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1 **TITLE:**

2 Growth and electrostatic/chemical properties of hybrid metal/LaAlO₃/SrTiO₃ heterostructures

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17 **KEYWORDS**

18 2D electron gas, oxide interfaces, lao, sto, magnetotransport, X-ray photoelectron
19 spectroscopy, pulsed laser deposition, sputtering

21 **SHORT ABSTRACT:**

22 We fabricate metal/LAO/STO heterostructures using a combination of pulsed laser deposition
23 and *in situ* magnetron sputtering. Through magnetotransport and *in situ* X-ray photoelectron
24 spectroscopy experiments we investigate the interplay between electrostatic and chemical
25 phenomena of the quasi two-dimensional electron gas formed in this system.

27 **LONG ABSTRACT:**

28 The quasi 2D electron system (q2DES) that forms at the interface between LaAlO₃ (LAO) and
29 SrTiO₃ (STO) has attracted much attention from the oxide electronics community. One of its
30 hallmark features is the existence of a critical LAO thickness of 4 unit-cells (uc) for interfacial
31 conductivity to emerge. Although electrostatic mechanisms have been proposed in the past to
32 describe the existence of this critical thickness, the importance of chemical defects has been
33 recently accentuated. Here, we describe the growth of metal/LAO/STO heterostructures in an
34 ultra-high vacuum (UHV) cluster system combining pulsed laser deposition (to grow the LAO),
35 magnetron sputtering (to grow the metal) and X-ray photoelectron spectroscopy (XPS). We
36 study step by step the formation and evolution of the q2DES and the chemical interactions that
37 occur between the metal and the LAO/STO. Additionally, magnetotransport experiments
38 elucidate on the transport and electronic properties of the q2DES. This systematic work not
39 only demonstrates a way to study the electrostatic and chemical interplay between the q2DES
40 and its environment, but also unlocks the possibility to couple multifunctional capping layers
41 with the rich physics observed in two-dimensional electron systems, allowing the fabrication of
42 new types of devices.

44 **INTRODUCTION:**

45 Quasi 2D electron systems (q2DES) have been extensively used as a playground to study a
46 multitude of low-dimensional and quantum phenomena. Starting from the seminal paper on
47 the LaAlO₃/SrTiO₃ system (LAO/STO)¹, a burst of different systems that host new interfacial
48 electronic phases have been created. Combining different materials led to the discovery of
49 q2DESs with additional properties, such as electric-field tunable spin polarization², extremely
50 high electron mobilities³ or ferroelectricity-coupled phenomena⁴. Although an immense body
51 of work has been dedicated to unravel the creation and manipulation of these systems, several
52 experiments and techniques have shown contradictory results, even in rather similar
53 conditions. Additionally, the balance between electrostatic and chemical interactions was
54 found to be essential to correctly understand the physics at play⁵⁻⁷.

55
56 In this article, we thoroughly describe the growth of different metal/LAO/STO heterostructures,
57 using a combination of pulsed laser deposition (PLD) and *in situ* magnetron sputtering. To
58 understand the effect of different surface conditions in the buried q2DES at the LAO/STO
59 interface, an electronic and chemical study was then performed, using transport and electron
60 spectroscopy experiments. This study shows a systematic way of probing both electronic and
61 chemical interactions, emphasizing the importance of crosschecking different approaches to
62 fully understand the many features of these types of systems.

63 64 **PROTOCOL:**

65 Note: All of the 5 steps described in this protocol can be paused and restarted at any time, with
66 the single condition that the sample is kept under high vacuum from step 2.4 to 4.

67

68 1. STO(001) Substrate Termination

69 1.1. Fill an ultrasonic cleaner with water and heat it to 60 °C. Ultrasound an out of the box
70 mix-terminated single-side polished (001)-oriented STO single-crystal substrate (5×5
71 mm² in lateral size, 0.5 mm in thickness) in acetone for 3 min. Repeat the
72 ultrasonication procedure in isopropanol, and then in deionized water. Dry substrates
73 using a nitrogen blow gun.

