Patterning Functional Oxides: Some Failures and Solutions in Fabricating a Hall Bar

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Functional oxides exhibit diverse useful properties, opening attractive prospects for electronic, magnetic and optoelectronic devices. However, the chemical instability of these oxides with some microfabrication processes, especially when dealing with thin films (<40 nm) or micron-scale lateral dimensions, can pose a considerable challenge. Here we describe the fabrication process of a Hall bar device used as a test structure for thin functional oxide films. The process employs photolithography and dry etching utilizing standard clean-room materials and methods. The device layout and fabrication process are described in detail, including conclusions and lessons gained from several failed attempts during process development. A key lesson is the advantage of employing an ultrathin protective layer to protect the oxide film surface. In addition, we encountered two common fabrication challenges: photoresist hardening during dry etching and edge accumulation of photoresist during spin-coating. Effective solutions to these issues are described. We hope that our lessons and conclusions, not limited to functional oxides, will help shorten the process development for other materials and devices.
I. INTRODUCTION

Electrical transport and magnetotransport measurements are crucial tools for characterizing various electrical and magnetic properties, including scattering mechanisms,\(^1\) magnetoresistance,\(^2-4\) various nontrivial Hall effects,\(^5-8\) and superconductivity.\(^9,10\) Two commonly used four-point schemes for such important measurements are the Van der Pauw and Hall bar geometries.\(^11\) While the Van der Pauw geometry is known for its simplicity and versatility, it can be limited by contact size and placements. Conversely, Hall bar geometry offers accuracy and directionality, thus emerging as a compelling alternative that addresses these challenges, with the tradeoff of a more complicated fabrication process.

Hall bar devices have been instrumental in the research of functional oxides, advancing the understanding of their exotic phenomena, such as topological and anomalous Hall effect,\(^12,13\) field effect,\(^14,15\) two-dimensional electron gas (2DEG),\(^16-18\) and spintronic functionality.\(^19,20\) With Hall bar geometry, the electric current flows between two contacts, e.g. from contact 5 to 6 in the schematic illustration in Figure 1a, and the longitudinal resistance is calculated by measuring the voltage between contacts 2 and 3 (or 4 and 1) for sheet resistance, and contacts 1 and 2 (or 4 and 3) for transverse or Hall resistance.

The microfabrication of Hall bars of conventional semiconductors is trivial using standard clean-room processes. However, as will be shown in this work, several standard patterning approaches are grossly incompatible with transition metal oxide (TMO) films. A key example is the goal of patterning a 2DEG system formed at the oxide interfaces without altering the interface properties.\(^21-28\) Previously employed solutions include
growing the film onto a pre-patterned inert layer,\textsuperscript{21–23} and ion milling at low temperatures.\textsuperscript{23,24}

This significant progress achieved with patterning 2DEG systems might not be fully applicable to thin films. The challenge becomes even greater for ultrathin films, with a thickness of a few tens of nm or below. One solution is the use of a liftoff process utilizing sacrificial water-soluble layers.\textsuperscript{29,30} Another approach is the application of wet etch schemes, which can produce excellent devices.\textsuperscript{31} However, dry etch is considered a more scalable approach, which, in principle, should allow future maturation into technologically-relevant dimensions. Thus, patterning, etching, and liftoff processes that are compatible with thin functional oxide films are of particular interest within this context.

In this work, we discuss the Hall bar fabrication process for functional oxides developed utilizing photolithography and dry etching. We used two different perovskite TMOs for the development: SrVO\textsubscript{3} (SVO) and 5-10% Ru-substituted La\textsubscript{0.70}Sr\textsubscript{0.30}MnO\textsubscript{3} (5-10% Ru-LSMO). Selective geometry, such as a Hall bar, is necessary to measure the anisotropic magnetic behavior of 10% Ru-LSMO. Whereas, the low resistivity of SVO makes it particularly sensitive to defects,\textsuperscript{32–34} allowing precise monitoring of film degradation by a simple electrical measurement. In Section A of the results, we present the fabrication process and device layout, explaining their underlying limitations and considerations. In Section B of the results, we discuss the main challenges encountered during the establishment of the fabrication process, and the solutions we developed to overcome them. We found that the key feature enabling the Hall bar fabrication without degrading the oxide thin film is the application of an ultrathin oxide protective layer.
Finally, in Section C of the results, we present experimental measurements to support our findings and conclusions. Suggestions for further improvement of the fabrication process are discussed in Section D. The development of a fully scalable TMO-based Hall bar fabrication process advances our capabilities to study functional oxides and lays the groundwork for large-scale fabrication, driving us closer to oxide electronics.

