements are in the frame. Nitrogen is a likely candidate, substituting for oxygen, but the presence of hydrogen either in the transport gas or in the doping precursor (e.g. NH_3) makes it difficult to avoid n-type compensation. Also, the acceptor level is relatively deep, resulting in low hole concentrations ($\sim 10^{17}cm^{-3}$) and hence high resistivity. Compounding this, hole mobilities are an order of magnitude smaller than for electrons — about $10cm^2/V$-s rather than $100–200cm^2/V$-s. Other acceptor doping materials that have been tried include phosphorus, arsenic and antimony.

Part of the problem is that n-type conduction is too easy; even getting intrinsic carrier levels is hard — the electron concentration in ZnO grown on sapphire is typically $10^{17}–10^{18}/cm^3$. The electron concentration can be reduced to $10^{16}/cm^3$ when ZnO is deposited on $ScAlMgO_4$. Nitrogen is seen as the best option for acceptor doping, because its small ion size reduces compensation effects. However, high-quality ZnO films require growth at more than 800°C, while high concentrations of N are only possible to achieve at temperatures below 500°C.

One method — alternating low- and high-temperature growth ('reverse temperature modulation' growth) — has achieved a hole concentration of $10^{16}/cm^3$ with a carrier mobility of $8cm^2/Vs$. The low-temperature phase grows 15nm of N-doped ZnO, while the high-temperature phase leaves 1nm of high-quality N-doped material. The process is repeated to achieve the required thickness. Some blue light-emitting diodes have been produced using this technique [5]. $ScAlMgO_4$ is insulating, so a mesa structure is used, with both contacts made through the top surface (Figure 1, left).

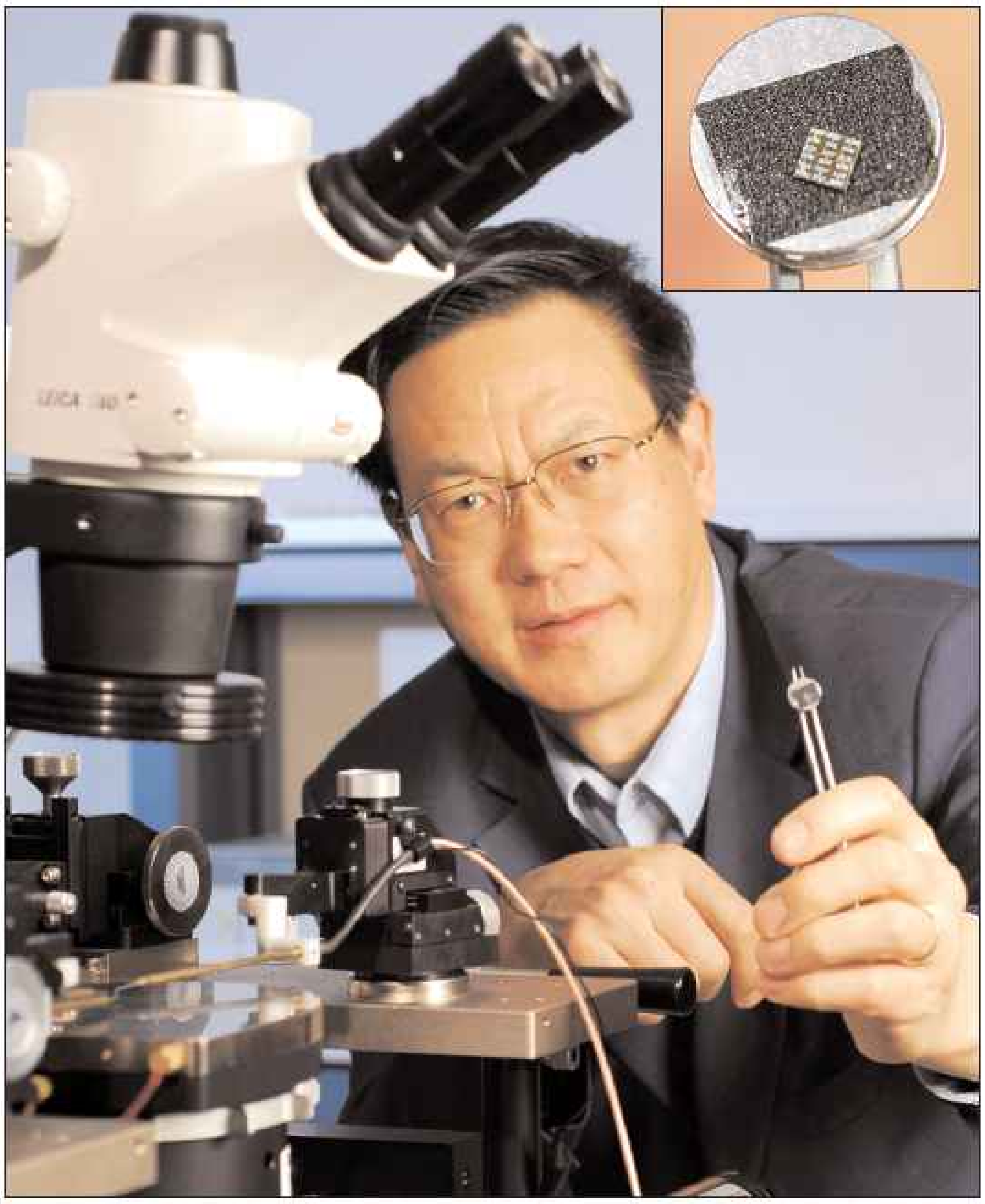

Figure 2. Zhong Lin Wang, Regents professor at the School of Materials Science and Engineering at Georgia Tech, holds a prototype DC nanogenerator fabricated using an array of zinc oxide nanowires. Inset: close-up image. (photos: Gary Meek)

Another attraction of ZnO would arise if high-quality bulk ZnO crystal substrates could be used, since then both top and bottom contacts could be made to the devices (Figure 1, right), as with bulk GaN laser diodes and more traditional GaAs and InP based light-emitting devices.

