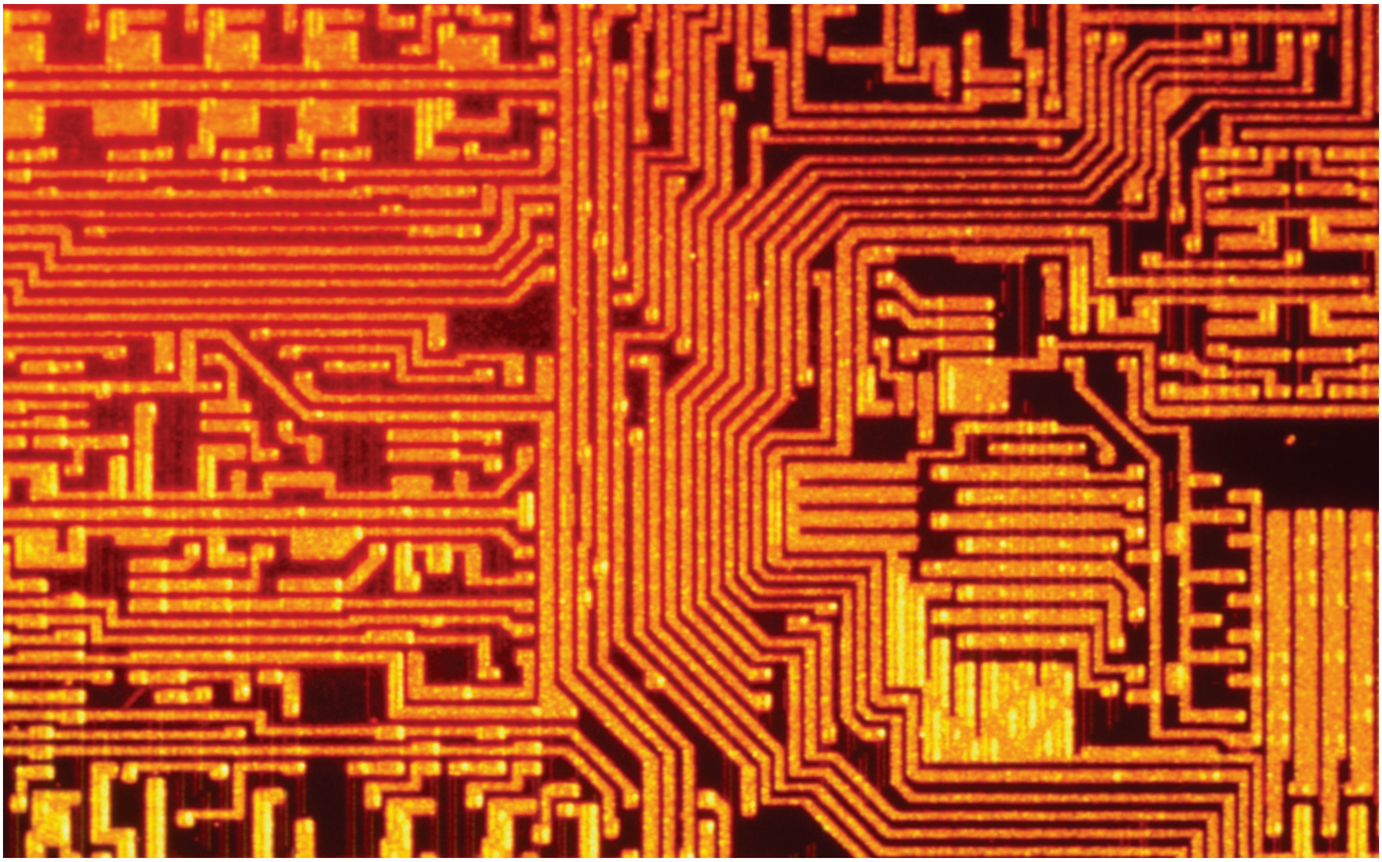

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MATERIAL HISTORY

Learning from silicon

Silicon is more than an incumbent technology competing with graphene — it also has a history researchers should remember.

