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**ABSTRACT**
Substrate surfaces terminated with a specific surface reconstruction are a prerequisite for the controlled epitaxial growth of most materials. Focusing on SrTiO$_3$ (001) substrates, it has recently been shown that *in situ* substrate termination by thermal annealing has decisive advantages over standard termination methods. We report here that *in situ* substrate termination is a generally applicable method not restricted to SrTiO$_3$ crystals. We specifically demonstrate the successful surface preparation of doped SrTiO$_3$ (001), LaAlO$_3$ (001), NdGaO$_3$ (001), DyScO$_3$ (110), TbScO$_3$ (110), MgO (001), and Al$_2$O$_3$ (0001) surfaces.

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**I. INTRODUCTION**
Epitaxial heterostructures of complex oxides feature a particularly rich spectrum of functionalities when grown in geometries that exploit size quantization, interface effects, and strain. Quantum matter functionalities rely critically on a highly perfect crystal structure to achieve the required properties such as perfect periodicity and large phase-breaking lengths. This, in turn, requires that the layer interfaces, and ultimately the interface to the substrate, be of excellent quality to achieve the desired performance of a device or to enable the detection of evasive new effects in structures designed for fundamental research. It is therefore imperative to study and continuously improve substrate preparation procedures and their integration into the heterostructure fabrication process.

The key importance of substrate preparation in oxide epitaxy was recognized early on in Ref. 12, and procedures have been developed to prepare surfaces with a uniform chemical composition of the top layer. This implies the formation of terraces separated by unit-cell-high steps, as the atomic arrangement in a crystal repeats every unit cell. It also implies a laterally uniform, and ideally single domain, atomic arrangement of the topmost layer, which is usually reconstructed and does not necessarily have the stoichiometry or lateral symmetry of the bulk. To make a process scalable for industrial production, factors such as throughput, simplicity, and robustness of the process as well as safety concerns such as the avoidance of toxic or hazardous substances are also important.

Traditional oxide substrate preparation schemes frequently involve aggressive chemicals and multiple *ex situ* process steps before the substrate is introduced into the growth system. These processes must be found and optimized individually for each substrate material and surface, which poses challenges in terms of complexity, reproducibility, and purity. *In situ* thermal annealing for substrate preparation has become the method of choice for compound semiconductor epitaxy, as it was found to be cleaner, faster, safer, and easier to control. Oxide substrate preparation using only thermal annealing was studied early on in a surface-science context, with more recent dedicated surveys aimed at obtaining good templates for epitaxial growth. We have found that annealing the pre-cleaned substrate in an oxygen partial pressure in the single-digit Pa range at high temperatures produces surfaces that are indistinguishable from surfaces prepared by the traditional procedure or even produce better results and may be used *in situ* for the subsequent deposition of heterostructures.

Here, we investigate the applicability of this method to a broader range of common substrate materials for oxide epitaxy. The oxide background pressure is chosen to match the typical values used for subsequent epitaxy so that no adaptations in pressure are necessary between substrate preparation and epitaxy. For the selected temperatures and oxygen pressures, we have found no evidence of oxygen deficiency in the as-prepared substrates. Therefore,
possible desorption of metal atoms at high temperatures does not change the bulk stoichiometry of simple oxides such as MgO and Al$_2$O$_3$. The substrate preparation process merely amounts to a redistribution of the surface atoms to form a minimum energy configuration, accompanied possibly by oxygen adsorption/desorption and bulk annealing. However, for binary or multinary oxides, the most volatile constituent will desorb preferentially, and this may result in a surface reconstruction that is poor in this component, in addition to the morphological rearrangement. These two processes are independent, in principle, and often a highly ordered terrace structure is formed at significantly lower temperatures than what is required to form a uniform surface reconstruction.\(^1\)

