MATERIALS SCIENCE

Changing face of the chameleon

A. Lindsay Greer and Neil Mathur

Chalcogenide materials form the basis of CD and DVD technologies. But an identity crisis looms in the wider field: what role do atomic reconfiguration, electronic processes and ionic movement play in these materials?

The chalcogens — the elements in group VI of the periodic table, particularly sulphur (S), selenium (Se) and tellurium (Te) — react with more electropositive elements, such as silver, to form chalcogenides. These are chameleon compounds: they can be crystalline or amorphous, metallic or semiconducting, and conductors of ions or electrons. Already important in optical storage discs and fibres, they are now being proposed as the basis for solid-state memory technologies. Two recent conferences — E*PCOS 05 in Cambridge*, UK, and Euromat 2005 in Prague†, Czech Republic — have demonstrated that devices using chalcogenides hinge on thermal and dynamic phenomena involving electronic, atomic and ionic processes. The links between these phenomena are not fully established, so unsuspected technological opportunities may well lie in store.

Electrical switching in chalcogenide semiconductors came to prominence in the 1960s, when the amorphous chalcogenide $Te_{48}As_{30}Si_{12}Ge_{10}$ was found[1] to display sharp, reversible transitions in electrical resistance above a threshold voltage (Fig. 1a). The switching mechanism remains unclear, but seems[2] to be initiated by fast[3,4], purely electronic processes. If current is allowed to persist in the material, it heats up, changing its atomic structure between the amorphous and crystalline states — equivalent to information being written on it. A crystalline region may be driven to become amorphous by exposure to a brief, intense heat pulse, leading to melting. The subsequent rapid withdrawal of heat sends the temperature plummeting so quickly that the melted region solidifies with the atoms still disordered. Conversely, a lower-intensity heat pulse of longer duration will crystallize an amorphous region — the crystalline state is more stable and the heat allows the atoms to mobilize just enough to assume crystalline order.

This thermally driven, amorphous–crystalline phase change, which can encode binary information, is already of great commercial significance[5], but uses thin films of chalcogenides that are switched locally by optical rather than electrical means. In write-once and rewritable CDs and DVDs, a laser beam supplies the heat pulse for write operations, whereas the read process exploits the relatively low optical reflectivity of amorphous data spots, or marks, in the chalcogenide film compared with that of the crystalline background. Contributions to E*PCOS 05 reporting optical-disc capacities as high as 112 gigabytes (A. Nakaoki, Sony Corp.) and data marks as fine as 20 nm (D.-P. Tsai, National Taiwan Univ.) show that current industrial trends could well continue.

Attempts[1] to induce the amorphous–crystalline transformation of chalcogenides by electrical means form the basis of phase-change random-access memory (PC-RAM). This incipient technology is on the brink of commercial exploitation by, among others, the pioneering company ECD Ovonics. For write operations, an electric current supplies the heat pulse. The read process is performed at sub-threshold voltages, and exploits the relatively large difference in electrical resistance between the amorphous and crystalline states. Recent advances in this area include a low-power device set up as a narrow line of material with the active region thermally isolated from the electrical connections, so that these are not degraded by heating[6]. There is also the prospect of much smaller data marks written with a beam of electrons[7] and, as announced at E*PCOS 05, continuing improvements in programming times (below 30 ns: K. Attenborough, Philips Res. Leuven) and writing currents (below 0.75 mA: B. J. Kuh, Samsung Electronics).

Although the electronic transitions and atomic rearrangements relevant to both optical discs and PC-RAM featured strongly at E*PCOS, contributions from ions were not considered — even though amorphous chalcogenides can have significant ionic conductivities. At Euromat 2005, however, it was shown that ionic transport can be useful for data storage in a solid chalcogenide electrolyte. At the nanoscale, this electrolyte consists of crystalline metallic islands of silver selenide (Ag_2Se) dispersed in an amorphous semiconducting matrix of germanium selenide (Ge_2Se_3) (M. N. Kozicki, Arizona State Univ.). The performance of a prototype electrolytic chalcogenide cell is described in Figure 1b.

Technologies exploiting phase-change and electrolytic chalcogenide devices are evolving convergently. Although the microscopic mechanisms seem rather different, the two technologies display similar measurable characteristics. The sudden onset of conduction — at V_t in Fig. 1a and V_{ON} in Fig. 1b — is, for example, associated with the formation of filamentary conducting pathways in both cases. In PC-RAM this onset is thought to arise electronically via the injection of charge carriers[2], but stems in the electrolytic device from the deposition of metal atoms (electrodeposition) to form conducting bridges between the islands. Another example of the similarity in characteristics but variation in underlying processes of the two types of chalcogenide device is that both show incremental changes in their structure, cumulative over time, when they are operated below their threshold voltages. These changes give rise to controllable intermediate conductivities and are in effect precursors to the binary memory effects that make chalcogenides useful as storage materials. In PC-RAM, this cumulative behaviour is readily explained by crystal growth; in the electrolytic variant, it is explained by electrodeposition.