Cermet, being based in Georgia, has worked with Georgia Institute of Technology on many ZnO projects. Most recently, the company announced an exclusive license agreement for ZnO/nitride semiconductor white LED technology that has been developed with the Georgia Institute of Technology (see February's issue 1, page 16). The devices use nitride emitter structures in combination with ZnO semiconductors to produce white light-emitting diodes. Another project with Georgia Tech and the US Air Force involves developing light emission on ZnO covering the infrared to UV in a single device. The US Army Research Office is also working with the company to develop ZnO p–n junctions for UV/blue emission. It is hoped that homoepitaxial growth of ZnO will result in devices with far fewer of the defects that seriously degrade performance of GaN devices. Also, Cermet believes that such devices will eventually cost less to produce than GaN-based technology.

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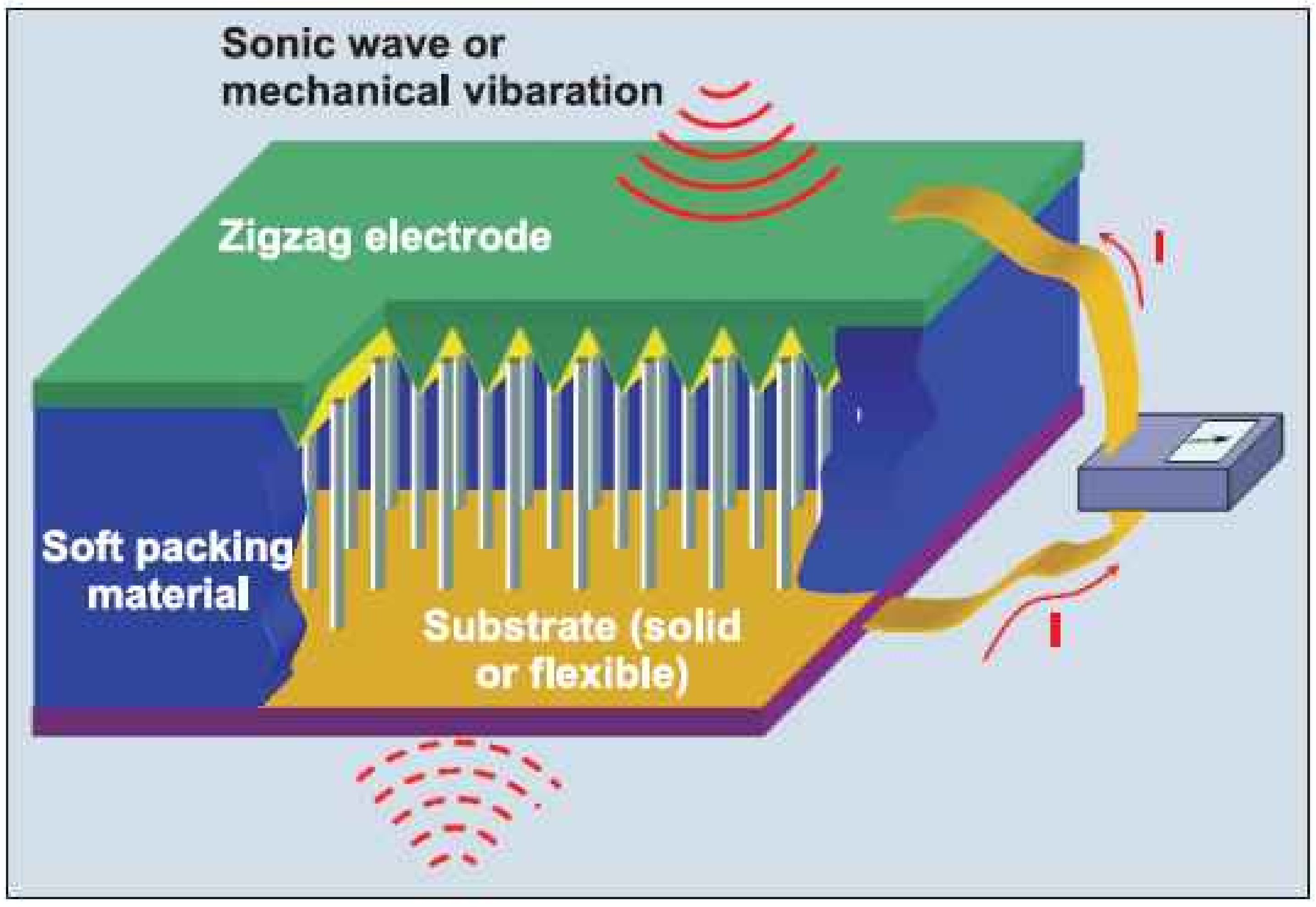

Figure 3. Schematic showing direct current nanogenerator built using aligned ZnO nanowire arrays with a zigzag top electrode. The nanogenerator is driven by an external ultrasonic wave or mechanical vibration and the output current is continuous.