74 1.2. Fill a large beaker with running deionized water. Wearing appropriate protection, fill a
75 second beaker (typically made of Polytetrafluoroethylene) with a buffered hydrofluoric
76 (HF) solution (HF:NH₄F = 12.5:87.5%). Submerge the substrates in HF for exactly 30
77 seconds and immediately move them into the deionized running water to stop any
78 subsequent chemical reactions. Dry substrates with a nitrogen blow gun. More details
79 can be found within Kawasaki's recipe⁸.

80 **Caution:** The HF solution used is highly corrosive and poisonous. Manipulation and disposal
81 of used HF solutions should always be carried out in appropriate working environments.
82 Symptoms of poisoning after contact with a body part might start to be visible up to one
83 day after exposure and may not cause any pain in the first few hours. An alternative acid-
84 free termination recipe might also be used⁹.

85 1.3. Bake the substrates in an oven for 3 hours at 1000 °C (20 °C/min ramp rate, for both
86 warming and cooling) in an oxygen rich environment (about 1 atm.). Ramping is not
87 included in the 3 hours procedure.

88 1.4. Repeat step 1.1. to remove subsequent surface contaminations promoted during

89 annealing.

90

91 2. Growth of LAO Ultra-Thin Films

92 2.1. Prepare the single-crystal LAO target (1-inch diameter).

93 2.1.1. Mechanically polish the LAO target gently using sandpaper and isopropanol
94 solution as a lubricant. Dry using a nitrogen blow gun.

95 2.1.2. Insert the target in the load-lock chamber. Let it degas in vacuum, while
96 continuously pumping the chamber, for up to a few hours. Transfer the target in
97 the PLD chamber and wait until it reaches a base pressure in the 10^{-9} mbar range.

98 **Note:** In the absence of a load-lock chamber and *in vacuo* transfer system, the typical waiting
99 time and base pressure can be severely affected.

100 2.1.3. Inspect the laser energy using an excimer laser sensor. Use the same energy (or
101 marginally higher) as the energy used during the growth. We use a pulsed KrF
102 excimer laser of wavelength $\lambda=248$ nm, with a characteristic pulse duration of 25
103 ns and operated at a minimum of 21 kV (for improved pulse-to-pulse
104 reproducibility).

105 **Note:** Absolute values of the laser energy might vary depending on the geometry of the setup.
106 However, for LAO target ablation, one should aim for a laser fluence of typically 1 J/cm^2
107 (fluence = energy/spot area).

108 2.1.4. Rotate the LAO target at about 10 rpm.

109 **Note:** It is advised to adapt the target rotation speed to the spot size and laser repetition rate
110 to avoid two consecutive overlapping shots, potentially leading to some local overheating or
111 melting of the target, and subsequent off-stoichiometry.

112 2.1.5. Shoot at 3 or 4 Hz for 20000 pulses at an oxygen partial pressure of 2×10^{-4} mbar.
113 The relatively long ablation of the LAO single-target we used was found to have a
114 determinant role in LAO/STO sample-to-sample reproducibility.

115 2.2. Perform an AFM scan of the STO substrate surface to verify morphology and cleanness.

116 2.3. Glue the substrate to a sample holder using silver paste. Heat it up to about $100 \text{ }^\circ\text{C}$ for
117 10 min so that the solvent evaporates and the paste solidifies (for optimum thermal
118 conduction). Let the sample holder cool down.

119 2.4. Insert the sample holder in the vacuum chamber. At this step, the first XPS
120 measurement can be performed to analyze the oxygen, carbon and titanium peaks
121 (refer to step 4 for more details).

122 2.5. Insert the sample in the PLD chamber.

123 2.5.1. Raise the temperature of the sample holder to $730 \text{ }^\circ\text{C}$ (at $25 \text{ }^\circ\text{C/min}$) in an
124 oxygen partial pressure of 2×10^{-4} mbar.

