from a single high-quality sequence from a Neandertal woman from the Altai Mountains in southern Siberia (*5*). With the sequencing of the Vindija individual, Prüfer *et al.* provide an important additional data point. The Altai Neandertal was highly inbred; her parents were related at the level of half-siblings. Furthermore, the background level of genetic diversity in her genome was also much lower than that of modern humans, suggesting a long history of small group sizes. The Vindija woman displays a similarly low level of genetic diversity, but no signs of recent inbreeding, suggesting that mating between close relatives was not a general feature of Neandertal groups, but small group sizes probably were. Prüfer *et al.* further show, by studying patterns of shared DNA, that the Vindija individual was more closely related than the Altai individual to the group of Neandertals who mixed with modern humans ~55,000 years ago.

"Population movement, mixing, and local extinction have been ubiquitous throughout prehistory and history."

Whereas the genetic relationships between ancient individuals can be gauged from DNA, their social relationships, if any, are challenging to assess. Sikora *et al.* tackle this problem by sequencing the genomes of four Paleolithic modern humans at the well-preserved Sunghir site. Two of these shared a single grave, which also contained the femur of the third human, whereas the fourth was buried in a nearby grave; they were very likely part of the same social group. Yet, none of these individuals were related at the level we would typically call family, that is, at third degree or closer, and they also did not show evidence of recent inbreeding. If the Sunghir group is representative of Paleolithic modern-human hunter-gatherer groups, it suggests that such groups consisted mostly of distantly related people and were connected to other groups via networks of movement. These findings mirror the conclusions from anthropological studies of present-day hunter-gatherer groups (*6*). The study shows that this social structure was already in place 33,000 to 35,000 years ago and may be a general feature of the modern-human hunter-gatherer lifestyle.

Neandertals went extinct soon after ~40,000 years ago, not long after modern humans had expanded into their Eurasian territory. The causes of their extinction (as well as that of the Denisovans, who vanished around the same time) are poorly understood, but competition with modern humans was probably a contributing factor. The current genetic studies (*1, 2*) raise the question of whether contrasting social structures played a role. This possibility is supported by previous archaeological analyses (*7*). Demographic modeling has suggested that whereas Neandertal groups might have been small and poorly connected, modern human groups had the sizes and network structures that allowed technology and culture to disseminate and persist over generations (*8*). Previous work has also shown that, as a genetic by-product of their long history of small group sizes, Neandertals suffered from a larger number of harmful mutations (*9, 10*).

The studies of Prüfer *et al.* and Sikora *et al.* demonstrate the promise of aDNA as a tool for understanding the social as well as genetic networks of past humans. Further research should provide more details about the structures of ancient human networks and how they changed across time and space. This should include studies of Paleolithic humans in Africa, where most of human evolution took place, and of the transition to agriculture and the growth of population sizes that followed. Such work might even inform the social and cognitive sciences. For example, it has been hypothesized that the human mind has an upper limit on the number of social relationships it can maintain (*11*), shaped by the group sizes of our Paleolithic ancestors. But as always with aDNA, we should not expect a simple picture (*3*). Even Neandertals, who seem to have had less far-reaching social networks in general, mated with modern humans, probably representing the extreme edge of their networks. ■

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The Wellcome Trust Sanger Institute, Wellcome Genome Campus, Hinxton CB10 1SA, UK. Email: ab34@sanger.ac.uk; cts@sanger.ac.uk

MATERIALS GROWTH

Epitaxy on polycrystalline substrates

The growth of new oxide phases is explored with multiple surface orientations

By **Shishir Pandya**[1] *and* **Lane W. Martin**[1,2]

Motivated by combinatorial and high-throughput approaches to the discovery of antibodies and drugs in pharmaceutical research, efforts like the Materials Genome Initiative (*1*) have been envisioned to develop similar algorithms for the discovery, design, and realization of next-generation materials, such as superconducting (*2*), magnetoresistive (*3*), dielectric (*4*), and luminescent (*5*) materials. However, such experimental approaches have not become pervasive across all classes of materials. For example, in the study of thin-film, functional complex oxides, systematic, small-scale exploration has remained the standard. However, studies like that of Wittkamper *et al.* (*6*), which explore many different substrates by using a polycrystalline substrate, stand poised to open the door for high-throughput studies of complex materials.

This new approach uses so-called combinatorial substrate epitaxy (CSE). In epitaxial growth, a crystalline film is deposited on a crystalline substrate with a well-defined orientation of the film relative to the substrate. Epitaxial growth of complex oxides not only produces high-quality materials, but also allows for the study of how strain can affect structure and properties, and even provides a route for stabilizing new materials with exotic properties (*7, 8*). In general, crystalline solids can exist in different structural forms (polymorphs), and epitaxial growth of a specific polymorph requires knowledge of the relative energies of the different polymorphs and the ability to identify and access the substrate that yields the desired structure.