Cermet also reports progress in producing the elusive p-type ZnO layers using metal-organic chemical vapor deposition (MOCVD) on its n-type substrates. While copper and phosphorus doping have been achieved, the company's efforts have focused on nitrogen doping using NH_3 and N_2O sources. Light-emitting diodes made from the resulting p–n junction were driven at 140mA to produce light with a peak wavelength of 384nm [6]. The published paper comments: "This, to our knowledge, is the first clear EL [electroluminescence] peak measured from a ZnO p–n junction LED."

This light is attributed to recombination between shallow donors and nitrogen luminescent centers on the p-side of the junction. Nitrogen-doped ZnO has a photoluminescence peak at around 380nm. Secondary-ion mass spectrometry (SIMS) of the p-type layer suggests a nitrogen concentration of $10^{20}/cm^3$. Hall measurements give a hole concentration of $9x10^{17}/cm^3$, but with a low mobility of $1.5cm^2/V\text{-}s$.

Cermet's president Jeff Nause believes ZnO will compete for high-end optoelectronic devices (power LEDs and laser diodes in the visible part of the spectrum) as a substrate for nitride emitters. "For UV devices, ZnO devices may compete if the community arrives at a long-lifetime p-doped ZnO," he adds.

Nano-piezotronics

At Georgia Institute of Technology, new electronic devices are being constructed from zinc oxide nanowires. The Georgia Tech researchers use both the electronic and piezoelectric properties of ZnO to create what have been trademarked as 'nanopiezotronics' [7]. Piezoelectricity describes the change of a material's charge distribution under mechanical strain.

Along with the usual suspects of diodes [8], field-effect transistors and sensors, the researchers have also constructed 'nanogenerators' (Figures 2 and 3) that produce currents operated by bending nanobelts and nanowires of ZnO [9]. Such devices could convert mechanical energy from body movement, muscle stretching, fluid flow or other sources into electricity. By producing current from the bending and releasing of zinc oxide nanowires, these devices could eliminate the need for batteries or other bulky sources for powering nanometer-scale systems.

In piezotronic transistors, current flow is controlled by changing the conductance by bending the nanostructure between the source and drain electrodes (Figure 4). The bending produces a 'gate' potential across the nanowire and the resulting conductance is related to the degree of bending applied.

"The effect is to reduce the width of the channel carrying the current, so you can have a ten-fold difference in the conductivity before and after the bending," explains Zhong Lin Wang (pictured in Figure 2), who is Regents professor in the School of Materials Science and Engineering at the Georgia Institute of Technology.

The change in transistor performance due to bending

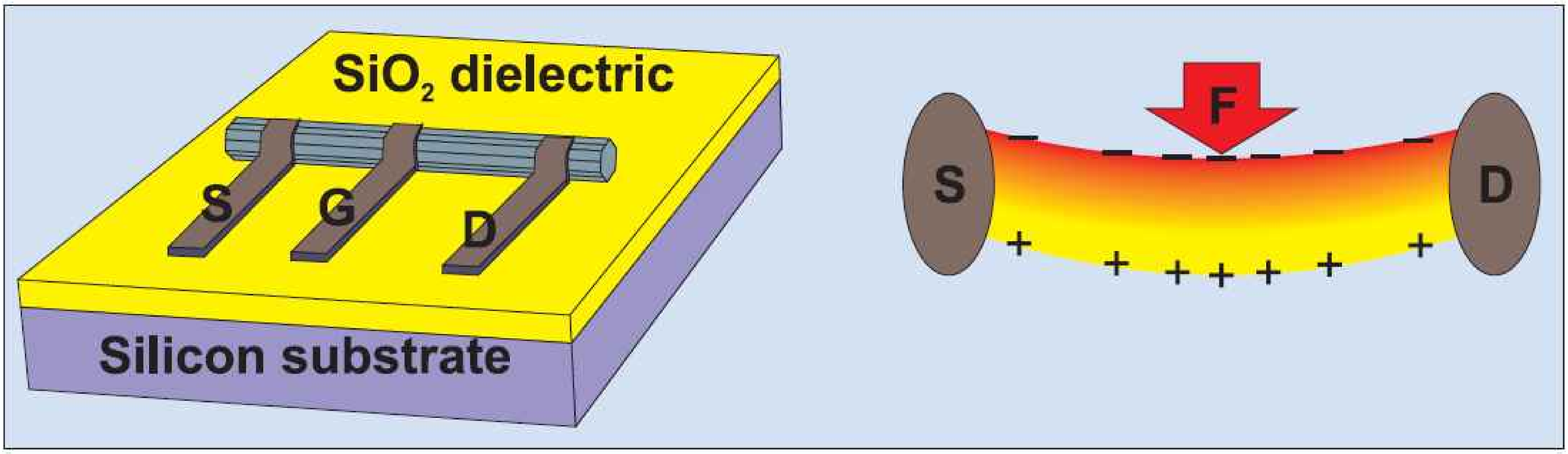

Figure 4. Diagram compares a nanowire/nanobelt based field effect transistor (FET) with a piezoelectric FET. The traditional FET has a gate electrode, either deposited (left) or using the substrate as a 'back gate'. In the 'piezotronic' device (right), the gate electrode is replaced by the piezoelectric field produced across the nanowire/nanobelt by an external force.

