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Size-controlled spalling of LaAlO$_3$/SrTiO$_3$ micromembranes

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Abstract

The ability to form freestanding oxide membranes of nanoscale thickness is of great interest for enabling material functionality and for integrating oxides in flexible electronic and photonic technologies. Sambri et al. recently demonstrated a route for forming conducting heterostructure membranes of LaAlO$_3$ and SrTiO$_3$; the canonical system for oxide electronics. In this route, the epitaxial growth of LaAlO$_3$ on SrTiO$_3$ resulted in a strained state that relaxed by producing freestanding membranes
with random sizes and locations. Here we extend the method to enable self-formed
LaAlO$_3$/SrTiO$_3$ micro-membranes with control over membrane position, their lateral
sizes from 2 to 20$\mu$m and with controlled transfer to other substrates of choice. This
method opens up for the possibility to study and use the two-dimensional electron gas
in LaAlO$_3$/SrTiO$_3$ membranes for advanced device concepts.

**Keywords:** LaAlO$_3$/SrTiO$_3$, two-dimensional electron gas, freestanding oxide mem-
branes, flexible electronics, thin-film spalling, micro manipulation.

**Introduction**

The realization and characterization of freestanding epitaxial oxide layers has recently re-
ceived significant attention due to potential applications in flexible electronics and photon-
ics.$^{1,2}$ The membrane geometry allows integration of oxide functional materials in technologi-
cally important platforms, such as silicon or flexible polyethylene terephthalate (PET), where
conventional epitaxial integration is challenging.$^{3-5}$ Most excitingly, however, the membrane
properties may be significantly altered compared to the bulk counterpart offering new op-
portunities for functional devices. Examples include enhanced ferromagnetic properties for
La$_{1-x}$Sr$_x$MnO$_3$ membranes$^6$ and giant flexoelectric response in freestanding BiFeO$_3$ and
SrTiO$_3$ films.$^7$ Recent advances towards single unit cell oxide membranes even join these
systems to the family of two-dimensional materials alongside graphene and transition-metal
dichalcogenides.$^8,9$

Most studies of freestanding oxide membranes have relied on the deposition of the ox-
ide layer of interest on sacrificial epitaxial layers such as La$_{1-x}$Sr$_x$MnO$_3$ or Sr$_3$Al$_2$O$_6$ which
subsequently can be dissolved in KI/HCl and water, respectively, to lift-off the oxide mem-
brane.$^3,11,11$

Using this approach, it has not yet been possible to realize freestanding membranes of the
conducting heterostructure LaAlO$_3$/SrTiO$_3$ (LAO/STO), which is the canonical system for
emergent electronic phases in oxides.$^{12-14}$ An alternative approach for the formation of thin
Figure 1:  

a Schematic illustration of the spontaneous (LAO/STO) membrane spalling. Adapted with permission from\textsuperscript{10} Copyright 2020 John Wiley & Sons. 

b Scanning electron microscope (SEM) image showing the spontaneous formed LAO/STO membranes of an as-grown sample with 70 nm LAO. 

c Distribution of lateral size ($D_x, D_y$) of membranes. No correlation is found between $D_x$ and $D_y$ and panel d shows the overall size distribution ($D_{x,y}$) displaying a clear preference for membranes with lateral sizes around $\sim 1.9 \mu m$. 