II. EXPERIMENTAL

Experiments were performed in two pulsed laser deposition (PLD) chambers designed for the epitaxy of complex oxides. Each chamber is equipped with a substrate heating system based on a 1.1 kW CO$_2$ laser operating at a wavelength of 9.27 $\mu$m and irradiating a circular area of 10 mm or 15 mm in diameter with a top-hat-shaped beam profile. For each chamber, a semitransparent Bragg mirror directing the beam into the recipient allows line-of-sight access of a coaxial long-wavelength pyrometer for measuring and controlling the temperature. The emissivity parameter of the pyrometer is set to 1.0. The stated temperatures therefore represent safe lower bounds for the actual temperatures at the back of the substrates. For reference, Al$_2$O$_3$ sent safe lower bounds for the actual temperatures at the back of the substrates. Laser pyrometer temperatures may therefore be corrected to a calibrated scale by multiplying the $\ell$K values by factors in square brackets. The temperature calibration/correction applies in the wavelength range $\circ\,\mu$m and emissivity varies substantially for different substrate materials at 2 $\mu$m and below, as we conclude from finding the required laser power for the same pyrometer temperature to vary by up to a factor of 5 for different substrate materials at 1300 $^\circ$C. This is visible to the naked eye during the experiment, appearing as strongly different brightnesses (emitted powers) at similar temperatures (colors) of the substrate.

The heating laser may be turned off abruptly at any power, allowing us to quench the surface rapidly from any temperature. We use this procedure to produce snapshots of a surface at any given state during a process, assuming that the cooling rate is high enough to stop surface diffusion effectively for subsequent room-temperature ex situ characterization. Sample sizes ranged from $5 \times 5 \times 0.3$ mm$^3$ to $10 \times 10 \times 1.0$ mm$^3$ in size. Their back surfaces were finished with a coarsely ground surface to optimize the absorption of the incoming laser radiation.

The front surfaces of the as-delivered substrates were first wiped with propanol using lint-free wipers.\(^2\) They were then degreased for 10 min in acetone and 10 min in propanol, followed by a 10 min bath in purified water (except for MgO) and subjected to ultrasonic agitation in glass beakers. The samples were blown dry using purified nitrogen and were then loaded into the vacuum system on metallic sample holders made of Haynes alloy 230.

For the annealing procedure, a background pressure of 7.5 Pa (0.075 hPa), unless otherwise stated, of purified molecular oxygen was set by the widely used combination of a mass flow controller and a turbomolecular pump behind an adjustable gate valve. Temperature profiles are presented together with the results for the different substrate materials. Laser heater optimizations were made during the time period in which the experiments were performed, reaching a control accuracy of better than 1 K rms at temperatures above 500 $^\circ$C toward the end.

Reflection high-energy electron diffraction (RHEED) images were acquired using a differentially pumped electron source operated at 30 keV and a digital image-acquisition system. The laser heater was ramped down linearly or turned off abruptly at various stages during the process, and the oxygen pressure was maintained until the substrates had cooled. Due to the low mass of the substrates and high radiative losses at high temperatures, initial cooling rates were of the order of several hundred K/s. The chamber was pumped down, and the samples were removed and immediately investigated by atomic force microscopy (AFM) under ambient conditions.\(^2\) The surface morphology was determined, and height profiles were taken to determine the step height between terraces. Line profiles were averaged laterally over three image pixels (px) for images, and 6 px for 1024 $\times$ 1024 px$^2$ images, corresponding to the line thicknesses drawn in the figures. Phase images were acquired simultaneously to investigate possible surface reconstruction domain patterns.

III. RESULTS

A detailed investigation of the thermal preparation of undoped SrTiO$_3$ (001) will be reported elsewhere. Here, we focus on how the method, developed and characterized with this material, can be applied to other substrate materials. The results are collected in Secs. III A–III G, material by material, discussing both the common features and the differences between the different substrates.
The investigated substrate materials are used as substrates for subsequent epitaxy. Therefore, not all materials are investigated in the greatest possible detail. However, common trends and the good reproducibility of the results demonstrate the general applicability of the method.