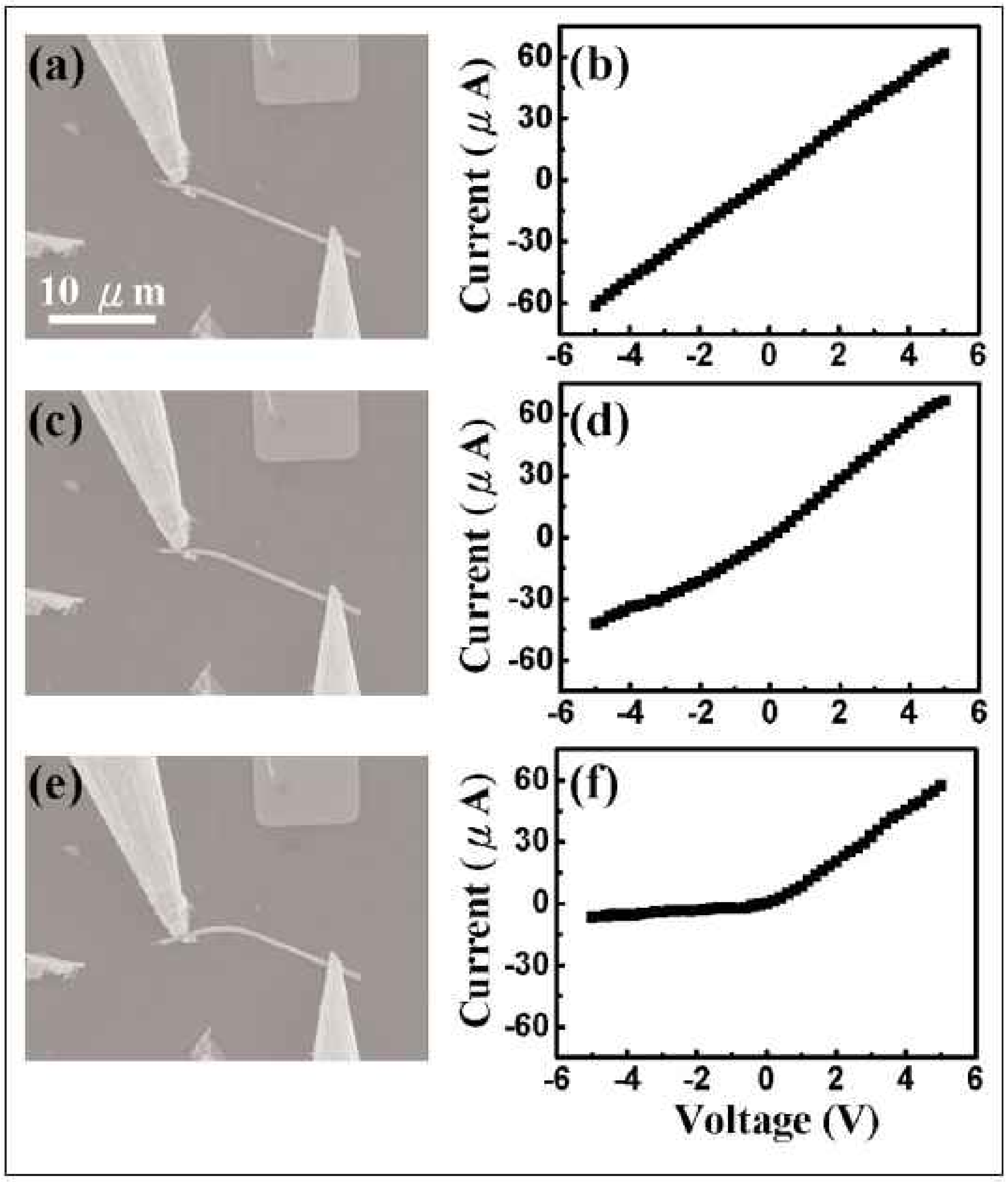

Figure 5. A piezotronic diode is shown (a, c and e) in a sequence of scanning electron microscope images of bending a single zinc oxide nanowire between two probes. The graphs (b, d and f) show the corresponding current flow through the nanowire.

could be used to create sensors for nano- or even pico-Newton forces, the researchers maintain. Another piezotronic sensor configuration could determine blood pressure by measuring the current flow, since ZnO materials are biocompatible, allowing their use in the body without toxic effects.

The diodes created through nano-piezotronic mechanisms take advantage of a potential barrier created at the interface between the electrode and the tensile (stretched) side of the nanowire by mechanical bending (Figure 5). The potential barrier created by the piezoelectric effect limits the flow of current to one direction.

Other ZnO-based nanosensors can detect very low levels of specific compounds by measuring the current change that is created when molecules of the target are adsorbed on to the nanostructure's surface. "Utilizing this kind of device, you could potentially sense a single molecule, because the surface area-to-volume ratio is so high," comments Wang.

Nanowire photodetectors

The University of California San Diego (UCSD) has also been studying ZnO nanowires with a view to producing single-photon detectors [10]. These researchers believe that the relatively large surface area of nanowires compared with their length and volume makes them extremely sensitive to light. In particular, surface states grab the holes from photogenerated electron–hole pairs, allowing the free electrons to transport charge under an electric field. ZnO nanowire UV photodetector arrays built at UCSD had an internal photoconductive gain as high as 10^8.