BY MICHAEL SEGAL

Every new technology faces an incumbent, and in electronics it is usually based on silicon. Because of its intrinsic properties, its abundance and the ease with which it can be processed, silicon has dominated the semiconductor industry. It would take remarkable optimism to believe that a new material could supersede it.

Yet graphene has inspired such optimism. Its unique electrical characteristics, thinness and processability have prompted speculation that it could be the next silicon (see 'Back to analogue', page S34) — a tall order indeed. But whether or not graphene succeeds, the comparison to silicon is relevant in another sense: silicon's history gives insight into what to expect from graphene.

First, silicon teaches us that it's hard to predict the strongest or most valuable use for a novel material. Although most people associate silicon with electronic and optical devices, that was not where the material first made its mark. Back in the 1890s, silicon was a 'poor man's alloying agent'[1] used in steel and aluminium metallurgy, competing with nickel, chromium and manganese. In the 1930s, US chemical giant DuPont intensively investigated silicon as an alternative to lead-based pigments in white paint.

These early uses were unrelated to the device in which silicon was to have its most profound impact — the transistor — but were essential for that technology's eventual development. That's because each application led to methods for producing large volumes of highly pure silicon. Research into silicon electronic devices began in the late nineteenth century with the discovery that electrical current between electrodes attached to silicon and other semiconductors flowed more easily in one direction than the other. This led to the development of semiconductor rectifiers, devices that convert alternating current into direct current, which were used for communication and radar in both world wars. However, because only impure and granular semiconductors were available, the rectifiers were unreliable and hard to manufacture. Bell Labs and other organizations applied or adapted the production methods developed to purify silicon for metallurgy and paint to crystal rectification. This convergence was instrumental in the development of the first germanium transistor in 1947, and the first silicon transistor in 1954.

Something similar is going on now with graphene. The Nobel-prizewinning work on graphene in 2004 included an electronic application — a transistor — and electrical devices were an early focus of research[2]. Since then, however, an increased understanding of graphene's mechanical, thermal and optical properties has broadened the scope of potential applications to include many in which graphene is not an actively controlled electronic component. These

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include conductive inks and composites, transparent or high-surface-area electrodes, impermeable membranes, nonlinear optics, and nanoscale pores.

Some of these applications have spurred improvements in the way graphene is manufactured, as was the case with silicon and metallurgy. For example, the most cited graphene publication in the past two years describes not a device but rather a way to make large pieces of graphene for large-area transparent electrodes[3]. But many of the papers that cite this work apply the technique to devices in which graphene is an active electronic component. Similarly, one of the first mass-market applications of graphene is likely to be a conductive ink whose performance depends on a unique processing approach.

As with silicon, then, early graphene applications do not rely on its more advanced electrical characteristics, and are closely tied to steps forward in material fabrication and processing that are being adopted by the broader community. And, as with silicon, these early applications may turn out not to be graphene's greatest hit.

SWITCH HITTER

Silicon has achieved its biggest success as an electronic switch. More than a million trillion transistors are made each year[4]. But the story of the switch goes beyond silicon: the development of an electronic switch capable of amplifying a signal precedes the silicon transistor by about 50 years. The vacuum tube triode was developed around 1906 and by the 1940s was found in radios, TVs and computers. And whatever technology brings, the switch should remain a central feature: digital information is created and processed with switches, after all, and even our brains rely on a sort of switch.

Therefore, even with all of graphene's potential applications, an electronic graphene switch has special status. And, at least on first blush, it appeared that the next great switch might run on graphene. Much of the initial optimism was based on graphene's remarkable charge mobility, which is about a thousand times higher than that of silicon. Although this mobility has led to high-performance radio-frequency devices[5], it may not be particularly useful for digital logic[6]. Moreover, graphene is missing a key characteristic required for building digital logic using traditional transistor designs: a bandgap (a range of energies in which electrons cannot exist). Already, other 2D crystals such as MoS_2, which does have a bandgap, are nipping at graphene's heels[7]. The situation recalls the competition between silicon and materials such as germanium, which has higher mobilities, and gallium arsenide, which is better suited to optical applications such as lasers. Despite these disadvantages, silicon dominated because it is easier to process, has a better oxide, and is more abundant. Graphene cannot depend on a single characteristic — electron mobility — for it to succeed as a material.