125 2.5.2. Using reflective high energy electron diffraction (RHEED) technique, align the
126 electron beam at grazing angle with the substrate so that the diffraction spots are
127 observed on the phosphor screen. Monitor in real-time the intensity of each spot
128 by using a CCD camera. *We used a source voltage of 30 kV and current of $40 \text{ } \mu\text{A}$.

129 2.5.3. *Place the target 63 mm away from the substrate.

130 2.5.4. *Calibrate the laser energy. Use a slit (6x16 mm) and an external attenuator right
131 after the laser exit to modulate the shape and energy of the beam.

132 2.5.5. Set the laser frequency to 1 Hz.

133 2.5.6. Ablate the target with the laser at constant energy (corresponding to about 1
134 J/cm²) and constant oxygen partial pressure of 2x10⁻⁴ mbar. Observe the RHEED
135 oscillations. Close the laser shutter at the peak of one of the oscillation depending
136 on the desired thickness. For the purpose of our experiment, we grew 1 and 2 uc
137 for transport and spectroscopic experiments, respectively.

138 2.6. After LAO growth, shutdown the RHEED gun. Proceed to the post-annealing step.

139 2.6.1. Increase the oxygen partial pressure in the chamber to 1x10⁻¹ mbar. Decrease
140 the temperature of the sample holder to 500 °C, and introduce a static oxygen
141 partial pressure of about 300 mbar. Post-anneal the sample in these conditions for
142 30 min.

143 2.7. Cool down the sample at 25 °C/min while keeping it in the same oxygen partial
144 pressure until it reaches room temperature.

145 2.8. The second XPS measurement can be performed at this stage to investigate possible
146 valence changes in the titanium peak or the relative La/Al concentration.

147 2.9. To ensure that the LAO surface is kept pristine, transfer the sample *in vacuo* to the
148 sputtering chamber. Performing these experiments *ex situ* will cause the accumulation
149 of carbon and water on the surface which ultimately leads to altered results.

150

151 3. Magnetron Sputtering of Metallic Overlayers

152 3.1. *Use a pure Ar atmosphere of 4.5x10⁻⁴ mbar.

153 3.2. *Position the substrate about 7 cm away from the target.

154 3.3. *Ramp the current up to about 100 mA (36 W) so that a stable plasma is created.

155 3.4. With the shutter closed, pre-sputter the metallic target for a few minutes to remove
156 any oxidized layer that may have formed at its surface.

157 3.5. At room temperature, deposit the desired metal at the lowest possible rate, while
158 keeping the plasma stable and uniform. For the purpose of our experiments we grew
159 films of 2.5 and 0.3 nm (at a typical rate of 2 Å/s) for transport and spectroscopic
160 experiments, respectively. For transport experiments, a subsequent capping layer of
161 about 3 nm of Al (whose surface passivates, forming an AlO_x protective layer upon
162 exposure to air) is grown to prevent oxidation of the underlying metallic layer.

163 3.6. Ramp the current down to zero, close the Ar source and pump the chamber.

164 3.7. A last XPS experiment might be performed at this stage to inspect a valence change at
165 the Ti 2p level as well as a possible oxidation at the metal/LAO interface.

166

167 4. X-ray Photoelectron Spectroscopy

168 4.1. Place the sample with the surface normal aligned parallel to the electron analyzer axis.

169 4.2. Turn on the X-ray gun and approach it as close as possible to the sample using a linear
170 shift (avoid mechanical contact between the end of the gun and the sample holder to
171 prevent damage).