\textsuperscript{3}
membranes, which obviates the need for a sacrificial layer and etching, is that of controlled spalling. This method relies on the deposition of a stressor layer and a flexible handle-layer to controllably delaminate the surface layers of a brittle crystal, and has been successfully used to release membranes from wafer scale semiconductors such as silicon, germanium, nitrides and III-V compounds.\textsuperscript{15–17} The spalling process relies on a stable fracture mode where a crack propagates parallel to the substrate at the equilibrium depth where the shear stress is minimized. The process self-corrections such that for a crack very close to the surface the top layer contracts and the crack tip is deflected downwards; conversely, for a crack very deep in the substrate the top layer will expand upon fracture due to the curvature and the crack is instead deflected upwards. The details of the crack propagation are reviewed in Ref.\textsuperscript{18} In Ref.\textsuperscript{10} some of us reported the spontaneous spalling of self-formed micrometer sized membranes of LAO/STO employing the lattice mismatched LAO top layer as the stressor layer. The process is schematically illustrated in Fig. 1a and a scanning electron microscope (SEM) micrograph of a typical sample is shown in Fig. 1b. Depending on the LAO thickness, the thickness of the micro membranes were \( \sim 140 - 200 \) nm and importantly, the interface conductivity remains intact after membrane release and transfer to a silicon platform. This creates qualitatively new opportunities for oxide electronics allowing integration with conventional semiconductor electronics and semiconductor processing. Furthermore, since each LAO/STO growth results in millions of individual membranes sufficient for multiple device generations, the results greatly improve the opportunities for device optimization, and reproducibility. The proof-of-concept developed in Ref.\textsuperscript{10} relies on spontaneous spalling of the surface and results in membranes of random sizes forming at random positions and subsequent uncontrolled transfer to silicon.

Here, we extend this work by introducing a new concept for pre-growth substrate preparation allowing control of where the LAO/STO membranes form on the substrate as well as their individual lateral dimensions. Further we demonstrate controlled manipulation of individual LAO/STO micro-membranes onto silicon substrates.
Results and Discussion

Initially we consider the as-grown, uncontrolled, spontaneously spalled LAO/STO sample with 70 nm LAO shown in Fig. 1b. The sample surface is fractured into approximately rectangular membranes with edges parallel to the [100] and [010] crystal directions of STO and lateral dimensions $D_x, D_y$. We note that all membranes in Fig. 1b and throughout this work exhibit curvature. This is a consequence of the different lattice spacings of the LAO and STO and thus directly confirms that all the membranes host the LAO/STO heterostructure and not just the LAO top film. The sizes of all 451 imaged membranes from three different regions of the sample were manually measured and the size-distribution is seen in Fig. 1c. No linear statistical correlation is found between $D_x$ and $D_y$ and the combined distribution of lateral membrane dimension ($D_{x,y}$) – i.e. the distance between spontaneous surface fracture events – is shown in Fig. 1d having an average of $\sim 1.9 \mu m$. Consequently the average membrane area and circumference follow distributions peaked at $4.5 \mu m^2$ and $\sim 8 \mu m$, respectively (see Supporting Information (SI) Figures S1,S2). The distribution in Fig. 1d, having a sharply peaked mean around $\sim 1.9 \mu m$ and low probability for larger and smaller dimensions, reflects that the driving force for membrane fracturing – the energy associated with the strain – increases with the lateral size. This makes it unlikely to find very large membranes as these will internally fracture and subdivide as a consequence of the energy balance between the membrane strain and the membrane surface energy$^{18-20}$.

For conventional spalling of semiconductors the initial fracturing is triggered by the discontinuity appearing at the edges of the stressor-layer.$^{15}$ Here, we instead investigate the possibility to control the position of fractures by topographic discontinuities predefined in the growth substrate. The process is schematically illustrated in Fig. 2a and relies on a combination of lithography and $Ar^+$-ion milling to define trenches in the STO substrate prior to LAO deposition. Each STO substrate was patterned with multiple $200 \times 200 \mu m^2$ fields, each consisting of a grid of 250 nm wide trenches milled to a depth of 20 nm. The trench grid thus outlines an array of square regions of pristine STO surfaces ready for epitaxially strained
growth. The dimensions of the squares $L_{x,y} = 0.5\text{–}20\,\mu m$ were varied between each field and Fig. 2b-d show typical characteristics of a $L_{x,y} = 2\,\mu m$ field before growth. As detailed in the Methods section, milling parameters were carefully chosen to prevent substrate conductivity caused by the Ar$^+$-ion bombardment, and resist-stripping and surface cleaning procedures were optimized to ensure that the patterned STO surface displayed TiO$_2$-terminated terrace structures (Fig. 2c) facilitating the epitaxial growth of LAO.

