**OXIDE HETEROSTRUCTURES**

**Atoms on the move**

The epitaxial growth of oxide heterostructures is generally thought to occur in a deterministic fashion. Recent results on the Ruddlesden–Popper phases show this is not always the case, and that a dynamic rearrangement of the layers during growth can spring up surprises.

Guus Rijnders

Complex oxide materials are a mixture of metal and oxygen ions that exhibit a wide variety of physical functionalities\(^1\). They are among the most abundant minerals on Earth, and are of interest in many commercial technologies, from displays to electronics and communication to sensors and actuators. The multifunctional nature of these materials has opened up many possibilities for fundamental research and created tremendous interest in the synthesis of novel materials. Among these, the \(A_{n+1}B_nO_{3n+1}\) Ruddlesden–Popper phases, where \(A\) and \(B\) are cations, and \(O\) an oxygen anion, have attracted a lot of attention, as they offer functionalities such as di-, ferro-\(^2\) and piezoelectric, magnetic, superconducting\(^3\) as well as catalytic properties\(^4\). The crystal structure of these Ruddlesden–Popper phases can be described by the stacking of a finite number \((n)\) of layers of perovskite \(ABO_3\) between rocksalt \(AO\) layers, as shown in Fig. 1.

One of the most promising techniques to synthesize Ruddlesden–Popper thin films is molecular beam epitaxy, an ultrahigh-vacuum growth technique in which molecular or atomic beams react to an epitaxial thin-film on a heated crystalline substrate. In the most ideal case, this film is grown atomic layer-by-atomic layer. Molecules or atoms impinge on the surface and two-dimensional islands nucleate. These islands grow by attachment of further atoms, until an atomic layer is completed by coalescence of these islands. This process, of nucleation and growth, is repeated for every subsequent atomic layer. For the growth of Ruddlesden–Popper phases, a shuttered deposition process is normally used, allowing for the control of the composition of each atomic layer. Writing in *Nature Materials* and *Nature Communications*, two independent collaborations now show\(^5,6\) that a set of dynamic phenomena occur during the growth process of Ruddlesden–Popper films, thus explaining why they have been challenging to grow in the past, but also expanding the range of materials that can be prepared as epitaxial heterostructures in the future.

The high degree of control over crystal growth provided by molecular beam epitaxy enables the precise control of surface composition and morphology, and therefore the reproducible synthesis of a large variety of heterostructures with extremely sharp interfaces. However, although many groups have successfully synthesized Ruddlesden–Popper phases using molecular beam epitaxy, fabricating these materials without defects, or indeed understanding the underlying mechanisms that govern the creation of such defects, has remained a challenge. At higher growth temperatures, both thermodynamic and kinetic effects are thought to disturb the atomic-layer control over the growth process, and therefore the resulting structure of the thin film. The work of Lee *et al.*\(^5\), however, now demonstrates that a dynamic rearrangement of atomic layers can occur during growth, leading to structures that are highly unexpected based on the intended layer sequence. Indeed, as Nie and colleagues\(^6\) independently demonstrate, the most atomically precise interfaces in \(Sr_{n+1}Ti_nO_{3n+1}\)

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**Figure 1** | Ruddlesden–Popper phases, \(A_{n+1}B_nO_{3n+1}\), where \(A\) and \(B\) are cations, and \(O\) an oxygen anion. The \(n = 1, 2\) and 3 members of the series are shown.
occur when deliberately using specific non-stoichiometric growth conditions. Until now, it had been generally thought that Ruddlesden–Popper phases grow in the same layer-by-layer order that their constituent monolayers are deposited. These latest results undermine this assumption, with dramatic consequences for the controlled production of high-quality thin films and their resulting properties. Understanding of the dynamic layer-rearrangement is a prerequisite for engineering atomically sharp interfaces at the desired location within the heterostructure. Based on these results, novel growth routes can now be envisaged, enabling the study of new interfacial phases containing any desired member of the Ruddlesden–Popper series, which can, in turn, lead to improved performance and new functionalities. Such growth routes are not only limited to layered oxides such as Ruddlesden–Popper phases, but can also be used to explore the structure and properties of oxide interfaces more generally.