172 4.2.1. We used an Mg K α source with an excitation energy of 1253.6 eV. *Set the
173 filament to achieve an emission current of 20 mA at an anode voltage of 15 kV.
174 Regarding the analyzer electron-optics, choose an entrance slit of 2 mm of
175 diameter and an exit slit with rectangular shape of 5x11 mm. If your analyzer has
176 different specifications, choose the slits in a way to avoid too high intensity in the

177 electron counting unit (refer to the respective manual to know the specific limits).
178 4.3. In ultra-high vacuum conditions (10^{-10} mbar range), collect the survey spectra (between
179 0 and 1200 eV binding energy) and locate the position of the relevant peaks. For
180 improved statistics, measure each peak several times and average the spectra
181 collected.
182 4.3.1. *Select a step of 0.05 eV, a dwell time of 0.5 s, a pass energy between 30 and 60
183 eV and an adequate lens mode to achieve the smallest spot size possible.
184 4.4. Analyze the spectra using an adequate XPS processing software.
185 4.4.1. In order to identify the electrons from a given transition, define an energy range
186 that comprises the peak to analyze.
187 4.4.2. Create an appropriate background curve (normally a Shirley background) and
188 subtract it from the original data.
189 4.4.3. Using bibliographic references¹⁰, locate the possible peaks that compose the
190 measured peak. Pay special attention to tabulated distances and relative
191 intensities for different peaks.

192
193 5. Magnetotransport Experiments
194 5.1. Wire-bond the metal/LAO/STO sample with Al or Au wires using an ultrasonic wedge-
195 bonding machine to contact the buried interface. Use an 8-wire geometry (4 in van der
196 Pauw –channel 1– and 4 in Hall geometry –channel 2–).
197 5.2. Check if contacts are good by measuring the resistance. To ensure that the sample is
198 uniform, verify that the resistance measured in different directions is the same.
199 5.3. Mount the sample in a transport setup.
200 5.3.1. Measure the resistance (channel 1) down to low temperature.
201 5.3.2. At low temperature, measure sequentially the magnetoresistance (channel 1)
202 and Hall effect (channel 2) by sweeping an external and perpendicular magnetic
203 field, sourcing a current of typically 10-100 μ A for metal/LAO/STO samples.
204 5.3.3. Repeat 5.2.2 for several different temperatures.
205

206 REPRESENTATIVE RESULTS:

207 The full experimental system used for growth and characterization is shown in figure 1. Having
208 different setups connected in UHV through a distribution chamber is highly recommended to
209 ensure that the surface of the sample after each growth process is kept pristine. The PLD
210 chamber (figure 3), magnetron sputtering (figure 4) and XPS chamber (figure 5) are also
211 described in detail. Additional information regarding the optical path in the PLD setup is
212 displayed in figure 3c (adapted from Ref.¹¹). The conditions discussed in the protocol for each
213 technique may vary depending on the exact geometry of each chamber, type of targets used or
214 the type of equipment. For this reason, we have marked throughout the protocol (*) all the
215 steps that highly rely on the features aforementioned and that ultimately will require some
216 degree of optimization by the user.

217
218 We confirmed atomically flat and clean STO surfaces, before starting the growth, through
219 atomic force microscope (AFM), as seen in figure 2a. A “step and terrace” like structure with
220 single unit cell step height is evidenced due to the miscut angle in respect to the (001) plane

221 orientation. All samples were grown on substrates with a step size of about 250 nm (for a
222 miscut angle between 0.01 and 0.02°). Both LAO and metal films reproduce the surface
223 morphology of the layers beneath, as seen in figure 2b, respectively.

224
225 During PLD growth, the plume generated through the process of ablating species from the
226 target towards the substrate is shown in figure 3d. Note that the intensity (and color) of the
227 plume depends on the oxygen pressure and fluence used. Altering the fluence was previously
228 shown to modify the La/Al cationic ratio, which might ultimately lead to a modulation of the
229 interfacial contacting properties^{12,13}. RHEED monitoring is used to ensure layer-by-layer growth.
230 Typical RHEED data is shown in figure 3e for a 2 uc growth of LAO on STO.

