

Tiny tubes of carbon could oust plasma in large flat-panel displays **By Gehan Amaratunga**

# Watching the Nanotube

**NOW THAT PLASMA TELEVISIONS ARE HERE,** their makers would have you believe the quest for the ultimate TV is over. After all, these big, flat screens are dazzlingly bright and have a wide viewing angle. They can be hung on a wall or even built right into it. What more could you want?

Well, for starters, how about a TV set that doesn't consume as much power as a toaster oven? For that matter, you would think that any TV technology worthy of the term "ultimate" would be free of significant flaws, which lower-end plasma screens are not. For example, many models costing less than about US \$5000 have a distracting tendency to render pure black with a greenish cast.

For reasons like those, bands of researchers in the United States, Europe, and Asia are insisting that the last word in TVs won't be plasma, but rather nanotubes. These exotic molecules of carbon, only a few nanometers wide and perhaps a micrometer long, are at the heart of a new class of big, bright experimental displays that could overcome the power and image quality problems of plasma screens while retaining their brightness and size.



*The author holds a wafer upon which carbon nanotubes, 1  $\mu\text{m}$  high and 0.1–0.2  $\mu\text{m}$  across, have been grown. Similar nanotubes will be used to make a prototype high-resolution flat-panel display.*

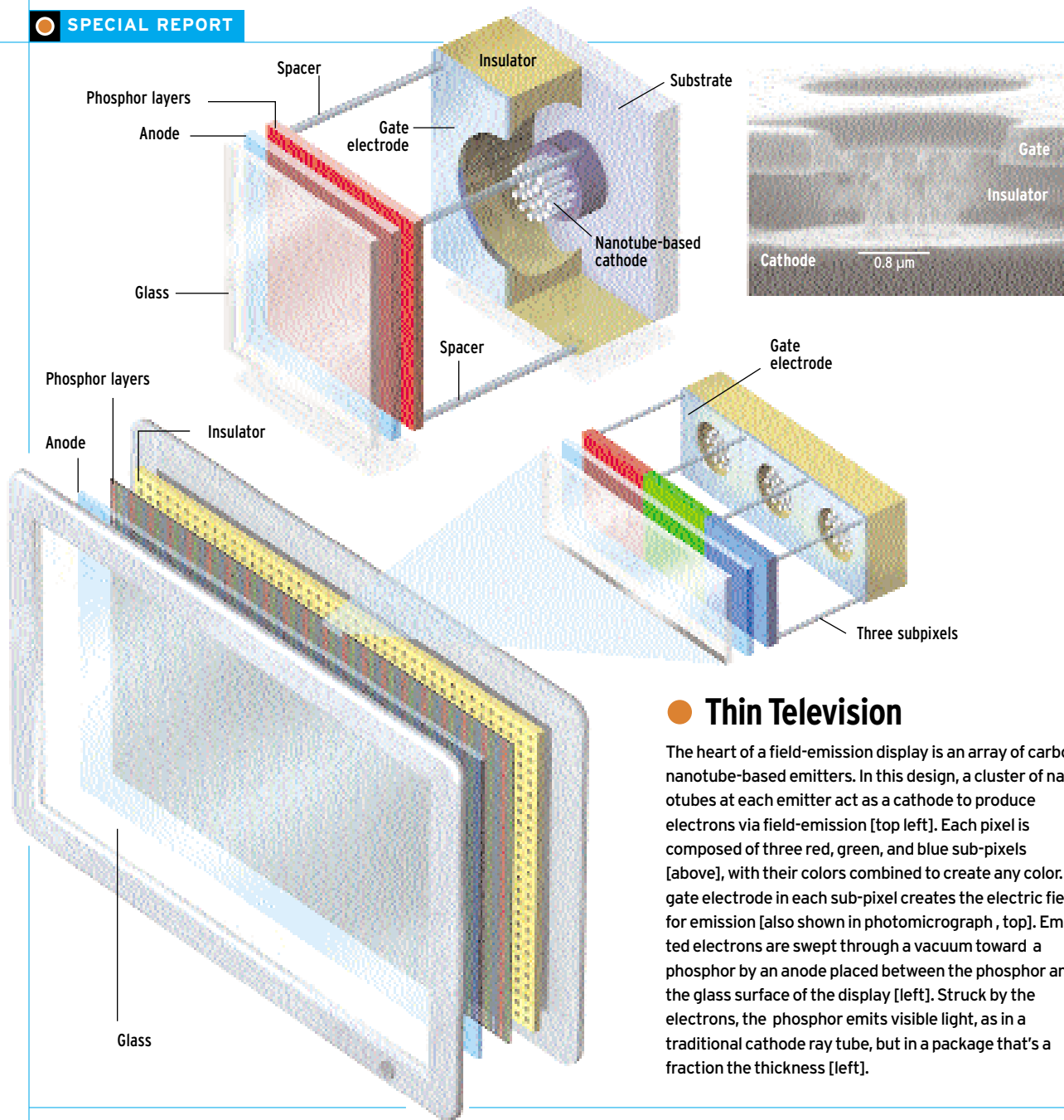
At stake is the richest consumer electronics category in the world: in the United States alone this year, people will buy at least 30 million analog and digital television sets worth more than \$12 billion, according to the Consumer Electronics Association (CEA) in Arlington, Va. Digital and flat models—precisely the category targeted by the emerging nanotube technology—are the fastest-growing category, the CEA says.