Like silicon, however, graphene brings with it a host of new physics that may change our understanding of the relevance of mobility and bandgap for transistors. Scientists are exploring alternative device architectures that exploit this new physics, including tunnelling transistors[8] and transistors that guide and focus electrons like light.

And switches may turn out not be an important part of graphene's story after all. Kroemer's Lemma of New Technology occasionally comes up in discussion of graphene. This principle, named after Nobel laureate Herbert Kroemer, states that the primary application of a new technology is one created by that technology. If it holds here, graphene's killer app may be something that nobody has yet imagined.

GRAPHENE INKS SOME PROFITS

Although the future may be murky, graphene is expected to make its consumer product debut in 2012. MeadWestvaco, a Fortune 500 packaging manufacturer based in Richmond, Virginia, is using graphene-based conductive inks to make a new kind of package with an integrated anti-theft security system. The technology enables 'open merchandising', in which products are readily available for consumers to hold or see up-close. Open merchandising has traditionally been associated with heightened security risks, particularly for high-value items packaged in paperboard or plastic.

Just a couple of years after the Nobel Prize was awarded, graphene is already on store shelves.

MeadWestvaco's solution is to use graphene-based inks to monitor whether the package has been tampered with. The inks form a conductive trace that winds around the inside of the package and sticks to the product itself. A plastic tab attached to the top of the package contains powered circuitry connected to the trace; if the packaging is cut, or the tab or product removed, an alarm built into the tab sounds. Carrying the package out of the store also triggers the alarm.

Previous attempts at secure packaging like this had foundered because the right conductive ink couldn't be found. Polymer and traditional carbon-based inks are not sufficiently conductive; silver inks are expensive and harder to process. The graphene inks (supplied by Vorbeck Materials of Jessup, Maryland) work well because they contain mostly single-layer graphene sheets that are deliberately wrinkled, preventing them from re-stacking into a graphite-like material. Instead, the sheets create a network of pathways for current to flow, resulting in films that are highly conductive even at thicknesses of a few hundred nanometres. Such thin, flexible layers can be printed using newspaper-style roll-to-roll presses that are capable of high-volume production. David W. Miller, global director of security packaging systems and supply chain at MeadWestvaco, says that major retailers have expressed an interest in deploying the packaging — and that one of them has already started testing it. Just a couple of years after the Nobel Prize was awarded, graphene is already on store shelves.

As was the case with metallurgical silicon in the nineteenth century, materials processing competence is allowing graphene to compete with established materials on this first foray into the mass market. Volumes are expected to be high, stimulating further improvements in manufacture. Vorbeck has indicated that almost all of the revenue it earns from its inks will be reinvested into research and development efforts to broaden the ink's appeal by, for example, increasing its conductivity to compete with silver inks used in solar cells. And Vorbeck's graphene inks leave the material's more exotic properties (Dirac fermions, valley polarization and so on) for future products to exploit.

ARE WE THERE YET?

So graphene is in the process of leaving the laboratory. But will we have to wait as long as we did with silicon — about 130 years from first isolation to the transistor — for graphene's golden age to arrive? Even if we must, we are already decades along the graphene development timeline. Thin graphite was being studied experimentally in the 1960s, and calculations on graphene were being performed earlier still. Much of the physics, chemistry and engineering of graphene are similar to that of nanotubes and fullerenes. In fact, many of the physicists who now study graphene have moved from research programmes on nanotubes — something reflected in the drop in growth of nanotube research papers just as the volume of graphene papers shot up after 2004.

At the same time, we are in the early or middle stages of graphene synthesis and processing. Key techniques, such as large-area chemical vapour deposition, have been developed in the past four or so years and continue to evolve (see 'Beyond sticky tape', page S32). And the number of potential applications continues to increase. Silicon's history teaches us to prioritize processing, allow for surprises, be patient, and keep a guarded (and resilient) optimism. Things are, after all, off to a good start.

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