OXIDE DIELECTRICS

A change of direction

Field-effect transistors, regardless of whether they use an organic or an inorganic semiconductor, require a gate dielectric with a large relative permittivity. A once-popular layered electrolyte may be just the right material for the job.

Hagen Klauk

Sodium beta-alumina (SBA) is a remarkable material with a fascinating history. It was first identified 100 years ago in the Bayer process for extracting alumina from its naturally occurring ore, bauxite. Similar to alumina, SBA is a polycrystalline ceramic with great mechanical strength and a very high melting temperature (~2,000 °C). Unlike alumina, however, SBA has a crystal structure that is distinctly two dimensional, with alternating thin layers of aluminium oxide and sodium ions (Fig. 1). Despite its unusual crystal structure, SBA roused little scientific or commercial interest until 1967, when researchers at Ford Motor Company discovered that the sodium ions in SBA are able to move through the crystal with great ease, endowing SBA with a very large ionic conductivity. Such a high ionic conductivity had previously been observed only in liquid electrolytes, never in a solid. Moreover, although having a large ionic conductivity, SBA has negligible electronic conductivity, which is an important prerequisite for its use in electrochemical cells. The discovery of large ionic conductivity in SBA jump-started the worldwide development of solid-state batteries with large energy density, and marked the beginning of a whole new research field — solid-state ionics. For roughly two decades, SBA enjoyed enormous popularity in science and engineering, but eventually better ionic conductors and more promising battery concepts came along, and SBA’s stardom faded.

On page 898 of this issue, SBA makes a refreshing comeback in an unexpected new role. As Howard Katz and colleagues from Johns Hopkins University report, SBA is not only an excellent ionic conductor, but also an outstanding dielectric. The sandwich structure of SBA dictates the movement of the sodium ions — they can move freely only in directions parallel to the lattice planes (Fig. 1). In the direction normal to the planes, however, movement of the sodium ions is restricted to a few angstroms by the adjacent alumina layers. Nevertheless, moving a large number of positive ions in unison inside a crystal in which the positions of all the negative ions are fixed produces a mammoth electric polarization, even if the ions move only a short distance. The degree to which a material polarizes in response to an external electric field is quantified as its permittivity; the larger the polarization vector induced by a certain electric field, the greater the material’s permittivity. The ionic displacement induced in SBA creates a polarization much larger than more common polarization mechanisms, such as dipolar or atomic polarization. Consequently, SBA has a very high relative permittivity, $\kappa$, of about 200; much larger than most known solid dielectrics, for example, SiO$_2$ (3.9), Al$_2$O$_3$ (9), HfO$_2$ (25), ZrO$_2$ (25) and TiO$_2$ (80).

Figure 1 | Crystal structure of SBA. Sodium, oxygen and aluminium atoms are coloured blue, red and yellow, respectively.

Field-effect transistors benefit considerably from a gate dielectric with a large permittivity, because a large permittivity means that the dielectric can be relatively thick and still provide a large capacitance. (Capacitance is proportional to the relative permittivity and inversely proportional to the dielectric thickness.) A large gate-dielectric capacitance is desirable so that when a voltage is applied to the transistor’s gate electrode a high electron density is induced in the semiconductor. If the permittivity of the gate dielectric is small, obtaining a high capacitance requires a very thin gate dielectric. However, if the dielectric is too thin, it loses its ability to block the undesirable flow of electrons between the gate electrode and the semiconductor. In fact, the difficult compromise between gate-dielectric capacitance and undesirable gate leakage has recently prompted the semiconductor manufacturer Intel to replace SiO$_2$ ($\kappa = 3.9$) with HfSiO$_2$ ($\kappa = 11$) as the gate dielectric in their microprocessors. This is because for the transistors in state-of-the-art chip-manufacturing technology (where the lateral circuit dimensions are only 45 nm) a gate dielectric made from SiO$_2$ would have been too thin (~2 nm) to provide sufficient reliability. A dielectric with a relative permittivity of 200 is just what is required to eliminate the need for compromise; it allows field-effect transistors to have both a large gate-dielectric capacitance and small gate leakage. Therefore, using SBA as a high-$\kappa$ dielectric is timely and noteworthy.