**A. Doped SrTiO$_3$ (001)**

We do not observe great differences in the thermal preparation between doped and undoped SrTiO$_3$ (001). In particular, we have not seen any direct evidence of enrichment, clustering, or...
preferential migration of dopant atoms during thermal annealing. We investigated the thermal preparation of commercial substrates measuring $10 \times 10 \times 1$ mm$^3$ and doped with 0.5% of Nb. The results are summarized in Fig. 1. Figure 1(a) shows a substrate after the initial degassing and water rinsing steps. The surface already features atomically flat terraces, indicating an exceptionally good mechanical polish. After thermal annealing at 1400 °C [1460 °C], a slightly irregular terrace system forms, the average terrace width of which is limited by the sample miscut [Fig. 1(b)]. Profiles [Fig. 1(e)] taken at higher magnification [Fig. 1(c)] confirm step heights of 0.4 nm, in agreement with the lattice parameter $a_{\text{STO}} = 0.3905$ nm. The phase contrast image in Fig. 1(d) shows some noise but is otherwise featureless. In particular, no contrast is observed from the step edges, unlike our measurements of undoped SrTiO$_3$ (001) substrates. It is unclear whether this is due to an insufficient signal-to-noise ratio or an effect of doping. Higher magnification images also show some height variations on the terraces [Fig. 1(f)], but it is not apparent whether these features are real or caused by measurement noise. To save time, the temperature profile during annealing was chosen to increase initially to 700 °C at a high rate of 3 K/s, then to 1100 °C at 2 K/s, and finally to only 1 K/s as we approached the final annealing temperature [Fig. 1(b)]. After the 200 s anneal, the temperature was lowered again to 1100 °C at 2 K/s and then to room temperature at 3 K/s. As the doped samples are thicker than the reference (1 mm compared to 0.3 mm in Ref. 21), we needed an annealing temperature of 1400 °C [1460 °C], compared to 1300 °C [1356 °C] to achieve similar surface morphologies.

The RHEED pattern at the end of the annealing plateau at 1400 °C [1460 °C] is indistinguishable from the patterns observed at the same point of the annealing sequence on undoped substrates. We observe the best results for a pattern with blurred Kikuchi lines, weak but very narrow streaks vertically connecting multiple reflections perpendicular to the substrate. This spot pattern, usually interpreted as a roughened surface, is accompanied by an emergent weak 2× reconstruction pattern.

B. LaAlO$_3$ (001)

Below its phase transition temperature at 540 °C, LaAlO$_3$ shows twinning, leading to clearly visible domains with different inclinations even at room temperature in its polished state [Fig. 2(a)]. Commercial $5 \times 5 \times 1$ mm$^3$ substrates reveal a terrace structure before thermal treatment. The measured step heights in Fig. 2(a) are 0.2 nm, in agreement with the expected mixed termination in this state. After performing the temperature ramp shown in Fig. 2(b) at a constant oxygen pressure of 0.0075 hPa, we obtained the surface morphology shown in Figs. 2(b)–2(f) in addition to uniform terrace trains with uniform terrace widths and large curvature radii. The step heights [Fig. 2(e)] are just below 0.4 nm, which matches the LaAlO$_3$ lattice constant of 0.38 nm. The RHEED pattern recorded at 1500 °C [1565 °C], directly before the end of the annealing plateau [Fig. 2(g)], shows sharp reflections on the Laue circle, in agreement with the large, flat terraces observed in the AFM scans. The pattern at room temperature (not shown) looks very similar, except that the peaks are doubled along the streaks normal to the surface due to twinning. This doubling disappears at 530 °C [553 °C] and reappears upon cooling to room temperature, in agreement with the phase-transition temperature. No in-plane superstructure reflections are observed at high temperatures or at room temperature. The terrace edges produce a sharp, positive contrast in the phase image [Fig. 2(d)].

