# Engineering strontium aluminate sacrificial layers for fabricating monocrystalline complex oxide freestanding membranes

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Citation: Lu D. (2024). Engineering strontium aluminate sacrificial layers for fabricating monocrystalline complex oxide freestanding membranes. The Innovation 5(4), 100646.

There was a long history of releasing various monocrystalline semiconductor structures from their hosting substrates to form "freestanding" structures, in order to change the substrates and for other special purposes. The release was achieved by breaking the bonds between the film and the substrate, through methods such as forming interfacial gas bubbles ("smart-cut" technology for fabricating semiconductor-on-insulator wafers) or chemical etching (selectively etching epitaxial AlAs underlayer for fabricating GaAs-on-silicon photonic devices). The exfoliation of layered van der Waals materials in recent decades also produced another class of freestanding monocrystalline materials—two-dimensional (2D) materials. In addition to changeable substrates, being freestanding also allowed unique methods to manipulate the 2D materials; for example, transferring them on flexible substrates and directly stretching them controls the strain in their lattice, as well as their strain-dependent physical properties.

And now it is the turn for complex oxides. Complex oxides manifest exotic physical properties such as multiferroicity, various magnetic orders, and high-$T_c$ superconductivity, which are generally believed to be the results of the interplay between the charge, the orbital, and the spin of the electrons, as well as the lattice structures of this type of material. These oxides often hold perovskite ($ABO_3$) or perovskite-related crystal structures; their similar atomic arrangements and lattice constants enable epitaxial growth on each other, yielding different epitaxial heterostructures and various accompanying emergent phenomena. The combination of such rich features from complex oxides and the advantages from freestanding membranes requires the fabrication of oxide freestanding membranes, which would bring tremendous opportunities in both fundamental research and device applications.

There are quite a few approaches for fabricating oxide freestanding membranes. Natural weak bonds between certain oxides allows cleavage at the interface, such as those in Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ (PMN-PT)/SrRuO$_3$ epitaxy; growing a double-layer graphene on single-crystal substrates and then growing epitaxial films on top using "remote epitaxy" also facilitates release, resembling the exfoliation of 2D materials. Currently, the most widely used fabrication method of oxide freestanding membranes is the sacrificial layer etching method; namely, using an etchant to remove the middle layer in an epitaxial heterostructure consists of a bottom substrate, a sacrificial layer, and a top film (Figure 1). By carefully choosing the combination of the sacrificial layer and the etchant, it is possible to selectively dissolve the middle layer without damaging the top film, yielding excellent-quality oxide freestanding membranes. Perovskite or perovskite-related oxides suitable for such sacrificial layers include (La,Sr)MnO$_3$, YBa$_2$Cu$_3$O$_{7-x}$, and SrCoO$_{2.5}$.

There were still challenges. One of the main challenges was that the chemical properties of many perovskite oxides are similar, causing difficulties in selective etching and fabricating certain kinds of freestanding membranes; for example, the typical etchants of many perovskite oxides, including manganites, ferrites, cobaltates, nickelates, and cuprates, are acids (H$^+$). This fact suggested that engineering a non-perovskite sacrificial layer is more advantageous to achieve selective etching, in terms of generality. Strontium aluminate (Sr$_3$Al$_2$O$_6$) was the first non-perovskite sacrificial layer for fabricating oxide freestanding membranes (Figure 1).[1] It holds a complicated yet somewhat highly symmetric cubic structure. Although the Al ions form 4-coordinated tetrahedral AlO$_4$ in Sr$_3$Al$_2$O$_6$ instead of the typical B-site ion in forming 6-coordinated octahedral BO$_6$ in perovskites, the atomic arrangement in Sr$_3$Al$_2$O$_6$ still matches those in perovskites. Detailed analysis reveals that one unit cell of Sr$_3$Al$_2$O$_6$ is effectively 4 × 4 × 4 unit cells of cubic perovskite, and the lattice constant $a$ (15.844 Å) also matches 4$a$ of typical perovskites (for example, 3.905 × 4 = 15.620 Å, for SrTiO$_3$). Furthermore, Sr$_3$Al$_2$O$_6$ dissolves readily in water, a solvent benign to most of the perov-

skite oxides. Its chemical reactivity and solubility in water is likely due to the high Sr content interrupting the Al-O-Al framework in aluminates, forming unconnected multialuminate ions (ring-shaped Al$_6$O$_{18}^{18-}$ here); as SrO hydrates into soluble Sr(OH)$_2$, Sr$_3$Al$_2$O$_6$ also dissolves.