Figure 2: a Schematic illustration of the surface patterning by Ar$^+$-ion milling. b Atomic force microscopy (AFM) topography map of the STO surface following Ar$^+$-ion milling and cleaning procedures for a field with $L_{x,y} = 2\,\mu m$ squares (scale bar is $2\,\mu m$). The dashed square and line correspond to the zoom in c and height profile in d, respectively. c High-resolution AFM image of area in b showing clear terraces characteristic of clean TiO$_2$-terminated STO (scale bar is $200\,nm$). d Height profile along dashed line in b show an average milled depth of $20\,nm$ and trench width of $w = 250\,nm$.

Figure 3a shows typical scanning electron micrographs of patterned samples after growth of $70\,nm$ of LAO$^{10}$ (see Fig. S3 for additional images). Clear directed formation of LAO/STO
micro-membranes following the intended substrate pattern are observed for all fields proving the viability of the concept. However, membranes did not form at all the intended positions, indicating that the patterned surface discontinuity can be further optimized to trigger surface fractures more efficiently. For fields with $L_{x,y} = 0.5–2\,\mu m$, which is equal to or smaller than the average unpatterned membrane size shown in Fig. 1d, only very few free-standing membranes were found. We associate this to strain relaxation at the edges of the pattern and an elastic energy of the small membranes below the threshold for spontaneous spalling. This thus sets a lower limit on the size of controlled membranes, however, we expect this limit will depend on the pattern and the LAO thickness; these smallest membrane patterns are excluded from the analysis below.

For the fields with $L_{x,y} = 4–20\,\mu m$, 1146 membranes were imaged by SEM and manually counted using the same procedure as for Fig. 1 (see SI Figure S4). The resulting membrane size distributions, $D_{x,y}$, for each patterned grid size ($L_{x,y}$) is presented in Fig. 3b. For $L_{x,y} = 4\,\mu m$, the LAO/STO membranes clearly display a narrow size distribution closely matching the patterned size. A smaller but significant population of membranes also appear with lateral sizes around $D_{x,y} \sim 8\,\mu m$ i.e. twice the patterned $L_{x,y}$ due to two neighboring membranes remaining merged. For $L_{x,y} = 7\,\mu m$, a different behavior is apparent: the size distribution show two characteristic populations - one corresponding to the intended patterned size of 7$\mu m$ and one of smaller sizes around $\sim 3.5 \mu m$ corresponding internally fracture of the patterned squares. By comparing, the size-distribution of the as-grown sample in Fig. 1b where the average size was around $\sim 1.9 \mu m$, it is clear that these internally fractured membranes are affected by the proximity of the trenches to dictate their resulting larger size. As the patterned square size is increased to $L_{x,y} = 10\,\mu m$ and $20\,\mu m$, it is clear that the likelihood of forming correspondingly large membranes is reduced while the population of smaller internally fractured membranes increases. For $L_{x,y} = 20\,\mu m$ the distribution approaches that of the as-grown sample with an average lateral size around $\sim 2.5 \mu m$ and only very few membranes of the intended size were observed (see inset in lower panel of Fig. 3b). Thus, this
Figure 3: a Representative SEM images of the different patterned sizes investigated with $L_{x,y} = 4$–$20\mu$m. Scale bar corresponds to 5$\mu$m. b Size distributions ($D_{x,y}$) of membranes measured in SEM for each $L_{x,y}$ investigated with success-rate (SR) indicated for each. For smaller patterned sizes, the resulting membranes appear with a size close to the intended. As the patterned size is increased, smaller membranes are formed as a result of internal fracture inside the patterned square that ultimately approaches the as-grown membrane size distribution.
method has both an upper and lower limit for the size-control with the yield of intentionally sized membranes reducing as the pattern sizes becomes much larger the average 1.9 µm. Also stated on the respective panels of Fig. 3b is the success-rate (SR) defined as the fraction of spalled membranes with dimensions $D_{x,y}$ within ±0.25 µm (i.e., the trench width) of the defined pattern dimensions $L_{x,y}$ out of the total number of membranes. With this definition - reflecting the peak area of the distributions - the success rate is decreasing monotonously from 75% for the 4 µm pattern to 25%, 8% and 0.7% for the 7 µm, 10 µm and 20 µm patterns, respectively. This is clearly significant compared to the unpatterned sample (Fig. 1c) where the corresponding SR for the same sizes would be (2.7%, 0.3%, 0.1%, 0.0%). This is also consistent with direct inspection of SEM images which confirm that membranes found with the intended sized indeed result almost exclusively from directed formation along the milled pattern and not random spalling which occasionally having a similar size. An alternative definition of SR is the area covered by correctly spalled membranes with respect to the total imaged area. This definition is insensitive to the failure mode (e.g. whether membranes failed to fracture at all or the degree to which a patterned membrane sub-divided). With this definition, the corresponding success rates are ($\sim 10\%, 25\%, 20\%, 5\%$) for $L = 4, 7, 10, 20 \mu$m. The failure mode for the smaller membranes are thus primarily due to intended membranes not forming at all, while for $L = 20 \mu$m a sizable fraction of the number of possible membranes did form although a large number of smaller membranes are also present. We note that both definitions of SR would yield 100% in the case of perfect controlled spalling, and we expect that the numbers can be greatly improved in the future by optimizing the patterning and growth parameters. To summarize, for all grid sizes membranes were found which were spalled along the intended pattern. While this serves as proof of the concept, the histograms in Fig. 3b quantify its efficiency as discussed above.