Figure 2(f) shows small protrusions at the terrace edges, together with hints of patches of slightly different heights on the terraces themselves. As LaAlO$_3$ and SrTiO$_3$ have very similar melting points, the annealing parameters for SrTiO$_3$ were examined first also for LaAlO$_3$. The results are shown in Fig. 3.

This figure compares two samples annealed at the same oxygen pressure of 0.075 hPa. Figures 3(a) and 3(b) show the AFM results for annealing at 1300 °C [1356 °C], followed by a rapid quench, whereas Figs. 3(c) and 3(d) show an otherwise nominally identical sample annealed at and quenched from 1500 °C [1565 °C]. Whereas the surface morphology of the 1500 °C [1565 °C] sample consists of flat terraces with straight edges, the edges of the 1300 °C [1565 °C] sample are wavy, and the terrace plateaus phase-separate into patches of two different heights. The height difference of the patches amounts to just over 0.1 nm. This appears to indicate that an insufficient amount of the volatile species (lanthanum oxide) has desorbed at the lower temperature, which does not yet allow uniform coverage by the lanthanum-poor surface reconstruction. At the higher temperature, enough lanthanum oxide has desorbed to form a uniform termination.

To test the stability of the surface formed in this way, in another experiment, a nominally identical substrate was annealed with the same temperature profile until the end of the plateau at 1500 °C [1565 °C], but then gradually cooled to 1000 °C [1043 °C] within 15 min. Then, the sample was rapidly quenched to room temperature by turning off the laser beam. The results are shown in Fig. 4. During the entire run, the oxygen pressure was 0.075 hPa. In contrast to the directly quenched sample, the lower sides of the surface steps are now decorated by stripes, which are quite similar in appearance to the elevated terrace areas in Figs. 3(a) and 3(b). As there is no volatile lanthanum or aluminum in the background atmosphere of the chamber under these conditions, the seeming (re)appearance of the material forming these layers cannot be due to adsorption from the gas phase. One possibility could be a surface reconstruction containing a mixture of lanthanum and aluminum atoms at high temperatures, which phase-separates into two distinct lanthanum-rich and aluminum-rich reconstructions at lower temperatures. Another possibility could be the exchange of materials with the bulk, leading to variations in the relative surface concentrations of the two elements as a function of temperature and possibly oxygen pressure. Such a mechanism is supported by TEM studies$^{27}$ that report on precipitates in bulk LaAlO$_3$ that disappear at higher temperatures and reappear when the specimen is cooled.

The hypothesis that such a bulk–surface exchange mechanism may also depend on the oxygen pressure is supported by the experiment shown in Fig. 5. This sample was processed similarly to the one shown in Fig. 4, except that the gradual cooling extended down to 850 °C [887 °C] and the oxygen pressure was kept at 0.0075 hPa. Although the temperature at which quenching began is even lower than for the sample shown in Fig. 4, no surface phase separation occurs. Even the AFM phase image [Fig. 5(b)] is featureless, similar to the Nb-doped SrTiO$_3$ shown in Fig. 1(d). The line profiles [Fig. 5(c)] confirm the absence of additional sub-steps on the terraces: Only step heights corresponding to the full bulk unit cell parameter are present. The RHEED pattern taken during
Annealing demonstrates the good reproducibility of the process compared to the one shown in Fig. 2(g). The reflections are nearly circular, with a high contrast between reflections and background, indicating that the highly ordered surface morphology is already present during annealing.

The bulk domain structure present during the initial polishing of the surface leads to areas with different and gradually varying slopes of the atomic planes and therefore different terrace widths. A sample subjected to an intermediate temperature anneal is shown in Fig. 6. Such a sample allows us to determine the maximum...
terrace width that can be achieved by a given annealing temperature profile. In this case, full monolayer-high islands remain on the terraces wherever they exceed a width of approximately 0.9 μm. The AFM scan shown in Fig. 6(a) was acquired in the central trough between the two ridges in the overview scan of Fig. 6(b). Figure 6(d) was acquired near the top-left corner of Fig. 6(b) and rotated in keeping with the convention established in this paper of step trains descending from left to right. Higher temperatures are
required to produce uniform step trains without islands on the terraces for smaller miscut. This also serves to estimate the migration lengths at given annealing temperatures. For typical terrace widths below 1 μm, islands on the terraces vanish and straight terrace edges develop before the uniform reconstruction on the terrace is achieved.