Although high-quality oxide freestanding membranes were fabricated by using Sr$_3$Al$_2$O$_6$, crack formation was common, causing film discontinuity, complicating further characterization, manipulation, and application. The mechanism remained not fully clear; research suggested that shrinking the lattice constant mismatch between the sacrificial layer and the top film mitigates the crack formation.[2] For example, for BaSnO$_3$ freestanding membranes, using Ba$_3$Al$_2$O$_6$ (mismatch −0.2%, also dissolvable in water) instead of Sr$_3$Al$_2$O$_6$ (mismatch 3.9%) significantly lowered the crack density. One possibility of crack formation is due to the incoherent epitaxial growth of both Sr$_3$Al$_2$O$_6$ on perovskite oxide substrates and films on Sr$_3$Al$_2$O$_6$ in many cases, creating periodic dislocations,[3] which destabilizes the crystal.

With such advances, various electronic devices based on monocrystalline oxide freestanding membranes have been demonstrated, including ferroelectric transistor memories, ferroelectric tunnel junction memories, and high-$k$ dielectric transistors. Strain has also been applied on these oxides, achieving metal-to-insulator transition in (La,Ca)MnO$_3$ and dielectric-to-ferroelectric transition in SrTiO$_3$. Novel phenomena requiring the "freestanding" geometry, such as super-elasticity and polar skyrmions, were also reported in freestanding oxides.

Very recently, a sacrificial layer based on another strontium aluminate, Sr$_4$Al$_2$O$_7$, has also been reported.[4,5] With more Sr content, Sr$_4$Al$_2$O$_7$ divides Al-O-Al framework into smaller trialuminate anions (Al$_3$O$_{10}^{11-}$) and monoaluminate anions (AlO$_4^{5-}$), providing even faster dissolution rate in water. The crystal structure of Sr$_4$Al$_2$O$_7$ is more complicated than Sr$_3$Al$_2$O$_6$, and its unit cell has lower orthorhombic symmetry (Figure 1). Even though, the atomic arrangement of Sr$_4$Al$_2$O$_7$ still matches those in perovskites: when aligning the [110], [1−10], and [001] orientations of Sr$_4$Al$_2$O$_7$ with the [100], [010], and [001] orientations of a cubic perovskite, each Sr$_4$Al$_2$O$_7$ unit cell corresponds to $2\sqrt{2} \times 2\sqrt{2} \times 6$ unit cells of cubic perovskite; its in-plane lattice constants $a$ and $b$, although orthorhombic, are very close to each other, forming a nearly tetragonal lattice, and also are close to lattice constants of typical perovskites. Furthermore, Zhang et al.[4] have found that in contrast to Sr$_3$Al$_2$O$_6$, Sr$_4$Al$_2$O$_7$ typically forms coherent epitaxy with perovskite. With greatly reduced interfacial dislocation density, Sr$_4$Al$_2$O$_7$ is able to decrease the crack density of various oxide freestanding membranes of the lattice constants ranging from 3.85 to 4.04 Å (Figure 1). The maximum size of oxide freestanding membranes without crack formation can be as large as millimeter scale, even close to the size of the substrates (typically 5 × 5 mm$^2$). The released freestanding membranes enjoy excellent physical properties, such as the metallicity and magnetism of (La,Ca)MnO$_3$ and SrRuO$_3$, close to their ideal values.