II. Experimental

SVO thin films (~60-75 unit cells, or 24-30 nm) were epitaxially grown on (LaAlO$_3$)$_{0.3}$(Sr$_2$AlTaO$_3$)$_{0.7}$ (LSAT) substrate using an oxide molecular beam epitaxy (MBE). The films were *in situ* coated with an ultrathin (~ 3 nm) TiO$_x$ protective layer deposited at low temperatures. Details of the MBE growth and the growth of the protective layer can be found elsewhere.$^{32,35}$

5% and 10% Ru-LSMO were grown on LSAT substrates using pulsed laser deposition (PLD), with the parameters described in a recent work.$^{36}$ The Ru-LSMO growth was followed by epitaxial growth of 2 nm of SrIrO$_3$ (SIO) at an oxygen partial pressure of ~0.13 mbar, a 1 Hz repetition rate, and a substrate temperature of 650°C.$^{37}$ Following the SIO growth, the samples were cooled to room temperature, where 2 nm of amorphous SrTiO$_3$ (a-STO) were deposited.

Hall bar devices were fabricated using photolithography and dry etching. The device dimensions are $L = 130 \mu$m, $W = 30 \mu$m, and $t = 10 \mu$m, as defined in Figure 1a (the design principles are detailed in Section III.A.3). See supplementary material for the full details of the optimized Hall bar fabrication process, materials, and tools.

The electrical and transport measurements were performed using a Quantum Design Physical Properties Measurement System (PPMS). The atomic force microscopy
(AFM) images were acquired with an Asylum Research/Oxford Instruments Cypher ES Environmental operated in tapping mode.

III. Results and discussion

TMO films (SVO, Ru-LSMO) were employed to develop a Hall bar fabrication process using photolithography and dry etching. Our goals were to achieve micron-scale dimensions and make the fabrication easily accessible for clean-room users. To that end, we rely on standard clean-room photolithography processes and materials. As it turned out, some of the materials and processes are entirely incompatible with functional oxides, requiring adjustments and workarounds. In the following sections, we introduce the device layout and the fabrication process, review the main development, and present the device performance to establish the success of the photolithography by comparing them to unpatterned films. Last, we discuss several suggestions for further optimization of the fabrication process.

A. Fabrication Process and Device Layout

We adjust the fabrication process and device layout to improve device yield and address fabrication challenges. Figure 1b-e illustrates the different masks that were used for the fabrication of nine Hall bars on a ~5×5 mm² sample. We start with the zero layer by creating Ti alignment marks (Figure 1b, pink) via a liftoff process performed on the TMO layer. Then, a preparatory step to the reactive ion etching (RIE) process is performed, where only the edge and corners of the sample are exposed and developed (Figure 1c, cyan) to remove photoresist accumulation. This step significantly reduces the exposure gap between the mask and the sample, as elaborated in Section C. Next is the oxide patterning process (Figure 1d), where the TMO thin film is etched. Finally, the
metal contact deposition is done using a liftoff process (Figure 1e). See supplementary material for the details of each process.

FIG. 1. (a) Schematic structure of a Hall bar device in top view (top) and perspective view (bottom). The patterned Hall bar is orange, the metal contacts used to access the Hall bar's legs are blue, and the exposed oxide substrate is gray. (b-e) The process flow and the different masks that were used during the Hall bar fabrication process. (b) Alignment marks for liftoff. (c) Edge exposure and removal of the photoresist accumulation. (d) Etching of the Hall bar devices via RIE. (e) Metal contact deposition.

The area layout of each Hall bar device is ~1x1 mm², with a total footprint (defined as the total area of the metal pads) of ~3x3 mm² for nine devices. We note that the large metal pads, deliberately designed for ease of bonding, can be substantially reduced.

The suggested layout allows magnetotransport measurements along the [100] and [010] directions of the film. However, the large and square area of the metal pads (about 1x1 mm² for each Hall bar device) allows adjustments, if needed, to one of the devices (e.g., an additional orientation) without changing the entire scheme. The choice of large
contact pads was a conscious choice, motivated by the ease of wire bonding and probing; the pads can be made much smaller without compromising performance, allowing for more devices and orientations to be fabricated on the same footprint. The following subsections will elaborate on the different fabrication processes, and the device layout considerations and suggestions.