As an example of the RHEED pattern evolution during thermal annealing, we discuss the LaAlO$_3$ sequence shown in Fig. 7.
The main differences between the patterns taken before and after the highest temperature was reached in the anneal are an increase in contrast, a sharpening of the streaks, and a reduction in diffraction spot sizes. Due to the phase transition in this particular case, the room temperature patterns show split peaks. It is therefore more appropriate to compare the patterns at 900 °C [939 °C] before and 840 °C [876 °C] after annealing, the latter being our substrate temperature for PLD homoepitaxy. Comparing these two panels (c) and (g) in Fig. 7, one can see a transfer of intensity from the streaks to the reflections, leading to larger red (overexposed) areas there, and
a clearer definition of the Kikuchi lines. This agrees well with the observed flattening and structural improvement of the surface as observed by the AFM measurements.

Figure 7(f), taken at the highest temperature during annealing, shows characteristic features that we have found to be common to all binary oxides we studied. The streaks become faint, but very narrow close to the reflections. At the same time, the Kikuchi lines blur, and the reflections on the Laue circle elongate normal to the surface. In Fig. 7, this becomes particularly clear when comparing the (10) reflection (third from the left) in panels (e) and (g) with panel (f).
On reconstructing surfaces with fractional-order reflections in RHEED such as SrTiO$_3$, the final surface reconstruction just begins to faintly appear under these conditions.

We find that the optimized surface morphology with large terraces, straight terrace edges, and a uniform phase image in AFM is only achieved after annealing at a temperature such that these three characteristic features begin to appear. Substantially higher temperatures usually deteriorate the surface. These changes may therefore be used in addition to tight temperature control and precise timing to ensure and improve the reproducibility of the process.

The elongation of the reflections and blurring of the Kikuchi lines indicate an increased disorder. At the same time, the narrowing of the streaks is typical for an increasing long-range order. It is therefore likely that the disorder is due to a high mobility and/or large oscillation amplitude of the atoms at or near the surface. A high mobile adatom concentration similar to what is observed on III–V surfaces, however, is less likely, as we have never observed islands due to condensation of mobile adatoms even when very rapidly quenching the surface from this high-temperature annealing state [see Fig. 2(h)].

C. NdGaO$_3$ (001)

Commercial $5 \times 5 \times 0.5$ mm$^3$ substrates were used to explore the in situ thermal preparation of NdGaO$_3$. The surface orientation was (001). (110)-oriented substrates $5 \times 5 \times 1.0$ mm$^3$ in size were also investigated [shown only in Fig. 8(a)] and found to produce qualitatively similar results. The optimized preparation procedure is illustrated in Fig. 8. The substrates supplied by the vendor [Fig. 8(a)] feature little roughness, but no discernible terrace structure. After annealing to 1000 °C [1043 °C] and rapidly quenching as shown in Fig. 8(h), terrace structures formed. The terraces are very uniform over large distances [Fig. 8(b)] but are wavy on a medium-range scale. The measured step heights match the bulk lattice constant of NdGaO$_3$ [Fig. 8(e)]. As with many other substrate materials, the phase image [Fig. 8(d)] displays a sharply localized, positive signal at the step edges, but otherwise shows no clearly distinguishable structure. A close-up of the terraces in topography mode [Fig. 8(f)] reveals a contrast variation on the terraces without a clear line or patch structure, most probably resulting from reactions with ambient moisture before and during the ex situ AFM measurements. RHEED shows a 2× superstructure at all temperatures up to and including the annealing temperature of 1000 °C [1043 °C] [Fig. 8(g)].