To study the fundamental physics of the dynamic rearrangement in detail, a strong degree of collaboration between experimental and theoretical solid-state scientists was necessary. Both teams used an oxide molecular beam epitaxy system with in situ growth-monitoring capabilities for the fabrication of Ruddlesden–Popper phases. Their crystalline properties, as well as the atomic stacking, were studied using state-of-the-art synchrotron X-ray scattering and high-resolution scanning transmission electron microscopy. Moreover, to support the experimental evidence for the rearrangement of the surface layer, density functional theory calculations were performed. It is by combining various experimental approaches with theory that provides the insight and mechanistic understanding that no individual research group or institution can hope to achieve alone.

PEROVSKITE SOLAR CELLS

Continuing to soar

The dream of printing highly efficient solar cells is closer than ever to being realized. Solvent engineering has enabled the deposition of uniform perovskite semiconductor films that yield greater than 15% power-conversion efficiency.

Michael D. McGehee

The emergence over the past four years of solar cells made by solution casting thin films of light-absorbing methylammonium lead halide perovskite semiconductors has captured the attention of materials scientists and researchers in renewable energy. The 15% efficiency values reported nearly a year ago ignited an explosion of research in this field (Fig. 1). Unsurprisingly, researchers quickly identified challenges that needed to be addressed for these materials to be technologically successful. Writing in *Nature Materials*, Nam Joong Jeon and colleagues report a deposition approach that, by significantly improving the morphology control of the perovskite layers, provides a feasible strategy to overcome some of these problems and raises expectations for these semiconductors.

Casting uniform thin films of perovskites using the originally reported procedures is not trivial. These perovskites, unlike other commonly cast materials like polymers, are made from ionic solutions that exhibit low viscosities and lead to rapid formation of perovskite crystals. In many cases, as the crystals grow the material dewets from the surface — meaning that it is pulled away from the regions surrounding the crystals — and openings in the film are formed. These openings cause the electrical contacts — which, in a common photovoltaic architecture, are conducting films deposited on top and on the bottom of the light-absorbing layer — to touch each other, forming an electrical short that lowers the voltage of the cell. The variability in voltage caused by poor control of the formation of these openings has raised concerns about the possibility to make large solar panels based on these materials. Jeon and co-workers have resolved this dewetting problem by casting an intermediate thin film containing an extra-coordination solvent. This precursor film fully wets the surface and can slowly be converted into the perovskite film by thermal annealing. The resulting films are remarkably uniform and have enabled the fabrication of solar cells with an average power-conversion efficiency of 15.5% and a relatively small standard deviation around 1%.

The researchers also address another problem made apparent during the past year: the hysteretic behaviour observed in the current–voltage curves of perovskite solar cells. For reasons that are not yet understood, the current often depends on the bias voltage applied to the cell seconds before the measurement is taken. Consequently, a current–voltage curve taken with increasing voltage (forward scan) tends to exhibit lower currents at each voltage than a curve taken with decreasing voltage (reverse scan; Fig. 2a). It is quite possible

![Figure 1](https://example.com/figure1.png)

**Figure 1** | The world record power-conversion efficiency of perovskite solar cells over time. Earlier data points were reported in the literature, but not validated. More recent data has all been validated by Newport or the National Renewable Energy Laboratory.

Taken as a whole, these two studies clearly underline the role of thermodynamic factors during the atomic-layer-by-layer growth of complex materials, and provide a clear route for expanding the base of materials that can be prepared by design, with precise interface control. The range of quantum phenomena accessible in oxide interfaces is already enormous. With an even richer variety of oxide interfaces to explore, this will continue to be fertile ground for fundamental studies in the future.