But what really adds to the work is that films of SBA can be prepared without the need for expensive vacuum equipment. Instead, the team describe a sol–gel process in which films of SBA are prepared simply by dipping the substrates into a gel solution, followed by thermal annealing. For the field-effect transistors demonstrated so far, the authors have employed SBA gate dielectrics with a thickness of ~70 nm (compared with ~4-nm-thick HfSiO$_2$ in the Intel® Core™ i7 microprocessor). Despite this, they achieved almost the same large capacitance (~2 μF cm$^{-2}$) that provides excellent gate control of the channel conductance at relatively small gate-source voltages (2–5 V). Staying with the general theme of solution processing, Katz et al. fabricated transistors with several different semiconductors that can be prepared in the form of thin films from solution, zinc oxide, zinc tin oxide and indium zinc oxide. As well as transistors on glass substrates, the authors also made flexible transistors using a conjugated organic semiconductor with SBA as the gate dielectric.
Nevertheless, a few hurdles must be overcome before SBA dielectrics will make a significant impact on large-scale transistor manufacturing. Perhaps the biggest problem at the moment is the slow response of the sodium ions to an external electric field. Consequently, the capacitance of the SBA films is reduced at higher frequencies. Solid-polymer electrolytes typically suffer from a similar problem, and in this case the frequency response can be substantially improved by increasing the ions’ concentration and mobility.

Another limitation of the SBA process reported by Katz et al. is that the temperature required to anneal the sol–gel-deposited SBA films (400 °C or more) is at present too high for large-area transistor applications, such as flat-panel displays. If this temperature can be lowered to near 250 °C, SBA may again become as popular as it once was.

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References

MAGNETIC SHAPE MEMORY

Magnetoelastic sponges

Nickel–magnesium–gallium foams connected internally by sizeable single-crystalline elements provide magnetic-field-induced strains comparable to free-standing bulk single crystals, and demonstrate feasibility for the application of magnetic shape memory.

Mehmet Acet

The discovery of giant magnetic-field-induced strains of about 10% in single crystals of the magnetic shape-memory alloy Ni–Mg–Ga under 2-T magnetic fields (attainable by permanent magnets) brought a new dimension to the concept and design of field-triggered actuators. However, because Ni–Mg–Ga single crystals are difficult to grow, costly and brittle, investments in wide-spread applications of such actuators have been very limited. The good news is that many of these problems can be overcome by using foams of these materials, as reported by Chmielus and coauthors on page 863 of this issue.

The authors demonstrate that polycrystalline foams of Ni–Mg–Ga prepared under certain conditions create a network of single crystals that can collectively show magnetic-field-induced strains up to an impressive 4% — surpassing by far any field-induced strain in polycrystalline materials (in particular in Terfanol D with 0.15% strain).

Magnetic-field-induced strain in Ni–Mg–Ga relies on the presence of a diffusionless, solid–solid phase change, otherwise known as the martensitic transformation. The transformation temperature separates the high-temperature, high-symmetry cubic austenite phase (with low magnetic anisotropy) from the low-temperature, lower-symmetry-modulated orthorhombic martensite phase (with high magnetic anisotropy). The martensite phase has a twin structure and strong magnetocrystalline anisotropy. The twin boundaries are highly mobile and are set into motion when an external magnetic field is applied. Crystallographically, several twin variants are possible. If a single crystal of Ni–Mg–Ga is prepared so that it has only a single variant, giant magnetic-field-induced strains can occur.

The origin of magnetic-field-induced strains is shown schematically in Fig. 1. For simplicity, we show a single-variant single crystal with a tetragonal unit cell with lattice dimensions a and c, such that c/a < 1, and the c-axis is the easy magnetization direction. If the magnetocrystalline anisotropy is large, rotating an applied field H will cause a gradual growth of a variant (coloured blue) with the c-axis along the field direction at the expense of the original variant (coloured grey). This can lead to a large change (Δl) in the external dimensions of the crystal.

The situation in foams is essentially the same. Foams are prepared by selecting an appropriate salt or ceramic ‘space holder’ with given size, around which the material is filled. The space holder is subsequently etched away. Figure 2a depicts a foam with monomodal pore size (shown as circles). Such Ni–Mg–Ga foams were previously studied by the same groups reporting in the present issue. The material between the pores (the blue area outlined by a bold line, Fig. 2a) is the foam consisting of single-crystalline ‘struts’ connected to each other at polycrystalline nodes, resulting in a ‘bamboo like’ structure as the authors had earlier described. In such foams, the easy-magnetization axes of neighbouring crystallites do not necessarily coincide, as shown by the red arrows. It was reported that the maximum field-induced strain in these foams did not exceed 0.15% because of the presence of node constraints that hinder domain-wall advancement and therefore a uniform magnetization. Nevertheless, this size, still considered ‘large’ with respect to strains observed in regular bulk polycrystalline material, was the source of motivation for further trials.

**Figure 1** | Schematic of magnetic-field-induced strain. A magnetic-field-induced length change Δl occurs when a field H, originally parallel to the c-axis, is gradually rotated (red arrows indicate the easy-magnetization axes). A new variant (coloured blue) with the c-axis parallel to the field grows at the expense of the original variant (coloured grey).