231
232 A first XPS analysis of the substrate allows us to confirm the virtual absence of additional
233 features in the oxygen peak, usually present due to attached water and hydrogen molecules, as
234 well as a very small amount of adsorbed carbon. The heating process used during the PLD
235 growth normally removes/reduces these features. A second analysis reveals the appearance of
236 La and Al peaks and an additional intensity decrease of Ti and Sr peaks, due to the attenuation
237 introduced by the LAO film. One last XPS analysis after metal deposition shows clear
238 attenuation of all peaks coming from the LAO/STO. As we discuss ahead, analysis of the peaks
239 associated with the deposited metal gives us information regarding its oxidation state. All
240 survey spectra addressed are displayed in figure 5c.

241
242 Transport experiments are performed at low temperature using an 8-wire geometry (4-wires
243 for transverse measurements and 4-wire for Hall measurements), as shown in figure 6a.
244 Measurements show strikingly different behavior depending on the metallic capping layer
245 chosen. LAO(2 uc)/STO samples capped with noble metals such as Au, Pt or Pd showed a linear
246 Hall trace with a change in resistance of a few tens of mΩ over 9 T (figure 6b). However, similar
247 samples capped with reactive metals such as Ti, Ta, Co, Ni₈₀Fe₂₀ and Nb (2.5 nm) showed
248 signatures of a 2DES, namely S-shaped Hall traces (figure 6c). We conclude that from a
249 transport point of view, LAO/STO samples below the 4 uc critical thickness (that in regular
250 conditions are insulating) form an interfacial 2DES if a reactive metal is added on top. Capping
251 with noble metals leads to an insulating interface, where only the metal layer is detected (see
252 figure 6b and inset of figure 6c). Indeed, these results are consistent with theoretical prediction
253 performed on similar heterostructures¹⁴. Simultaneously fitting the extracted Hall and
254 magnetoresistance for the 2DES enables us to extract values for carrier densities and mobilities.
255 The results are summarized in table 1 for three LAO(2 uc)/STO samples capped with Au, Co or
256 Ta. We observe that the carrier densities scale with the work function of the metal capping.
257 Electrostatically, the Fermi level of lower work function metals will stay above the Fermi level of
258 the STO, which ultimately promotes electron transfer towards it. Lower metal work function
259 (higher Fermi level) leads therefore to stronger electron transfer, which explains the trend seen
260 for these 3 samples.

261
262 Although, an electrostatic approach seems to fully describe this system, chemical reactions
263 must be considered¹⁵. For this purpose, XPS allows us to investigate possible oxidation
264 processes occurring at the metal/perovskite interface, as well as valence changes occurring at

265 the interfacial Ti atoms in the STO (figure 7a). The results are summarized in table 2. The
266 likeliness of the metal to oxidize, given by the enthalpy of oxide formation $\Delta_f H^0$, scales with the
267 Ti^{3+}/Ti^{4+} intensity ratio, translating in an increased number of electrons at the Ti interfacial
268 atoms for highly reactive metallic capping layers, as seen in figure 7b and 7d. As expected, the
269 quantity of metal oxide formed at the metal/LAO interface scales similarly, although we suspect
270 oxidation would continue for Ta capped sample if the metal layer was thicker (figure 7c).
271 Additionally, from angle-dependent XPS experiments (inset of figure 7b) we observe that the
272 thickness of the 2DEG formed extends beyond the XPS maximum probing depth. This result
273 contradicts the transport experiments, since more carriers translate in a larger interfacial
274 confining electric field that should shorten the 2DES thickness¹⁶. The large spatial extension
275 might be described through oxygen vacancies created by the highly reactive metal capping.
276 Since the LAO layer is only 1 μ c thick, if the concentration of vacancies formed is high enough
277 then they might reach the 2DES region, expanding it while maintaining a high carrier
278 concentration.

279 These results clearly show the importance of backing transport experiments with electron
280 spectroscopy and vice versa. For more details on the analysis refer to Ref.⁷.