1. Centering the Hall bar devices

The photoresist accumulation at the corners of the substrate, stemming from the spin-coating of a small and square substrate, leads to a non-uniform photoresist thickness, which becomes significant at the edge of the substrate (to be further discussed later in the text). To overcome this issue and improve device yield, we chose to avoid the sample perimeter by centering the patterned Hall bar devices relative to the substrate area. As can be seen in Figure 1e, out of the lateral 5x5 mm$^2$ sample area, we centered the Hall bar devices on a ~3x3 mm$^2$ area. Another advantage of centering the devices is to avoid non-uniform growth that sometimes occurs at the perimeters, and shadowing from MBE substrate holder clamps.

2. Geometry considerations

The choice of a four-point probe, where the current and voltage electrodes are separated, ideally eliminates lead and contact resistances. In practice, the contact size and placement can severely affect the accuracy of the four-point probe measurement.$^{11}$ However, for a Hall bar device, these geometrical errors can be minimized by choosing the recommended aspect ratios, as follows.$^{11}$

- $t \leq W/3$
- $L \geq 4W$
\[ p \approx t \]

Where the parameters used here are defined in Figure 1a.

3. **Wide overlap between the bar and the metal contact**

Another approach to increase device yield is to minimize errors stemming from misalignment and handling. To address this issue, we increased the overlap area between the patterned film and the metal pads as much as possible. As can be seen in Figure 1d, we increased the length of the patterned film underneath the metal pads while keeping the “active” leg length (p) similar to its width (t) to maintain the aspect ratio.

4. **Patterned test areas**

Since the Hall bars are at the center of the film, the remainder of the film perimeter can be patterned into testing areas for additional measurements, e.g., AFM, electrical measurements, and more. During the development of the Hall bar fabrication process, we used these areas (visible in Figure 1d on the sample perimeter) to measure the film’s conductivity prior to the metal contact deposition. Monitoring the state of the film during the fabrication process via resistance measurements allowed not only the prevention of additional redundant work in case of a fabrication failure, but also pinpointing the problematic stage.

**B. Major Challenges and Solutions**

The main pitfalls we encountered during the process development were:

1. Chemical instability of the thin functional oxide during different steps of the fabrication process.

2. Hardened photoresist residue on the patterned device during dry etching.
3. Excess accumulation of photoresist at the samples’ edge after spin-coating due to the square shape of the oxide substrate. This accumulation prevents optimal contact between the mask and the film (exposure gap).

These challenges will be described in the following subsections, along with our proposed solutions.

1. Ultrathin protective layer – the key enabler

Early during the process development we found that SVO and Ru-LSMO thin films exhibited chemical instability with the standard materials used for photolithography. While it might not be noticeable for thick enough films, our 10-40 nm TMO films were strongly affected by it. An example of such damage is presented in Figure 2a, where much of the SVO part of the Hall bar is gone. To overcome this challenge, we deposited an oxide ultrathin protective layer. The protective layer, ~2-3 nm thick, was grown in situ inside the growth chamber to prevent the formation of a near-surface region. We successfully tested ~3 nm of amorphous TiO$_x$ and AlO$_x$ for SVO films, and 2 nm a-STO for Ru-LSMO films. We note that in the absence of a protective layer, there was no consistency between the failure modes of the photolithography. In one example, the process failed during liftoff with hot NMP, and in another example, it failed during photoresist stripping (post-etching) using acetone.

While the photolithography damage to the patterned SVO thin film can be visible optically (Figure 2a), the absence of visible damage is insufficient on its own. Additional characterizations are required, and one such example is the use of AFM. Figure 1b and c present a bare (uncapped) 5% Ru-LSMO film, before and after Hall bar patterning. While the film exhibits a smooth surface with visible atomic steps prior to the patterning, wide
(~1 μm) pits are observed in the film after patterning. These pits degrade the quality of the film and undermine the reliability of the transport measurements. These pits might originate from a chemical reaction between the TMO film and the materials used in that preliminary fabrication process, such as the photoresist stripper (hot NMP). On the other hand, when a protective layer was employed, there was no sign of film degradation. See supplementary material for additional AFM analysis and an x-ray photoelectron spectroscopy (XPS) study of the surface (Figures S1 and S2, respectively). It is important to note that the presence of a protective layer is not a guarantee for a successful photolithography process; however, we find it impossible to succeed without it.
FIG. 2. (a) Optical image of patterned Hall bar device with an unoptimized photolithography process. The Hall bar was fabricated from 27 nm SVO films with a 3 nm TiOₓ protective layer. (b,c) Surface topography of 42 nm bare (uncapped) 5% Ru-LSMO film before (b) and after (c) patterning. We point to the severe damage during fabrication when the 5% Ru-LSMO film does not have a protective layer. (d,e) Representative examples for SVO etched geometries with hardened photoresist after unsuccessful photoresist stripping. (d) When performing the etching process in one cycle, and (e) when performing the etching in ten short cycles, where each cycle includes oxygen plasma. The feature in (d) is an old version of the Hall bar.
2. **Photoresist hardening during RIE**