It is intriguing that Sr$_4$Al$_2$O$_7$ can grow coherently on perovskite more easily than Sr$_3$Al$_2$O$_6$. Zhang et al.[4] attribute the reason to the higher deformability and stronger bonding to the perovskite of Sr$_4$Al$_2$O$_7$: density functional theory calculations show that both biaxial strain and in-plane anisotropic strain deform Sr$_4$Al$_2$O$_7$ easier (lower elastic moduli); the bonding energy between Sr$_4$Al$_2$O$_7$ and perovskites is similar to the perovskite-perovskite bonding energy and more than 2 times larger than the bonding energy between Sr$_3$Al$_2$O$_6$ and perovskites. As a result, Sr$_4$Al$_2$O$_7$ tends to deform under the strain generated by the bottom substrate and the top film, instead of creating dislocations, as observed for Sr$_3$Al$_2$O$_6$.

In some cases, Sr$_3$Al$_2$O$_6$ is able to form coherent epitaxy on perovskite substrates.[5] As the growth conditions of incoherent and coherent Sr$_3$Al$_2$O$_6$ are similar, the difference is likely caused by other factors, such as the growth
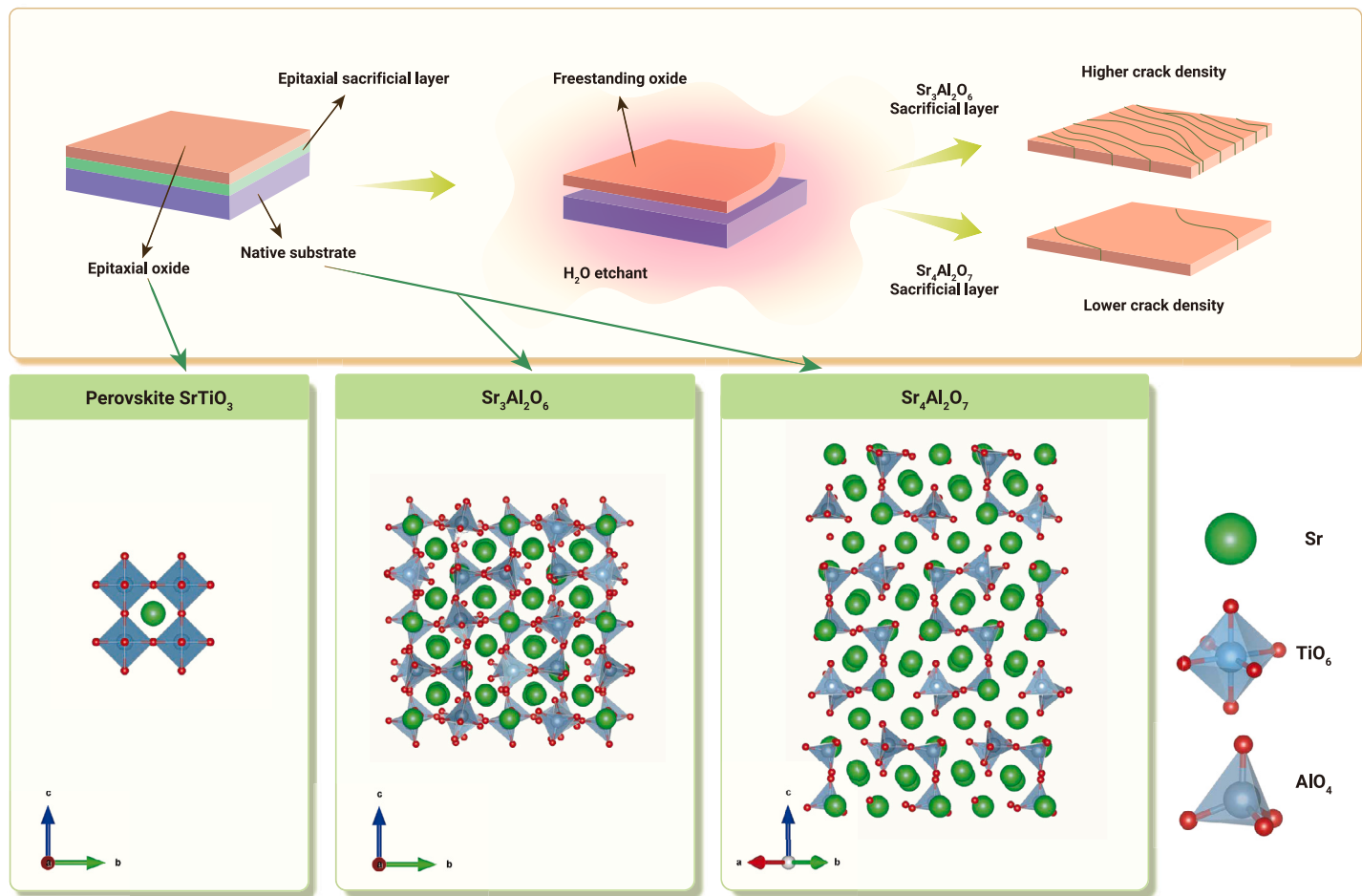
**Figure 1. Strontium aluminate sacrificial layers for fabricating monocrystalline complex oxide freestanding membranes** (Top) Schematics of the fabrication process for oxide freestanding membranes. (Bottom) Crystal structures of a typical perovskite ($SrTiO_3$, viewed along [100]), $Sr_3Al_2O_6$ sacrificial layer (viewed along [100]), and $Sr_4Al_2O_7$ sacrificial layer (viewed along [110]). The similarity between the perovskite unit cells and the perovskite-like "unit cells" in these strontium aluminates suggests an epitaxial relationship.