281

282 **FIGURE AND TABLE LEGENDS:**

283 **Figure 1 – Complete setup including the pulsed laser deposition chamber, magnetron**
284 **sputtering and X-ray photoelectron spectroscopy.** The three setups are connected through a
285 cluster that allows for sample transfer without breaking vacuum (10^{-9} mbar range).

286

287 **Figure 2 – Atomic force microscopy of (a)** a STO substrate used for the growth of **(b)** a
288 Co(2nm)/LAO(2 μ c)/STO sample.

289

290 **Figure 3 – Pulsed laser deposition system. (a)** Exterior of the PLD chamber. Although not
291 visible, the phosphor screen and camera used to monitor the RHEED diffracted electrons are
292 behind the chamber, aligned with the RHEED gun. **(b)** Interior of the PLD chamber. An infrared
293 laser is used to locally heat the back-side of the sample holder. X and y positioning is controlled
294 through knobs on the outside of the chamber. The target carousel allows us to have 5 different
295 targets inside the chamber at the same time. **(c)** Detailed sketch of the optical apparatus. The
296 beam exits the laser and is immediately reduced in size through a slit. The variable attenuator
297 allows the control of the beam energy without varying the source laser parameters. Two
298 converging lenses are then used to focus the beam on the target. Modified from Ref.¹¹. **(d)**
299 Characteristic plume-shaped plasma formed after ablating the LAO target with a single beam
300 pulse, at 2×10^{-4} mbar of oxygen. **(e)** Typical RHEED oscillations and diffraction spots. For
301 consistency, monitoring is always performed on the (0-1) diffraction spot, located inside the
302 yellow dotted box.

303

304 **Figure 4 – Magnetron sputtering system. (a)** Exterior of the sputtering chamber. **(b)** Interior of
305 the sputtering chamber. Ar atoms are accelerated towards the metal target, located inside the
306 shown cylinder and mounted on a dc-magnetron source, hence generating a plasma.

307

308 **Figure 5 – X-ray photoelectron spectroscopy system. (a)** Exterior of the XPS chamber. Emitted

309 electrons enter the transfer lens of the analyzer. There, they are retarded/accelerated to match
310 the analyzer pass energy before entering the analyzer itself and being finally collected by the
311 electron detector. A preamplified signal is then sent to the optical receiver before reaching the
312 amplifier and computer. **(b)** Interior the XPS chamber. The X-ray gun can be retracted to allow
313 positioning of the sample holder. **(c)** Typical survey scan performed on a bare STO substrate, an
314 LAO(1 uc)/STO and a Co/LAO(1 uc)/STO. Note the evolution of the peaks. Ti and Sr peaks are
315 gradually attenuated as the top layer thickness increases. La and barely visible Al peaks appear
316 after LAO growth. The addition of an ultra-thin layer (3 Å) of Co rapidly attenuates all the other
317 peaks. An additional zoomed O 1s peak (STO substrate) is displayed on the right.

318
319 **Figure 6 – Transport properties of metal/LAO/STO heterostructures. (a)** Wire bonding of a
320 sample in an 8-wire geometry (4-wire for Hall resistance and 4-wire for longitudinal resistance).
321 This geometry allows the collection of both Hall and magnetoresistance, sequentially sourcing
322 between the two channels, yet in a single measurement run. Hall resistance R_{xy} as a function of
323 applied perpendicular magnetic field $\mu_0 H$ of LAO(2 uc)/STO samples capped with **(b)** noble
324 metals and **(c)** reactive metals. The inset shows a schematic circuit after wire bonding, where
325 R_M and R_{q2DES} represent the longitudinal resistances and $V_{H,M}$ and $V_{H,q2DES}$ the Hall voltages
326 generated in each layer. More information in ref.⁷.