The annealing temperature for NdGaO$_3$ substrates is significantly lower than the ones of the other materials discussed above. This is in agreement with the significantly lower melting point of NdGaO$_3$, indicating that the entire temperature scale for surface and epitaxy processes has shifted correspondingly. The structures shown in Figs. 9(a) and 9(b) for 1100 °C [1147 °C] and in Figs. 9(c) and (d) for 1050 °C [1095 °C] for higher annealing temperatures are observed on the surface. The surface breaks up into strongly elongated, at times filamentary, rectangular terraces with flat top surfaces [Fig. 9(b)]. The thin wires decorating some of the steps may present limiting cases of such filaments. The boundaries of these rectangles often align over large distances, suggesting that dislocations form at the edges of these features [Fig. 9(a)]. At lower temperatures, the pattern is not yet as uniform and shows a large variety of terrace sizes and aspect ratios [Fig. 9(e)]. In some areas, the high-temperature structures coexist with the usual terrace pattern, allowing us to observe the morphological transition [Fig. 9(d)] at which the direction of the steps first rotates out of the usual
orientation normal to the surface miscut to align with the axes of the bulk crystal structure. The corners then become increasingly sharp until inverted steps opposite to the miscut direction appear. At this point, the surface has probably lost so much of the volatile component of the compound that the surface phase separates, and crystal structures with different lattice constants form that, in turn, form a heterostructure with dislocations in and near the top layer.

**FIG. 10**. Thermal preparation of a DyScO$_3$ (110) surface at 1400 °C [1460 °C]. (a) AFM topography of the initial substrate surface in the as-received state. (b), (c), and (f) Topography of the final surface at various magnifications. (d) Phase image acquired simultaneously with (c). (e) Height profiles taken along the lines marked in (c). (g) RHEED image at the end of the plateau at 1400 °C [1460 °C]. (h) Temperature profile during the process.
D. DyScO₃ (110)

Commercial DyScO₃ (110)-oriented substrates produced the data discussed in this section. The substrate size was 5 × 5 × 1 mm³. After ex situ precleaning as described in Sec. II, the substrates were heated to 600 °C [626 °C] at a rate of 2 K/s and then to 1400 °C [1460 °C] at 1 K/s [Fig. 10(h)], at which temperature they were annealed for 200 s, until the laser was turned off to quench the surface for ex situ AFM. The O₂ pressure was kept at 0.08 hPa. The as-delivered surfaces already show a terrace structure [Fig. 10(a)] with steps of full unit cell height determined from the AFM image. This specific substrate was subsequently used for the experiment shown in Fig. 11(d). Both figures show the same terrace widths, which confirms the assignment of full unit-cell-high steps in the precleaned state. The presence of such unit-cell-high steps implies that either the vendor’s polishing procedure or the crystal structure itself favors one termination. It also implies that this favored termination is stable in contact with ambient conditions. Small circular bumps in Fig. 10(a) may be due to precipitates similar to the SrO surface precipitates frequently observed on SrTiO₃ surfaces.

Under optimized conditions, the surface morphology shown in Figs. 10(b), 10(c), and 10(f) is obtained. The terrace steps have some short-scale waviness but are straight on the multi-μm scale. The step height equals 0.4 nm [Fig. 10(e)], which matches the full unit cell of the bulk crystal structure. The phase image exhibits a uniform signal, except for the frequently observed, sharply defined positive signal seen at the step edges. Even at high magnification [Fig. 10(f)], the terraces are featureless and smooth, indicating a uniform surface reconstruction. Together with the nicely preserved step structure of the polish in Fig. 10(a), this indicates the good stability of DyScO₃ in air. The RHEED pattern recorded at the end of the annealing plateau at 1400 °C [1460 °C] shows elongated reflections and a relatively high background intensity, indicating more dynamic disorder than what is suggested by the AFM images of the quenched surfaces.