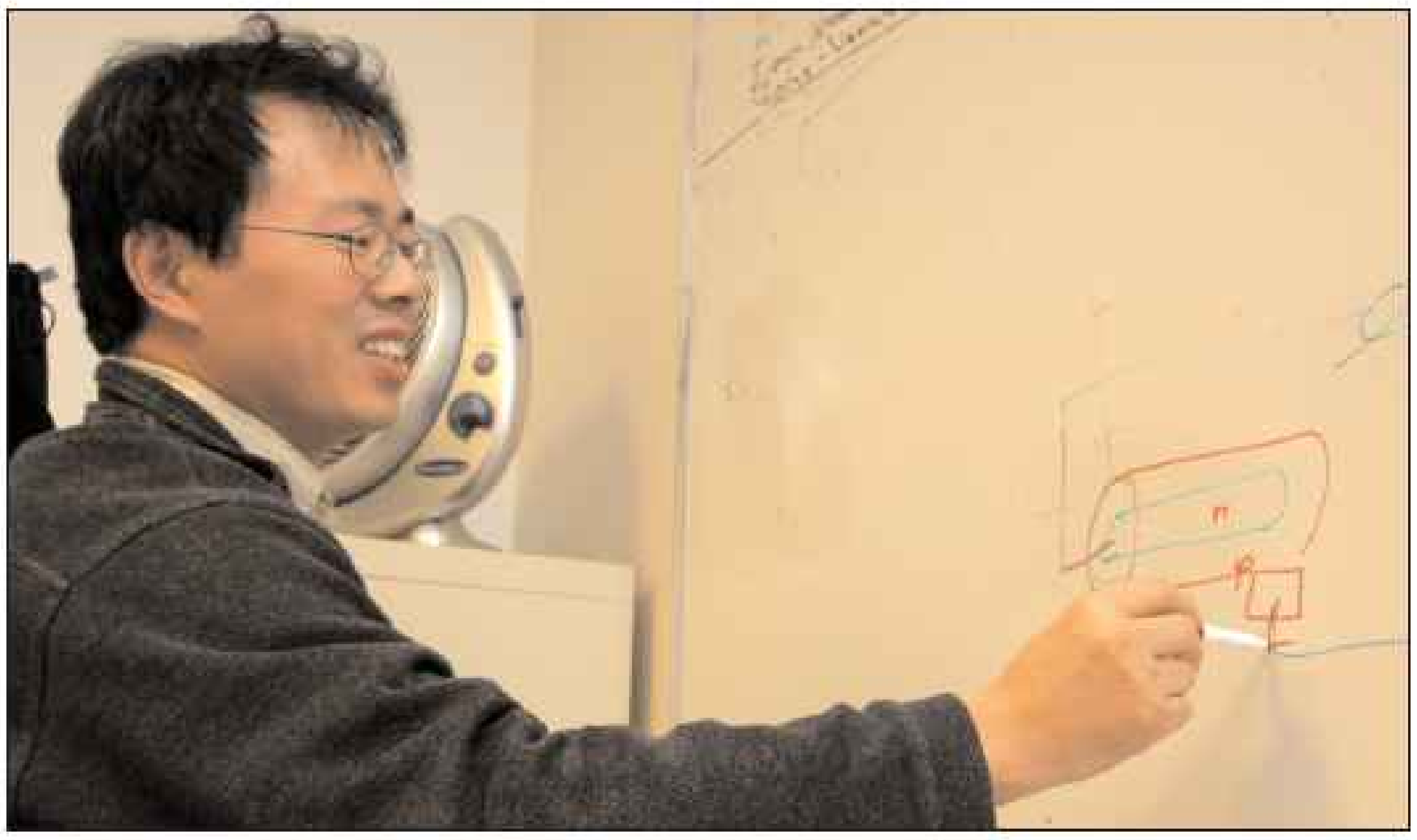

Figure 6. UCSD professor Deli Wang sketches a design for an LED made with a single ZnO nanowire.

"The surface trap states that help to make nanowires such sensitive light detectors are the very same surface features that engineers desperately avoid when manufacturing semiconductors for computer transistors, where they hamper performance," comments UCSD professor Deli Wang (pictured in Figure 6).

The diameters of the nanowires were of the order of 150–300nm, and the lengths were about 15μm. The nanowires were transferred to thermally oxidized silicon substrates (600nm SiO_2) after growth. Titanium/gold (Ti/Au) electrodes (20nm/160nm) were deposited and patterned (at a spacing of 2μm) on top of the nanowires (see Figure 7).