It will be the first consumer application in microelectronics for these sheets of carbon atoms seamlessly wrapped into infinitesimal cylinders. They have been proposed as the basis for a whole host of technologies, including hydrogen storage, interconnects for chips with ultradense components, and a new breed of transistor.

They're also breathing new life into an old idea—displays based on the phenomenon of field emission. Unlike the liquid-crystal displays common in laptops and small video devices, field-emission displays can offer wide viewing angles, and they are inherently less power-hungry than plasma displays, making them cheaper to operate.

With advantages like those, it's no wonder that companies such as Motorola Inc. (Schaumburg, Ill.) and Samsung Group (Seoul, South Korea) are aggressively pursuing field-emission display technology using nanotubes. Samsung, for example, has already demonstrated a full-color 38-inch field-emission display capable of handling normal video frame rates. What's more, a Japanese government-funded consortium has announced earlier this year to develop similar displays, and Sony Corp. (Tokyo) is developing its own nanotube display technology as well.

Plasma demands considerably more electricity than regular television cathode ray tubes (CRTs). A 38-inch color CRT consumes approximately 70 W. A similarly sized plasma display consumes some 700 W—a level of power consumption normally seen only in home appliances, like vacuum cleaners, that are typically in use for only a few minutes a day. Apart from the impact on consumers' wallets, if plasma technology became commonplace, it would result in significant implications for electricity generation and distribution, given that most people watch television for several hours a day and homes (at least in the West) often have multiple televisions. However a 38-inch field-emission display should be able to provide the same performance as a plasma display while consuming only 50 to 70 W.



## ● Thin Television

The heart of a field-emission display is an array of carbon nanotube-based emitters. In this design, a cluster of nanotubes at each emitter act as a cathode to produce electrons via field-emission [top left]. Each pixel is composed of three red, green, and blue sub-pixels [above], with their colors combined to create any color. A gate electrode in each sub-pixel creates the electric field for emission [also shown in photomicrograph, top]. Emitted electrons are swept through a vacuum toward a phosphor by an anode placed between the phosphor and the glass surface of the display [left]. Struck by the electrons, the phosphor emits visible light, as in a traditional cathode ray tube, but in a package that's a fraction the thickness [left].

Field-emission displays use much less power than plasma displays because they're intrinsically more efficient. Generating visible light from the surface of a plasma display is a three-step process that requires a gas to be ionized, which in turn emits ultraviolet light that stimulates a phosphor to produce visible light. Field emission allows TV makers to do away with the energy-hungry ionization step and stimulate the phosphors directly with electrons.