FIG. 11. Surface morphology of DyScO₃ (110) as a function of preparation temperature.
A twofold superstructure is present even at these high temperatures, indicating a reconstructed surface. The reconstruction persists at all temperatures down to room temperature.

The surface preparation process was analyzed as a function of the plateau temperature used for the annealing. Different substrates were heated to different annealing temperatures, remained there for 200 s, and then rapidly quenched for AFM as shown for 1400 °C in Fig. 10(h). The results are collected in Fig. 11. These results show in a prototypical manner the behavior we qualitatively see for all substrate materials. A terrace system forms already at low temperatures [Fig. 11(a)], but the terrace edges meander strongly, and isolated islands remain in regions where the underlying terrace is broader. Under these conditions, not all atoms on the terraces are mobile enough to reach the terrace edges. With increasing temperature [Figs. 11(b)], the islands have disappeared, and the terrace edges begin to straighten. This continues with increasing temperature [Figs. 11(c) and 11(d)], leading to increasingly straight terrace edges, until finally the desired state with the smallest curvature of the terrace edges and uniform terrace widths is achieved [Fig. 11(e)]. At yet higher temperatures [Fig. 11(f)], the terrace widths begin to fluctuate, introducing an instability that leads to step bunching.

E. TbScO$_3$ (110)

We used commercially available $24 5 \times 5 \times 1 \text{ mm}^3$ TbScO$_3$ (110) orthorhombic substrates. The results of the thermal substrate preparation are displayed in Fig. 12. Using a dwell temperature of 1300 °C [1356 °C] and an oxygen pressure of 0.08 hPa, we obtained a terrace structure very similar to that of the other substrates. Cooling rates of 1 K/s, 4 K/s, and abrupt cooling were investigated, but no difference in surface morphology between the final surfaces was observed. Using AFM operated in tapping mode at a scan rate of 0.8 Hz similar to the other scans shown here, the surface morphology of TbScO$_3$ substrates was investigated ex situ before and after the cleaning and annealing procedure. Figure 12(a) depicts a $10 \times 10 \mu\text{m}^2$ AFM image. The image shows the typical surface morphology of the as-received TbScO$_3$ (110) substrates. The substrate surface reveals no step or terrace features. AFM images [Figs. 12(b), 12(c), and 12(d)] of TbScO$_3$ substrates annealed at 1300 °C [1356 °C] for 200 s show clean surfaces consisting of flat, equidistant terraces with an average step height of about 0.4 nm, corresponding to the unit cell height of TbScO$_3$ (110).$^{23}$ This step height, together with the clean terrace morphology, indicates a homogeneously reconstructed surface most probably rich in TbO. The step edges show a characteristic mid-range waviness but are straight on the long scale. A comparison with Fig. 11(b) indicates that further optimization utilizing higher annealing temperatures may be possible.

F. MgO (001)

Previous studies$^{21}$ indicated that thermal annealing under ambient oxygen pressure is feasible for the surface preparation of MgO, thereby suggesting that in situ thermal annealing should also work for such a simple oxide. Detailed studies of chemical ex situ cleaning, in selected cases followed by in situ thermal annealing, have demonstrated that annealing is capable of removing surface contaminants such as carbonates and hydroxides.$^{22}$ We used commercially available MgO (001) single-crystal substrates $^{23}$ (5 × 5 × 1 mm$^3$). The ex situ substrate preparation steps after the preoxygen treatment described in Sec. II were avoided to minimize exposure to water. The substrates were immediately blow-dried with purified nitrogen and loaded into the vacuum chamber to keep them as dry as possible. Figure 13 provides an overview of the annealing experiments and their results. Thermal annealing took place at an oxygen pressure of 0.09 hPa according to the temperature profile shown in Fig. 13(b). To save time, the substrate was initially heated at a rate of 2 K/s, followed by an approach to the final temperature at a rate of 1 K/s. After the 200 s anneal, slow cooling at 1 K/s, fast cooling at 4 K/s [shown in Fig. 13(h)], and abrupt cooling by turning off the laser were all tried during the optimization process. However, no significant difference was found, and therefore, all subsequent runs were performed using a cooling rate of 2 K/s. Annealing temperatures between 700 °C [730 °C] and 1700 °C [1773 °C] resulted in regularly stepped surfaces such as the ones shown in Fig. 13.