327
328 **Figure 7 – X-ray photoelectron spectroscopy of metal/LAO/STO heterostructures. (a)**
329 Schematic sketch of the measurement performed. Photoelectrons emitted by X-ray excitation
330 carry information on both the LAO/STO and the metal/LAO interface. **(b)** Spectra collected on
331 Ta/LAO/STO samples at the Ti 2p level show an additional (Ti^{3+}) shoulder at lower binding
332 energy, associated with extra electrons hosted at the interfacial Ti atoms. The inset additionally
333 shows the weak angle-dependence of the Ti^{3+} shoulder, revealing that the extension of the
334 q2DES formed at the LAO/STO interface is larger than the maximum electron probing depth. **(c)**
335 The Ta 4f spectra informs on the oxidation level of the metallic capping used. The spectra can
336 be fitted exclusively with different Ta oxide peaks, indicating that ~100% of the metal layer has
337 oxidized on top of the oxide heterostructure. **(d)** Fitting the Ti 2p peak with two components,
338 4+ and 3+, allows us to extract a Ti^{3+}/Ti^{4+} intensity ratio of ~20%. More information in ref.⁷.

339
340 **Table 1 – Relation between metallic capping used, the work function of the metal and the**
341 **carrier density found in the q2DES at the LAO/STO interface.** Smaller work functions translate
342 in a larger energetic difference between Fermi levels (metal and STO), which leads to stronger
343 charge transfer, after band alignment, and ultimately an electro gas with higher carrier density.

344
345 **Table 2 - Relation between metallic capping used, the enthalpy of oxide formation $\Delta_f H^0$, the**
346 **intensity ratio between Ti^{4+} and Ti^{3+} peaks (extracted from XPS) and the relative**
347 **concentration of metal oxide in the metallic capping.** Higher (negative) enthalpies of formation
348 mean that the oxide has a higher tendency to oxidize, which leads to a higher Ti^{3+} shoulder in
349 the Ti 2p XPS spectra (more electrons transferred towards the interface) and larger
350 concentration of metal oxide formed.

351
352 **DISCUSSION:**

353 During substrate termination, one should be extremely careful with the submerging time in HF
354 solution. We observed under- and over-etched surfaces by varying just 5s with regard to the
355 original recipe. Additionally, we observed a dependence between substrate step size and
356 submerging time. For smaller step sizes (less than 100 nm) submerging 30s might lead to over-
357 etching, even though afterwards the annealing procedure might be sufficient to properly
358 reconstruct the surface. Due to the risks of using HF based acids, we also advise the
359 optimization of an acid-free termination technique such as the one described in Ref.⁹ which
360 should lead to similar results.

361
362 Concerning the growth of LAO, we advise the use of single crystal targets to avoid the possible
363 preferential ablation of specific species, which might occur for example in ceramic/sintered
364 targets. In our case, samples grown with a ceramic target resulted in insulating samples, most
365 likely due to off stoichiometry of the grown films¹³. The 20000 pulses pre-ablation step we
366 describe might seem overly long, however we observed that the transport properties
367 deteriorate extremely quickly by overlooking this step. Pre-ablating with less than 10000 pulses
368 repeatedly showed insulating LAO/STO interfaces. As expected from PLD growth we
369 additionally advise not to grow on substrates larger than 10x10 mm in lateral size. 4-point
370 electrical probing on different regions of these 10x10 samples showed slight inconsistencies
371 likely due to off-stoichiometry issues at the samples corners. We also note that all samples
372 were grown with the center of the plume vertically aligned with the substrate. At low oxygen
373 pressure (lower than 10^{-2} mbar) and due to the low target-substrate distance, ablated species
374 travel in a ballistic regime, which might also justify why the fluence utilized affects so drastically
375 the properties of the interfacial conductivity¹².

376 Finally, since the laser energy measurement is done outside the chamber and the laser
377 entrance window gets coated over time, which yield to a loss of transmission, we guide
378 ourselves by targeting a constant growth rate value instead. The optimized growth rate for LAO
379 was found to be approximately 25 pulses/unit cell for our specific PLD growth process.