Researchers have pursued field emission as a prospective flat-screen technology for over 20 years, but reliability and longevity issues have prevented it from leaving the laboratory. The central element of this type of display is the field-emission cathode, which works by combining the mysterious phenomenon of quantum tunneling with the operating principle of a traditional lightning rod [see "Field Emission in a Nutshell," p. xx]. In essence, as in a normal CRT, a cathode is induced to emit electrons, but unlike a normal CRT, field emission doesn't rely on heating the cathode to boil off electrons. Cathodes can therefore be packed close together

with their supporting electronics without causing the entire display to melt. The forest of cathodes can then be placed close enough to the glass face of the display that the bulky electromagnetic beam-steering setup used in a CRT can be eliminated.

Emitted electrons are instead swept through a vacuum by a much larger voltage—5 kV—toward a positively charged anode just behind the glass face of the display glass, the rear of which is coated with an array of phosphors that lights up when struck, forming a visible image.

What you end up with is a display that has the brightness and image quality of a CRT without any of its problems of distortion or blurriness near the screen edges (caused by the difficulty of steering an electron beam precisely over the entire screen) in a package a fraction of the thickness [see illustration, opposite page].

The fly in the ointment is that field-emission cathodes have to survive a punishing electrical environment. Initially, such cathodes for displays were made using metals such as

molybdenum shaped in the form of tiny cones. However, problems arose because during field emission, the cathode tips often got hot enough to cause local melting, ultimately deforming the tip and damaging the geometric characteristics necessary to create the electric field required for emission. Additionally, in metals resistivity rises with temperature, creating more heating in turn, leading to a feedback cycle that can destroy the cathodes. Another problem is that the heated cathodes will begin to react with residual gases in the vacuum, which can chemically poison the cathodes, further reducing their field emission.

The ideal material for a field-emission cathode, then, is one that conducts electricity, can be produced in the desired pointed shape, doesn't suffer from a resistive heating feedback cycle, isn't chemically reactive, and can withstand high temperatures without deforming.

Enter the carbon nanotube.

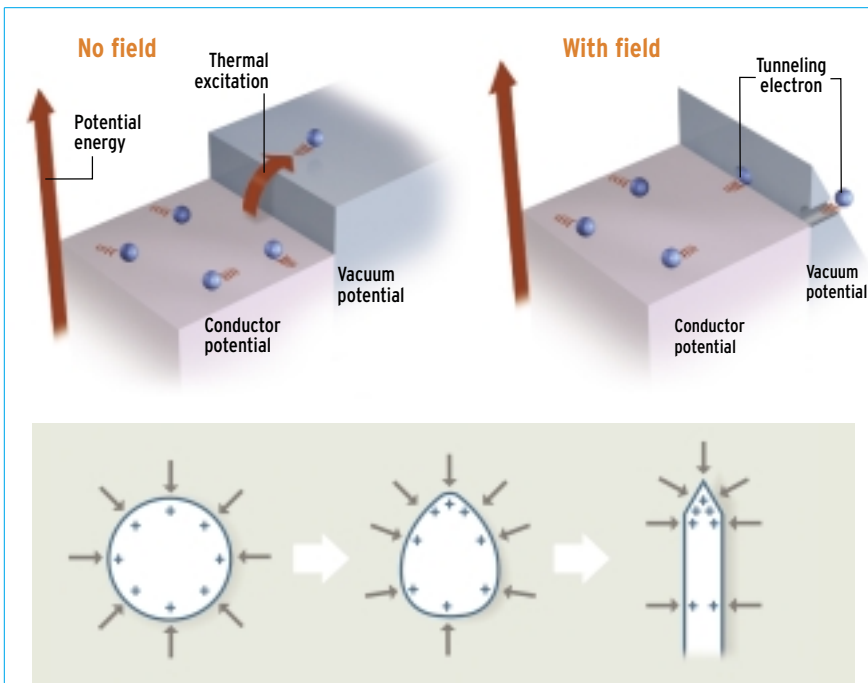
### Of soccer balls and nanotubes

Carbon nanotubes were discovered in 1991 by Sumio Iijima while working at NEC Research Laboratories in Tsukuba, Japan. This remarkable find followed on from the groundbreaking work of Harold Kroto, Richard E. Smalley, and Robert F. Curl Jr. in 1985 that discovered Buckyballs—molecules consisting of 60 carbon atoms arranged in the shape of a soccer ball.