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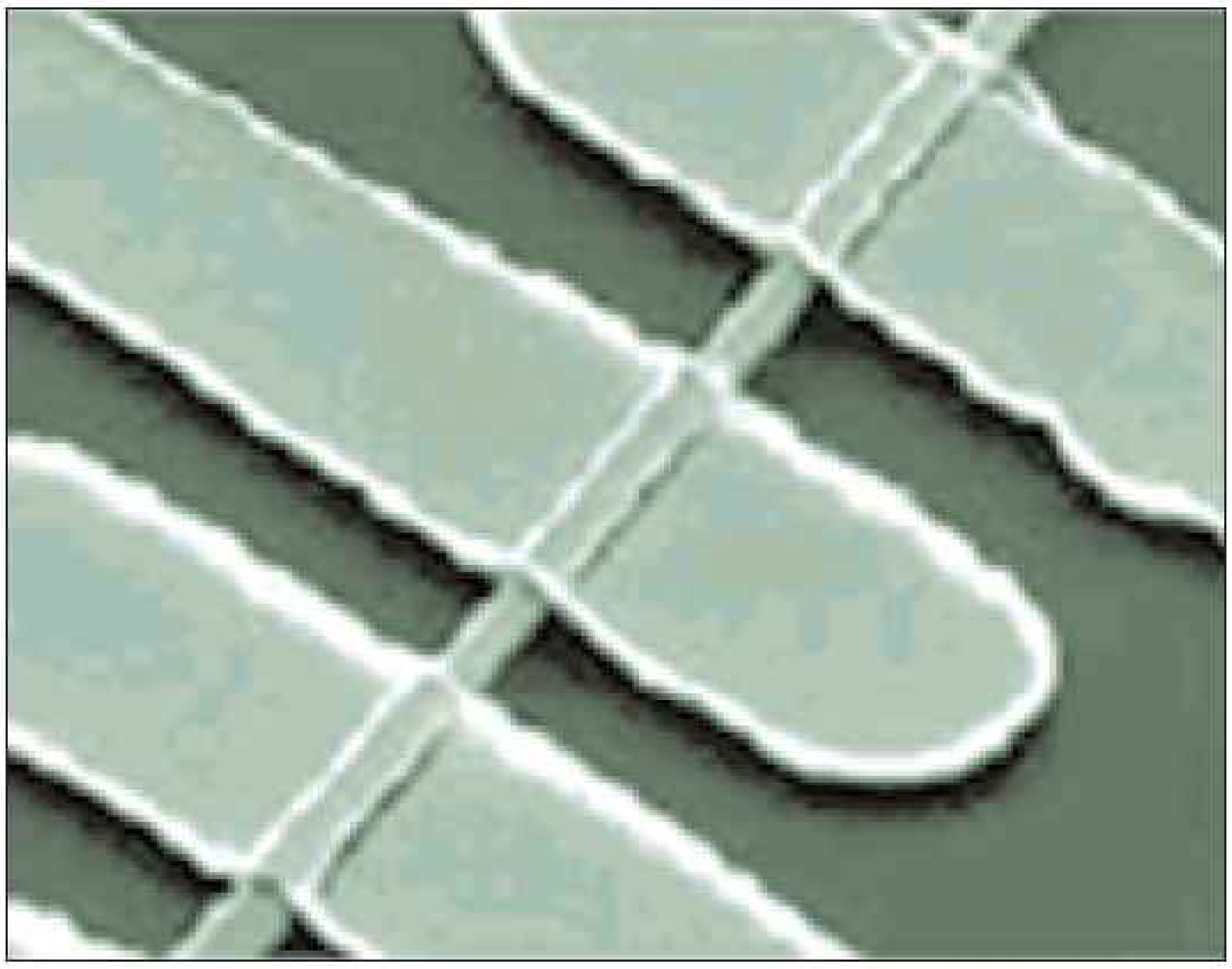

Figure 7. A single zinc oxide (ZnO) nanowire held down by metal contacts. Nanowire segments between the contacts can serve as photodetectors.