Both chalcogenide technologies present exciting opportunities that are not restricted to memory, but include cognitive computing[1,8] (E*PCOS 05: S. R. Ovshinsky, ECD Ovonics) and reconfigurable logic circuits[9]. It is too early to tell which technology will be selected for which niche, but scientific interest alone should motivate a closer look at chalcogenide materials to investigate correlations between phase-change and electrolytic behaviour. To take one example, the migration of dissolved ions is required in the electrolytic case, but could degrade the performance of a phase-change device. Fluxes of both electrons and ions participate in electromigration — widely studied as a degradation mechanism of the electrically conducting lines for integrated circuits. Thus, a unified approach to the study of chalcogenides, assessing the roles of atoms, ions and electrons, may prove crucial for both device performance and reliability. ■

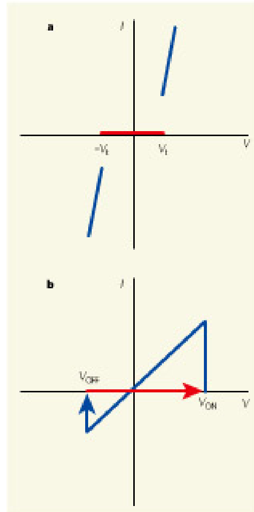

Figure 1 | Two types of chalcogenide device. **a**, Electronic switching associated with phase changes. At moderate frequencies, the alternating current–voltage (I–V) characteristic of a suitable amorphous chalcogenide material shows symmetric switching above a threshold voltage V_t from a highly insulating regime (red) to a more conducting regime (blue, gradient reduced for clarity). (Modified from ref. 1.) Optically addressed phase-change materials form the basis for CD and DVD technologies. **b**, Ionic (electrolytic) switching. A solid electrolyte of two chalcogenide phases can also encode information. In the cycle shown, the insulating state (red) switches at V_{ON} to a conducting state (blue) when nanoscale bridges of silver form between electronically conducting islands in an ionically conducting matrix. These bridges persist until they are dissolved at a sufficiently negative voltage, V_{OFF}. The asymmetric I–V characteristic shown here is reminiscent of symmetric I–V characteristics in phase-change random-access memory, where read operations in a working device would also be performed at low voltages. (Modified from ref. 10.)

*European Symposium on Phase Change and Ovonic Science, Cambridge, 3–6 September 2005; www.epcos.org

†Symposium on Memory Storage Materials, European Congress on Advanced Materials and Processes, 5–8 September 2005; www.euromat2005.fems.org/index.htm

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CELL BIOLOGY

Helices sculpt membrane

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Many proteins are carried within cells in bubble-like sacs. These are pinched off from membranes inside the cell, and it seems that the Sar1p protein is key in both starting and finishing this budding process.

The cell contains a network of membrane-bound compartments that exchange proteins with each other and with the cell surface thanks to several haulage systems, each providing a specific link between one station and another. At the departure point, specialized 'coat' proteins wrap up a small area of the lipid membrane, shaping it into a bulging 'bud' and gathering up proteins due to be transported inside it[1]. The bud detaches from the membrane — a stage called fission — to form a bubble-like 'vesicle' loaded with cargo. Lee *et al.*[2] report in *Cell* that a coat protein called Sar1p, whose structure contains several α-helices, initiates buds for one type of vesicle by thrusting one of its helices into the membrane, causing it to balloon outwards[1].

We knew that Sar1p begins the formation of so-called COPII vesicles, but quite how was unclear. These vesicles transfer proteins from a membrane-bound structure called the endoplasmic reticulum, where they are made, to another such structure, the Golgi apparatus, where they are processed into their final form. A common cellular fuel called guanosine triphosphate (GTP) activates Sar1p. When Sar1p binds to GTP, it exposes a short α-helix at its amino (or N) terminus that anchors the protein to the membrane of the endoplasmic reticulum. There, Sar1p recruits two large COPII protein complexes, Sec23/24p and Sec13/31p, which polymerize into a curved lattice. Studies using artificial lipid vesicles called liposomes show that adding all these components is sufficient to generate coated buds on the liposome and, less efficiently, free coated vesicles[3]. Now Lee *et al.*[2] report how Sar1p contributes to the initial moulding of the membrane and, less expectedly, to membrane fission.

Using electron microscopy, the authors first show that Sar1p alone can deform liposomes into long, narrow tubules, but only when it is bound to GTP, suggesting an involvement of the N-terminal helix. To demonstrate this, they swap this helix for a peptide that binds to an artificial lipid. As expected, the Sar1p mutant still binds to liposomes containing the artificial lipid but no longer deforms them.

Both normal Sar1p and the domain-swapped mutant can interact with the other COPII complexes, so the next step was to compare incubations conducted with the complete set of COPII proteins. Puzzlingly, though, buds do form in the presence of the

50 YEARS AGO

For some time past, the B.B.C. Research Department has been studying the technique of colour television, and recently a programme of experimental transmissions was started outside normal broadcasting hours. On October 20, Sir Harold Bishop, director of technical services, presented a special demonstration for the Press. This comprised the transmission over a closed circuit at the Alexandra Palace station, of still pictures, a short travel film and a number of 'live' camera shots, all of which were reproduced at the receiving end as attractive colour pictures.
From *Nature* 29 October 1955.

100 YEARS AGO

The Far East. By Archibald Little. — Of late years the Far East is only far in actual distance; it is very near to our thoughts, while the ignorance regarding these lands is being very rapidly dispelled... China stands now at the parting of the ways; for many years resolute in keeping out foreign inventions so distasteful to the old-fashioned mandarin, circumstances have proved too strong, and railways, the precursors of western life, are now being built or projected throughout the land... Consider the Yangtse Valley... This magnificent river will undoubtedly remain the great high road for commerce into Central China; but railways are and will be built to act as feeders to the main line, much to the profit of the shareholders and of the inhabitants, for Chinese are born traders, and already make use of the pioneer of Chinese railways — the line from Tientsin to Peking — in large numbers.

Finally, we have a vivid description of the southern basin, Canton, Hong Kong, and the provinces bordering on French territory. Yunnan, which adjoins our Burma, has a particular interest to Englishmen; but here, owing to our supineness in days gone by, we have allowed the French to get ahead of us with their railway, which will undoubtedly draw to itself all that is valuable of the trade of the province.
From *Nature* 26 October 1905.

50 & 100 YEARS AGO