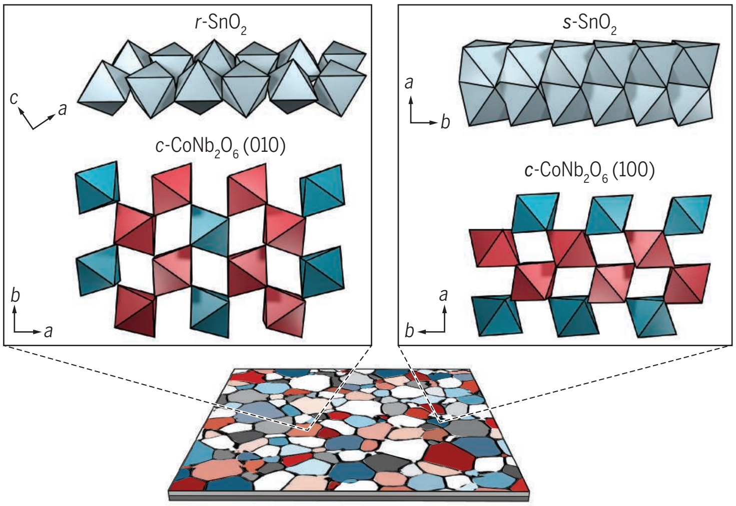
Although advances in computation can provide guidance on how to select to a specific structure for growth, experiments have

[1]*Department of Materials Science and Engineering, University of California–Berkeley, Berkeley, CA 94720, USA.* [2]*Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA. Email: lwmartin@berkeley.edu*

been limited by the dearth of commercially available substrates, which provide access to only a limited number of crystal structures, lattice parameters, and orientations. The CSE approach addresses these concerns by providing access to a wide range of materials and numerous orientations in a single pass, which greatly increases the search throughput. CSE relies on the creation of polycrystalline substrates. Such surfaces provide a large spread of surface orientations, and methods that probe local structure in a robust manner in a single-shot experiment can probe many epitaxial films at once.

High-throughput materials discovery

Polycrystalline substrates provide a wide array of templates upon which to explore epitaxial growth of a material, especially phases that are otherwise unstable.



Distinct from compositional-spread combinatorial approaches (*9*), which probe materials, structure, and property evolution as a function of chemistry in a single experiment, CSE probes a wide array of templated growths in the exploration of epitaxially stabilized materials and properties. Epitaxy allows one to go beyond traditional equilibrium phase diagrams, which are subject to the confines of ambient pressures, temperatures, and chemistry, to explore what phases can be created under a different set of boundary conditions. The key to such epitaxial stabilization is selecting the appropriate substrate that provides a favorable chemical environment (i.e., an interface that is chemically compatible and low in energy) as well as a favorable elastic environment (i.e., an interface that is dimensionally matched by having similar lattice parameters for the two materials) to promote the growth of the desired phase.

In turn, the substrate can drive the condensation of a specific atomic or molecular organization of a solid, even one that may not be the equilibrium-stable polymorph, because of the thermodynamic environment that is provided. For example, epitaxy has enabled the production of more photochemically active, but thermodynamically less-stable, polymorphs of titanium dioxide (TiO_2) (*10*) and provides a pathway to produce materials that are difficult (if not impossible) to produce in bulk, such as the Ruddlesden-Popper phase Ca_2MnO_4 (*11*) or layered cuprate superconductors like $Bi_2Sr_2Ca_{n-1}Cu_nO_x$ (*12*).

The CSE approach used by Wittkamper *et al.* leveraged these key features of epitaxy in a high-throughput study of the growth of tin dioxide (SnO_2), wherein a wide array of different possible epitaxial growth configurations (phases and orientations) were explored. Polycrystalline columbite (*c*-$CoNb_2O_6$) substrates were used to identify the epitaxial conditions most likely to produce exotic, metastable phases of SnO_2. That is, this work explored, in one sample, hundreds of different epitaxial conditions—a study that would take years of dedicated efforts to recreate in traditional single-crystal epitaxy.

In equilibrium, SnO_2 adopts a rutile (*r*) structure, but high-pressure studies have revealed a metastable scrutinyite (*s*) structure that is less stable by ~6 kJ/mol. Theoretical approaches have suggested that an epitaxial constraint can provide a route to stabilize materials by as much as ~20 kJ/mol relative to the equilibrium phase (*13*). Ceramic materials like SnO_2 can be considered as close-packed arrangements of anions, with cations filling some of the interstitials. In SnO_2, both the *r* and *s* phases have identical hexagonally close-packed oxygen lattices, but different cation ordering in the interstitial sites. This similarity would traditionally limit the ability of epitaxy to differentiate between these two structures. Faced with no obvious substrate choice to provide a route to select one phase over the other, Wittkamper *et al.* used their understanding of the differences in cation ordering in the two structures to select a candidate substrate (*c*-$CoNb_2O_6$) that possesses a similar cation ordering and lattice parameter to the desired *s*-SnO_2 phase. In turn, they applied CSE to rapidly explore a wide variety of epitaxial constraints to identify the best orientation to stabilize this phase.

Equally important to this high-throughput approach are methods that allow for rapid, local determination of the crystal orientation of the substrate and film. Wittkamper *et al.* used a combination of electron backscattered diffraction, long used in the study of polycrystalline bulk systems but rarely applied in epitaxial films, together with selective-area electron diffraction to produce a detailed picture of the grain-by-grain epitaxy (see the figure). This technique reveals grain-over-grain growth and provides for statistical analysis of the stabilization of both the *r* and *s* phases and for illumination of the underlying epitaxial relations. This approach identified the unit cell–over–unit cell epitaxial orientation relation wherein the film aligns its primary close-packed planes with the substrate close-packed planes to minimize strain and interfacial energies.

Ultimately, the power of this approach lies in simultaneously exploring various primary and secondary orientational and interfacial arrangements and elastic constraints (arising from the lattice mismatch between film and substrate) to establish the epitaxial orientation relations that can stabilize different phases. Thus, a single sample can provide the equivalent of many hundreds of samples produced by means of traditional epitaxial growth and allows for exploration of nonintuitive orientation relations in a systematic manner. The application of the CSE approach could greatly expand the throughput of epitaxial studies and usher in a new era for materials discovery and design in substrate-supported films. ■

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