But instead of a ball, you can make a cylinder—a carbon nanotube—by taking a sheet of graphite and reducing its size so that it becomes a narrow strip. When the strip's width approaches 30 nm, it becomes energetically favorable for the strip to curl up and join its opposing carbon bonds together, forming a tube approximately 10 nm in diameter. It's possible to make even thinner tubes, until the diameter reaches about 0.5 nm, below which bending the bonds between carbon atoms to form a tube requires more energy than can be saved by joining up the sides of the freestanding strip. However, although it's easier to consider so-called single-wall carbon nanotubes, which are made by curving a lone strip of graphite, in practice it's much easier to obtain tubes made by curving three to eight sheets to form concentric cylinders. Such tubes are referred to as

multiwall carbon nanotubes. Highly pure samples of single-wall tubes can cost \$500–\$1000 per gram—50 to 100 times as much as gold—while multiwall tubes are a relative bargain at \$100–\$200 per gram. Those are not bulk costs, but even the volume production of carbon nanotubes planned by such companies as E.I. duPont de Nemours and Co. (Wilmington, Del.) is unlikely to affect the cost differential.

Unfortunately, for those seeking to use the cheaper multiwall tubes, most of the theory regarding the electronic proper-



## Field Emission in a Nutshell

Unless a conductor is in the shape of a sphere, any electric charge it might have is not distributed uniformly across its surface. Rather, charge concentrates at the places of greatest curvature—in other words, the more pointy a conductor, the more charge will be found at the tip, effectively concentrating the electric field [see diagram, immediately above]. In a lightning rod, this allows charge to leak away during a thunderstorm, reducing the local electrical potential between the ground and clouds—hence, the likelihood of a lightning strike. It also provides a preferred path through the air for any lightning that does strike to follow.

If a small, but similarly pointy, negatively charged cathode is used in a field-emission display, the application of even modest voltages, 30 V or less, creates such a concentrated electric field at the tip— $10^7$  to  $10^8$  V/cm—that electrons can engage in a phenomenon known as tunneling and escape into free

space without the traditional CRT's need to heat the cathode to release electrons.

Tunneling relies on the fact that electrons can behave like waves as well as particles. In a conductor, some electrons are free to move about, but they're prevented from simply flying off into space by a potential energy barrier [see diagram, top left]. Normally, to escape the conductor, electrons have to be supplied with enough thermal energy to overcome that potential energy barrier.

But applying a strong electric field outside the conductor deforms the shape of the potential energy barrier, making it thinner and thinner as the electric field increases. Eventually, it becomes so thin that part of an electron wave can extend all the way through the barrier. Once that happens, the electron can simply appear on the other side of the barrier—think Dracula turning into smoke to get through a keyhole [see diagram, top right].

—G.A.

ties of carbon nanotubes has been formulated by considering the simpler, single-wall case, the most significant property of which is that electrical conduction occurs almost exclusively parallel to the nanotube's axis.

The degree to which multiwall tubes display the properties of single-wall nanotubes remains an open question. Some results show that the coupling between tubes is in fact strong enough to make multiwall tubes behave much more like conventional graphite, but conduction still occurs largely in the direction of the tube's axis. However, recent results suggest that because of the weak electronic coupling between the various graphite sheets in a multiwall tube, the tube's behavior is governed mainly by the outermost tube, allowing it to function like a single-wall tube.

### From theory to TV

Initially, it was thought that the runaway advantage of carbon nanotubes in field-emission displays would be that, being by nature long and skinny like a lightning rod and unidirectionally conductive, they would have the ideal shape for a field-emission cathode. However, the actual aspect ratio—the ratio of length to width and hence a measure of pointiness—of cathodes achievable with multiwall tubes isn't much better than what can be achieved using cone-tip cathodes made of molybdenum.