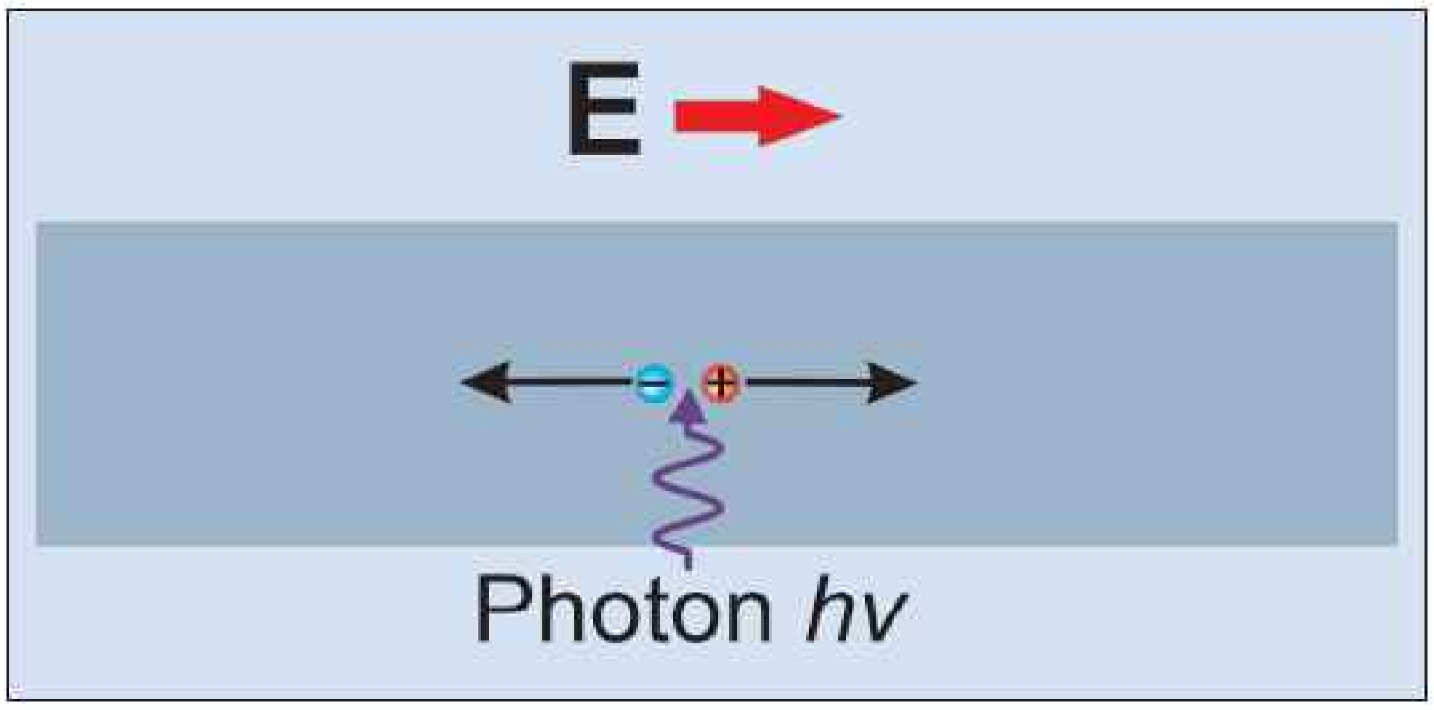

Figure 8. Photogeneration of electron–hole pairs in a section of a nanowire photodetector. The charge carriers run along the wire and increase the wire's current, and light is detected. However, if there are both electrons and holes present, they can recombine, reducing the current.

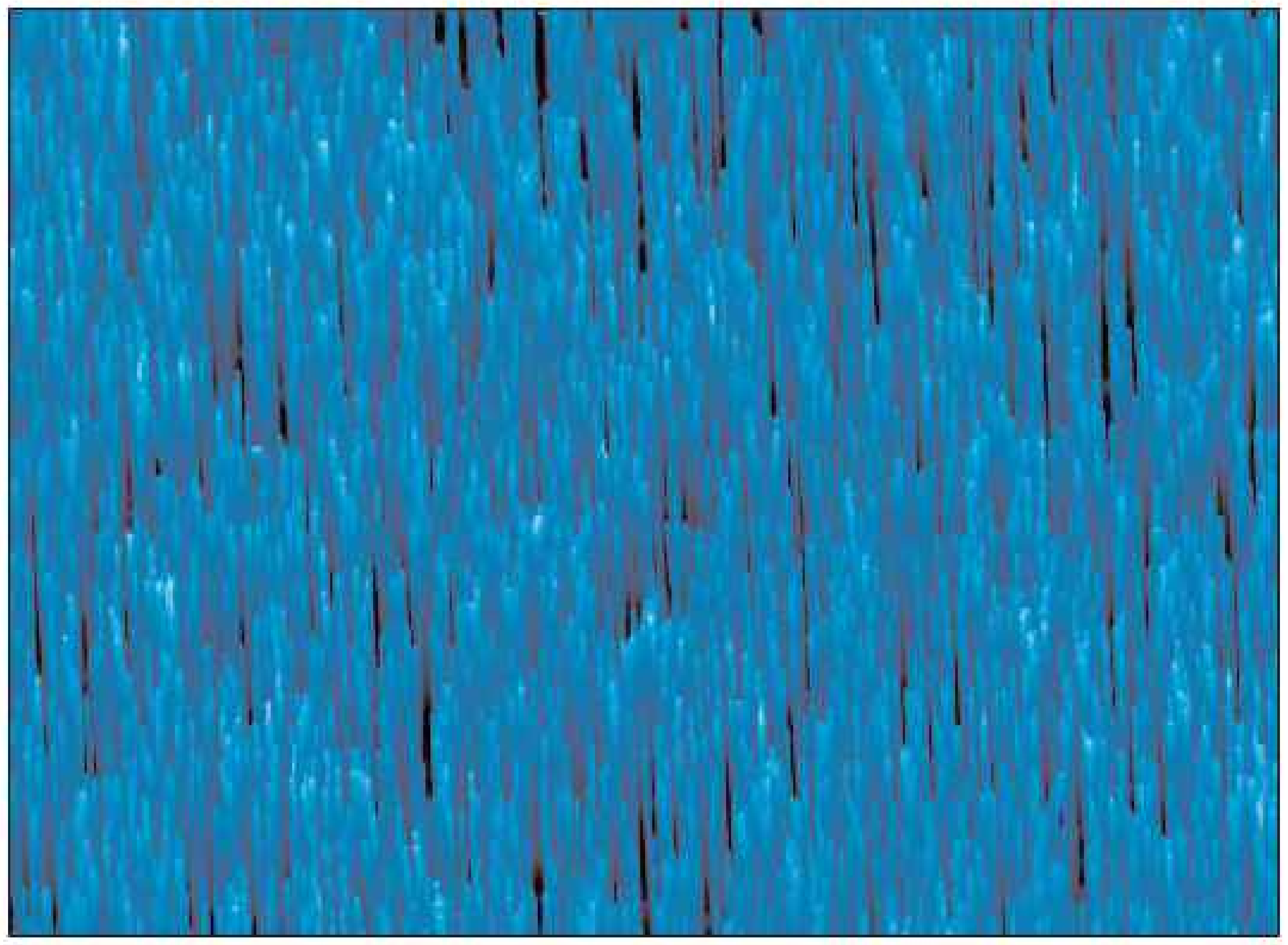

Figure 10. SEM image of p-type ZnO nanowires.