We employ RIE for the etching of the film using SF₆ and N₂. RIE can cause hardening of the photoresist (sometimes referred to as crusting).¹⁰,¹¹ The hardening forms a crust on the outer regions of the photoresist, top and side surfaces, to a point where it becomes insoluble in the stripping process. Examples of hardened photoresist are shown in Figure 2d and e, presenting patterned geometries after resist stripping.

To mitigate the hardening of the photoresist, we try to remove the crusted photoresist parts during the RIE process, before they become too hardened to be stripped. To that end, the etching time was split into ten short cycles of 1.5 minutes, and a short 12 seconds of oxygen plasma (descum) was added after each cycle. This descum step removes the hardened photoresist without removing too much of the bulk photoresist. This solution significantly reduced the residues of hardened photoresist to a point where they are negligible (mostly on the edges of the patterned shape), and in some instances, it solved this issue altogether. See Figure S3 for an example of a resist-free optimized outcome.

3. **Photoresist accumulation at the substrate edges**

Perovskite oxide substrates are almost exclusively available in square shapes of 10x10 and 5x5 mm², where the small and square shape makes them inconvenient for lithography processes. The spin-coating of these samples results in a considerable accumulation of photoresist on the corners. We employ a relatively thick photoresist layer (~4.5 µm) to withstand the etching (RIE) process. The thickness intensifies the photoresist accumulation problem, thus preventing suitable placement of the mask over the sample, resulting in a large exposure gap and degradation of the image transfer, which...
is seen as ill-defined pattern edges. To resolve this issue, a preliminary step was added to the photolithography process of the etching. This step is an adjustment to the commonly used edge-bead removal process. After the photoresist is deposited, we use a designated mask (Figure 1c, cyan) to expose only the edge of the sample. Accordingly, in this step, only the photoresist at the edge of the sample is developed and removed. The use of a designated mask allows long exposure and development times, enabling the removal of the excess thick photoresist at the edges. However, this extra exposure step can be made unnecessary by using ‘mask-less’ exposure methods such as laser lithography.

While the primary step of removing the photoresist accumulation on the corners significantly improves the exposure gap issue, the photoresist absence in these areas prevents the use of photolithography there. For that and other reasons specified in the previous section, we positioned the Hall bars in the center of the film (on a 3×3 mm² region out of a 5×5 mm² substrate).

C. Device Performance and Functionality

Sheet resistance (Rs) and Hall measurements were measured for an SVO film before (Van der Pauw geometry) and after the fabrication process (Hall bar geometry) to rule out the possibility of degradation of the film quality during patterning. Figure 3a illustrates the similarity of the results for unpatterned and patterned SVO. A small decrease in the patterned Hall bar sheet resistance is visible, which can be explained by the difference between averaging the resistance from the entire film and a small area in the center of the film (unpatterned and patterned, respectively). We calculate the sheet resistance as $Rs = R_{\text{meas}} \cdot \frac{W}{D}$, where $R_{\text{meas}}$ is the measured resistance, and W and D are defined in Figure 1a. A comparison of sheet resistance between two adjacent Hall
bars confirms the uniformity of the Hall bar fabrication (Figure S4, supplementary material).

The SVO Hall measurements presented in the inset of Figure 3a indicate that the carrier density was not affected by the fabrication process. We note that although the Hall bar configuration is expected to minimize the voltage misalignment, there was a small offset voltage, which was eliminated by subtracting the measured voltage for a given positive and negative magnetic field:

$$V_H = \frac{1}{2} [V(+) - V(-)].$$

**FIG. 3.** (a) Temperature-dependent sheet resistance of a 27 nm SVO film with 3 nm TiOx protective layer before and after patterning as a function of temperature. The inset
presents the Hall measurements of the same sample before and after patterning at 300K. The transport measurements indicate that the fabrication process did not degrade the SVO film. (b) Sheet resistance as a function of temperature in a patterned 10 nm 10% Ru-LSMO with 2 nm SIO and 2 nm a-STO protective layers. The resistance was measured along two in-plane perpendicular directions, namely xx and yy, as defined in the schematic illustration in the inset of the figure.