Much of the advantage of nanotubes turns out to lie in their electrical and physical similarities to their carbon cousin, graphite. Graphite shares important characteristics with semiconductors—its resistivity decreases with increases in temperature, preventing destructive heating feedback. Graphite does not melt and flow like a metal, but rather has a very high sublimation temperature—the temperature at which a solid material turns directly into a gas—of approximately 2500 °C. That reduces the problem of tip deformation. Graphite is also much less chemically reactive, significantly reducing the residual gas-poisoning problem that plagued metal cathodes.

The bottom line is that carbon nanotubes allow field-emission display manufacturers to reap the benefits of graphite in a cathode whose aspect ratio is at least as high as that of existing metal-tip technology.

The fact that carbon nanotubes are grown makes them different from most other nanoscale electronic devices, which use lithography to define their structure and dimensions. While that frees nanotubes from the scale limitations of lithographic processes, which allow features with a minimum of 500 nm on medium-area glass substrates, it means that controlling their structure and integrating them with other elements of a device is a trickier problem.

Using a method originally developed by NASA, my co-workers and I in Cambridge University's engineering department in the UK have grown single-wall tubes, almost all having a diameter of 1.3 nm, by decomposing a hydrocarbon gas, such as methane, in the presence of a catalyst composed of transition metals.

Although this technique allows us to grow uniform nanotubes, the problem of integrating them into fine structures like those used in conventional microelectronics remains. A way around the problem is to grow the nanotubes in situ on a substrate—for example, by using lithography to pattern a metal cat-

alyst layer. Subsequent nanotube growth will occur only in regions where the catalyst is present.

In many nanotube-based field-emission display designs (and in microelectronics in general), it is also important to control the orientation of tube growth as well as the tube's length. Working here at Cambridge and at Oak Ridge [Tenn.] National Laboratory, we have been able to grow single multiwall carbon nanotubes vertically that are 60 to 100 nm in diameter and 1000 nm long from lithographically defined catalyst regions. Under the right conditions, it's possible to reduce the diameter of the nanotubes relative to the patterned catalyst spot diameter by a factor of two or three. Such structures are ideal for use as field-emission cathodes.

Getting these devices out the laboratory and into the hands of the consumer is the goal of a number of consortium projects in Europe and Japan.

My laboratory at Cambridge is a part of a consortium called Takoff (which is a loose acronym for Technologies and Advanced materials for Kick-off in field-emission display manufacturing). We are producing carbon nanotubes grown vertically on glass for a high-resolution 7-inch display suitable for use in such applications as high-brightness car navigation systems and portable TV/DVD players. The program is coordinated by Saint Gobain Display Glass (Thourotte, France), with Samsung as the main integrator of new technologies into both large and small, high-resolution field-emission displays based exclusively on carbon nanotube cathodes.

Samsung has its own active program to develop field-emission displays, for which its European Takoff partners are providing specific assistance on various technologies. So far, the crown jewel of the Takoff program is Samsung's demonstration of its 38-inch screen.

The nanotube-based cathodes in this case are created using a process proprietary to Samsung in which a combination of multi- and single-wall tubes are mixed into a photosensitive resin. The resin is then screen-printed onto the cathode backplane and photoexposed to define the cathode regions. Samsung's device differs from most field-emission displays by placing the anode responsible for creating the emission electric field, not between the cathode and the phosphor, but beside the cathode, creating a so-called lateral field emitter.

The advantage of this approach is that many lateral field emitters can be manufactured together on large glass substrates with low-cost processes like screen printing. The disadvantage is, of course, that electrons are emitted perpendicular to the direction they need to go to hit the phosphor above. An auxiliary focusing grid electrode has to be placed above the emitters to make the electrons travel vertically. The challenges involved in getting the electrons to turn and hit only the desired red, green, or blue phosphor are significant (otherwise color mixing would result), but Samsung seems to have overcome them. Impressively, its display's pixel-to-pixel spacing is 0.8 mm, rather than the 1 mm typical of a plasma display, enabling better resolution.

Based on breakthroughs like that, it's a fair bet to say that the giant wall displays of the future could well be based on tiny slivers of carbon—the vanguard of the 21st century's nanotechnology revolution. ●