380
381 The RHEED oscillations measured during growth are extremely sensitive to the fine positioning
382 of the substrate. The exact same growth process might result in substantial differences in terms
383 of RHEED oscillations intensities. We advise using the same positioning parameters and probing
384 the same diffraction spots for every growth. For consistency purposes, we have grown all of our
385 samples monitoring only the (0-1) or (01) diffraction spots, off of the specular reflection. TEM
386 imaging showed good uniformity and confirmed, together with standard X-ray diffraction, the
387 correct corresponding number of LAO unit cells.

388
389 Concerning the sputtering deposition, we emphasize that different metals have different
390 wetting behaviors on top of oxides substrates¹⁵. Consider increasing the thickness accordingly
391 to achieve full coverage. Films under a few nm in thickness might result in non-percolated films.
392 Perform SEM characterization after deposition to verify good uniformity.

393 Using slower deposition rates and less energetic incoming species is also recommended, to
394 finely control the film's thickness and avoid possible penetration of sputtered species into the
395 sample. To do this, one might increase the target-substrate distance and/or reduce the plasma
396 excitation current.

397

398 Regarding the XPS measurements, since the measurements are performed *in situ*, there is no
399 electrical connection between the metallic overlayer (or the 2DEG) and the sample holder. This
400 means that charging effects will be severe due to the insulating nature of the STO substrate.
401 We therefore advise not to conclude on the position of the collected peaks, since they might be
402 shifted several eV. It is also known that metals tend to screen electrons quite efficiently so that
403 a 1 nm metallic capping might already impede probing other buried layers. An additional charge
404 compensation by a flood gun might help to avoid peak shifting and deformation. In our case,
405 peak deformation was negligible since we used a non-monochromated X-ray source providing
406 enough secondary electrons.

407 Angle-dependent studies can also provide valuable information on the depth profile. If the
408 electron takeoff angle is 90° (surface normal parallel with the electron analyzer axis) then the
409 maximum volume is probed. When the takeoff angle decreases (tilted sample) electrons from
410 the same depth will travel larger distances, so that the total volume measured is reduced. One
411 is then able to, for example, assess the thickness of a q2DEG through a valence state depth-
412 dependent analysis, as was previously shown for LAO/STO heterostructures¹⁷.

413

414 We also bring the attention to additional peaks seen in the survey spectra. If the sample size is
415 smaller than the detected area of the electron analyzer, traces of silver paste on the borders of
416 the sample and of the species deposited on the substrate holder, such as La or Al, are collected.
417 Note that these species will, to some extent, suffer different charging effects, which will lead
418 for example to the appearance of double peak features. This can be easily fixed by reducing the
419 entrance slit size for electron collection and increase the dwell time (for higher electron count).

420

421 Overall, although the instructions provided in this paper serve as a guide to grow LAO ultra-thin
422 films, they demonstrate a generic way of growing most ABO₃ perovskites with PLD. Even though
423 each material will require specific steps for optimized desired structural, electrical, or magnetic
424 properties, one should be especially attentive to some essential features: type and composition
425 of the target¹⁸, oxygen partial pressures during growth and annealing^{19,20}, substrate
426 temperature, ablation frequency and laser fluence^{12,21} and type of substrates (and previous
427 surface treatments).

428 Through a combination of transport and spectroscopy experiments, we are also able to draw a
429 more accurate and complete picture of a complex system where capturing the interplay
430 between electrostatic and chemical phenomena is essential to understand the intrinsic versus
431 extrinsic doping mechanisms. We reiterate that due to their strongly correlated character,
432 these complex oxide systems are extremely sensitive to small stoichiometry and electronic
433 changes such that their comprehensive study requires different complementary *in situ* and *ex*
434 *situ* techniques.

435

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444

445 **DISCLOSURES:**

446 The authors have nothing to disclose.

447

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