As clearly seen in scanning electron micrographs of the uncontrolled membrane growth in Fig. 1b, the natural fracture direction is along the $[100]/[010]$ high symmetry directions, and these were also chosen for orientation of the control patterns in Fig. 2 and 3. To investigate
the possibility of generating complex membrane shapes following other directions, a trench pattern was fabricated along [110]/[1-10] i.e., rotated by 45° with respect to the design in Fig. 2 and 3. The resulting membranes are shown in SI Fig. S5. While a significant fraction of membranes show internal cracks or corners truncated along the [100]/[010], the pre-growth patterning method is clearly feasible for directing also fractures along directions not along the naturally preferred [100]/[010].

Figure 4: **a** Schematic illustration of the controllable manipulation and transfer of LAO/STO membranes with a micro-manipulator needle onto a silicon substrate. **b** SEM image of transferred membranes arranged into a row on the pre-patterned silicon substrate.

Lastly, to demonstrate the perspectives of the self-formed membranes and the present patterning technique for electronic devices, we show in Fig. 4 the results of controlled membrane transfer onto a SiO₂/Si substrate by means of a micro-manipulator (see Methods for details): four individual membranes were selected on different patterning-fields of the growth substrate and transferred and arranged on a Si/SiO₂ substrate with respect to an existing alignment grid. This degree of control shows the feasibility of this patterning method for realising unique device principles involving the LAO/STO interface two-dimensional electron gas or for devices combining functionalities of different oxide heterostructures in the
same circuit. We note that despite the curvature, the membranes are sufficiently clamped to the substrate by van der Waals forces to allow standard device fabrication procedures (resist spinning etc). In device geometries the membranes are further fixed by contact materials etc. We also note that the micro-manipulator technique will allow routine transfer of the membranes to any substrate and expand the possible heteromaterial combinations. We expect that entire arrays of membranes may be simultaneously transferred keeping their mutual distances, by adapting the techniques of polydimethylsiloxane (PDMS) stamping developed for assembly of van der Waals heterostructures.