Figure 3b presents the transport anisotropy of 10% Ru-LSMO capped with thin SIO and a-STO. The anisotropy is the largest above 250K, which is attributed to the crystallographic anisotropy of the film, as discussed elsewhere. Here, the ultrathin SIO layer of 2 nm is unlikely to have a role in the observed electrical anisotropy. In the temperature range above 250K, we point to resistance variation of less than 3% between two Hall bars oriented along the same direction (either x or y), whereas the anisotropy between different orientations (x and y) is between 11-15%. Figure 3b exhibits the expected metal to insulator transition at about 280K, around which paramagnetic to ferromagnetic phase transition is observed for a 10 nm 10% Ru-LSMO film grown on LSAT substrate, which is familiar as the colossal magnetoresistance peak in doped manganite films. Moreover, the resemblance of the device performances to previous work confirms that there was no significant degradation to the film quality during fabrication, and that the variation between different devices on the same substrate is negligible.

While the isotropic SVO enabled an easy comparison between patterned and unpatterned films, the anisotropic electrical behavior of 10% Ru-LSMO thin film cannot be accurately measured in Van der Pauw geometry on the unpatterned film, as the anisotropic resistance measurement requires the flow of current in a specific desired
direction. Although various methods such as extended Van der Pauw\textsuperscript{44,45} and Montgomery\textsuperscript{46,47} have been developed for resistivity measurements in anisotropic blanket films, their precision is inferior compared to Hall bar measurements, and they are more prone to errors for Hall measurements.\textsuperscript{48} Hall bar geometry is therefore attractive and effective for the transport measurements of anisotropic materials.

**D. Further development**

We note that while a protective layer provides sufficient protection to the functional oxide film during the photolithography process, the patterning (Figure 1d) process exposes the perimeters of the underlying film. Ideally, this etching process should be the last step of the fabrication process, thus keeping the oxide protected under the protective layer throughout all photolithography stages. Although it requires certain adjustments, it is possible to reverse the fabrication process flow, i.e., first perform the liftoff and then the oxide patterning. In this scenario, the oxide film below the metal contacts will not be etched, which should not affect the Hall bar performance. The development of such a fabrication process can be beneficial for materials that are even too sensitive for the current suggested fabrication process, such as EuO, SrNbO\textsubscript{3}\textsuperscript{49} and others.

In some processes, oxygen plasma (ashing / descum) is used as part of or the main method for stripping the photoresist after lithography. Plasma ashing can be used as a preliminary step to the liquid stripping, and also as a final step when the photoresist is difficult to remove. Thus, it can make the stripping process easier and shorter, and therefore less aggressive for the patterned film. In addition, increasing the revolutions per minute (RPM) during the photoresist spin-coating should improve the photoresist uniformity, thus reducing its accumulation at the substrate perimeter.
It is also suggested that the number of “legs” on the hall bar be increased. While we used four terminals – the minimum needed for Hall effect measurements, there might be benefits to adding another pair of contacts for redundancy. For example, if one contact is damaged, there is still the possibility of having two longitudinal and two transverse measurements. However, such an upgrade would require a reduction of the contact size or the number of devices.

**IV. SUMMARY AND CONCLUSIONS**

We developed a photolithography fabrication process of Hall bar devices for thin functional oxide films based on standard clean-room processes and materials. Here, we present and discuss the fabrication process and device layout. The major hurdle in the development was found to be the TMO chemical instability with the photolithography chemicals, and the main solution for this difficulty was found to be the *in-situ* deposition of an ultrathin oxide protective layer following the oxide growth. We note that the TMO chemical instability is expected to become more significant as the thickness of the film or the lateral dimensions of the patterned geometry become smaller. In addition, a designated step to develop and remove the photoresist accumulation at the substrate corners was added to reduce the exposure gap. In order to minimize photoresist hardening during RIE, we divided the etching time into short cycles separated by oxygen plasma. We evaluated the Hall bar performance by comparing sheet resistances before and after patterning, and between different devices on the same substrate. The suggested fabrication process can be broadly applied to functional oxides and other material systems, enabling patterning of films without degradation, using scalable standard clean-room techniques.
SUPPLEMENTAL MATERIAL

The supplementary materials include a detailed description of the optimized Hall bar fabrication process, including materials selection and process parameters. A surface study of the patterned and unpatterned SVO and Ru-LSMO films, including AFM scans and an XPS analysis. Additional optical microscopy images for the results of the RIE process and sheet resistance variation of patterned SVO Hall bars are also provided.

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AUTHOR DECLARATIONS

Conflicts of Interest

The authors have no conflicts to disclose.
DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

REFERENCES