The photoconduction mechanism was studied using photon pulses of length 10^{-9}–10^{2} seconds. This study showed two main relaxation processes with widely different timescales (20 nanoseconds and 10 seconds). Oxygen-related hole traps form at the nanowire surface, delaying recombination. When holes are trapped (Figures 8 and 9), the oxygen is desorbed to gas, leading to saturation of the photoresponse at high intensity (since there is a limit to the amount of oxygen that can be desorbed) and increased photocurrent at low pressure (since oxygen cannot be reabsorbed, releasing holes).

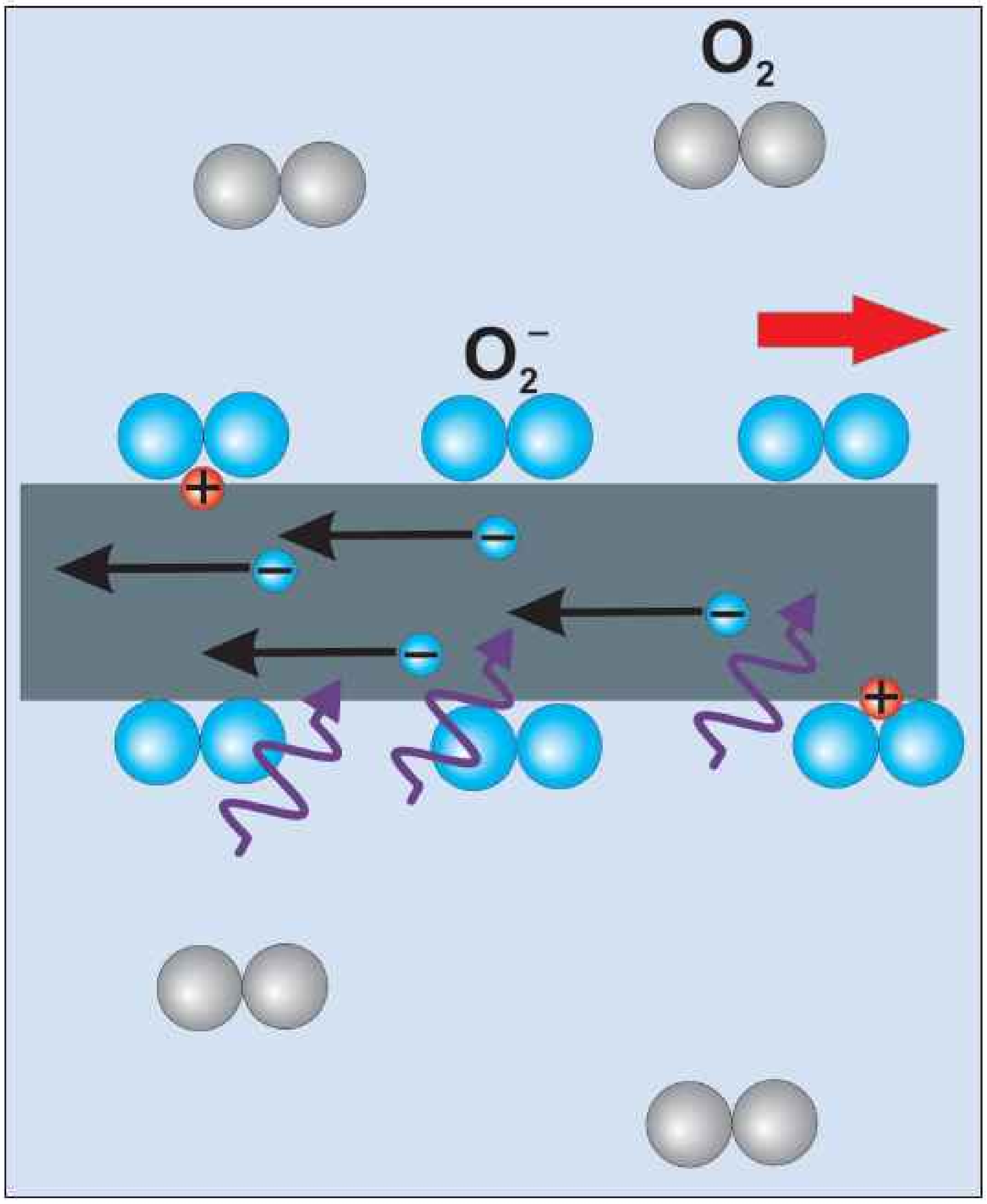

Figure 9. Schematic of proposed hole-trapping and photoconduction mechanisms in ZnO. In ZnO nanowires, the lifetime of the now unpaired electrons is increased by oxygen molecule desorption from the surface, taking away the holes that neutralize the oxygen ions.

Despite the long recombination time, the gain–bandwidth product is about 10GHz. Hence, UCSD engineers believe that the high gain and low power consumption of the arrays could lead to new phototransistors and sensing, imaging and intrachip optical interconnect applications. Other nanowire-based devices include field-effect transistors, optically pumped lasers and chemical/biological sensors.

UCSD scientists have also previously made progress in p-type doping of ZnO nanowires (Figure 10), using phosphorus pentoxide as the dopant source [11]. The p-type doping was confirmed by using photoluminescence and electrical measurements on single-nanowire field-effect transistors. Vertical arrays of p-doped ZnO nanowires were grown on A-plane sapphire. Phosphorus-doped nanowire FETs show a transition from n-type to p-type behavior on high-temperature annealing. ■

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