techniques. Reports show that dislocations start to form in $Sr_3Al_2O_6$ grown by pulsed laser deposition at the thickness of 2−5 nm[3] and continue to exist for thicker films,[1,4] while $Sr_3Al_2O_6$ films grown by molecular beam epitaxy (~10 nm) are coherent.[5] One speculation is that the high-energy laser supplies additional kinetic energy to the atoms ablated to the surface of the substrate, overcoming the energy barrier for dislocation formation. Comparing the crack density of oxide freestanding membranes fabricated by different growth methods could provide further insights for the mechanism of crack formation.

Although $Sr_4Al_2O_7$ sacrificial layers are able to produce oxide freestanding membranes of satisfactory quality with high efficiency, questions still remain: is $Sr_4Al_2O_7$ applicable for perovskite-related crystal structures, such as Ruddlesden-Popper phases? Is it just a coincidence that strontium aluminate family ($Sr_3Al_2O_6$ and $Sr_4Al_2O_7$) has atomic arrangements and effective lattice constants similar to those of perovskite oxides, or there are deeper reasons? Are there rational principles to design materials suitable for sacrificial layers in strontium aluminate family or out of this family (such as recently reported (Ba,Sr)O sacrificial layers) or even using some metastable phases that can be stabilized by epitaxy? Nevertheless, with a more powerful sacrificial layer, it would be possible to further extend the frontier of oxide freestanding membranes as a research field and to more strongly support the related research opportunities.

The crystal structures of complex oxides are not limited to perovskites. Oxides in spinel and garnet structures exhibit distinctive physical properties such as magnetic orders different from perovskites and unusual spin dynamics, and their crystals contain metal-oxygen tetrahedra in addition to octahedra. Using corresponding sacrificial layers to release these oxide films from native substrates could similarly enable related research opportunities such as novel spintronic devices and physical property modulation by deforming metal-oxygen bonds in unique modes through strain application. Heterogeneous integration of

monocrystalline materials of different crystal structures may further provide opportunities to fuse various physical properties in one system. Then come the questions: what can be used as the sacrificial layers for the complex oxides of non-perovskite structures? Can some members from the strontium aluminate family again fulfill this task?

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### DECLARATION OF INTERESTS

The authors declare no competing interests.