**Conclusion**

To conclude, we have demonstrated a proof-of-principle for directed spalling and size control of conducting LAO/STO heterostructure membranes. The method relies on patterning the stress discontinuities in the LAO/STO epitaxial heterostructure by locally altering the growth substrate using argon milling prior to the growth. The size control is constricted by an upper and lower limit with respect to the yield and reproducibility of membranes. We demonstrate also the capability of direction fracture formation also along directions different from [100]/[010] otherwise strongly preferred without the pre-growth patterning. Lastly, we show that the membranes can be manipulated in a controllable manner with a micro-manipulator needle and transferred onto a silicon substrate. Preliminary results (Supplementary Fig. S5) suggest that extending the trench width may increase the yield, and we expect that a systematic variation of all the design parameters (trench width, depth etc.) as well as LAO thickness will allow significant improvement of the yield and extend the method towards more complex structures. We note further that the membranes exhibit thickness variations determined by the propagation of the crack tip during spalling. At a distance from the edge which exceeds the thickness, the unevenness is not expected to depend on the nature of the crack triggering (spontaneous vs. controlled) and although no systematic study has been made, no significant differences have been observed also compared to previous work.
Thickness variations may, however, be related to the speed of the spalling process and we expect that introducing a sacrificial handling/straining layer onto the heterostructure stack, our method may be improved both towards membranes of larger lateral size and more uniform thickness.

**Experimental**

LAO with a thickness of 70 nm, used for both unpatterned and pre-growth patterned spalled micro-membranes, was grown by Pulsed Laser Deposition (PLD) on TiO$_2$-terminated (001) STO substrates heated to 730°C at a oxygen background pressure of $2 \times 10^{-2}$ mbar. The LAO was ablated from a single crystal target with a KrF excimer laser at a repetition rate of 3 Hz and a laser fluence around 2.5 J/cm$^2$. The laser pulse width was 20 ns, the ablation spot area was 0.78 mm$^2$, and the angle of incidence was 45°. The target-substrate distance was in all depositions fixed to 37 mm. Following LAO growth, the samples were annealed at 500°C in 50 mbar oxygen for 1 hour, before cooling to room temperature under the same oxygen partial pressure.

To prepare the pre-growth patterned sample for electron-beam lithography, the sample was first rinsed in acetone, isopropanol and finally dried with N$_2$. In order to direct the Ar$^+$-milling, the sample was prepared with a $\sim$900 nm trilayer e-beam resist stack consisting of copolymer El6, Czar 13% and a decharging top-layer of Espacer 300Z. The resist stack was exposed and developed using standard conditions. The Ar$^+$-milling was carried out with a Kaufman ion source using a beam voltage of 600 V and a beam current of 23 mA. Using these beam conditions, the sample was milled for 6 minutes. The remaining resist was stripped with N-Methyl-2-Pyrrolidone (NMP) and organic residues were removed by oxygen plasma ashing.

Individual LAO/STO membranes were transferred from the growth substrate to the silicon substrate in a home-build setup having a programmable motorized stage (x,y,z)+rotation where growth source substrate and the silicon target substrates are placed. In addition, the
system is equipped with an Eppendorf x,y,z manipulator equipped with a 0.1 µm disposable tungsten needle. The system is integrated into a long working-distance optical microscope, and nanostructures can routinely be picked-up from the source substrate and deposited on the target substrate with an accuracy of less than 1 µm.

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Supporting Information

Five supporting figures showing: histograms of membrane area (S1) and circumference (S2), SEM images of all $L_{x,y}$ studied (S3), recorded sizes ($D_{x,y}$) of all membranes investigated (S4) and effect of trench rotation respective to [100] lattice orientation (S5).

References


(20) Hu, M.; Thouless, M.; Evans, A. The Decohesion of Thin Films from Brittle Substrates.

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