Using AFM in tapping mode at a scan rate of 0.8 Hz, the surface morphology of the MgO substrates was investigated ex situ before and after the cleaning and annealing procedure. Figure 13(a) depicts a $10 \times 10 \mu\text{m}^2$ field of view, showing the typical surface morphology of the as-received MgO (001) substrates. The substrate surface exhibits no step-terrace features. Instead, a number of particles of different sizes and line defects, probably polishing scratches, are visible. The overview after the thermal preparation [Fig. 13(b)] shows a surface with flat terraces separated by steps with a slight curvature.

The magnified area displayed in Figs. 13(c) and 13(d) reveals a rougher morphology on the terraces compared to the other substrates. The greater roughness is most probably caused by post-annealing reactions with ambient moisture$^{24}$ occurring when the substrates were removed from the deposition chamber for the AFM measurements in air. Nevertheless, the surface steps can be clearly resolved, and the profiles extracted from Fig. 13(c) and plotted in Fig. 13(e) show a step height matching the expected 0.21 nm half lattice parameter of MgO. The phase image in Fig. 13(d) shows a fine dark (negative) contrast at the step edges in the upper half but is otherwise quite noisy with strong intensity fluctuations on the terraces. Given the strong reactivity of MgO with moisture, it is impossible to determine the original surface quality of the in situ prepared state. The RHEED image at the end of the annealing interval in Fig. 13(g) shows a high contrast and thin Kikuchi lines, but also transmission reflections, indicating a rough surface. Once the substrate has cooled; however, these reflections disappear, and only 2D reflections, narrow streaks, and Kikuchi lines remain.

Morphology changes arising from variations of the annealing temperature are shown in Fig. 14. Very similar to the other substrates, terraces with meandering step edges and occasional remaining islands on larger terrace areas form if a lower annealing temperature of 900 °C [939 °C] is used [Fig. 14(a)]. Terrace edges tend to align with the in-plane crystallographic axes [Fig. 14(b)] if the miscut is oriented in intermediate directions. In the investigated temperature range up to 1700 °C [1773 °C], we have not observed a tendency toward step bunching.

G. Al$_2$O$_3$ (0001)

In addition to the aforementioned materials, we also investigated sapphire because it is one of the few oxide substrates available
in high crystalline quality and large wafer diameters. All substrates were (0001)-oriented and $5 \times 5 \times 1$ mm$^3$ in size. The substrates were prepared as stated in Sec. II. We found the initial wipe and final water rinse to be unnecessary. An overview of the results is shown in Fig. 15. In several runs, a temperature profile similar to the one shown in Fig. 15(b) was used in which the temperature was first ramped to $1100^\circ$C $[1147^\circ$C] (chamber 2) or $970^\circ$C $[1130^\circ$C] (chamber 1) at a rate of up to 4 K/s, then ramped to the dwell.
FIG. 13. Thermal preparation of an MgO (001) surface at 1700 °C [1773 °C]. (a) Initial substrate surface in the as-delivered state. [(b), (c), and (f)] Topography of the final surface at various magnifications. (d) Phase image acquired simultaneously with (c). (e) Height profiles along the lines marked in (c). (g) RHEED at 1700 °C [1773 °C]. (h) Temperature profile during the process.

A temperature at 1 K/s. After 200 s dwell time, the temperature was ramped to 1100 °C [1147 °C] (chamber 2) or 970 °C [1150 °C] (chamber 1) and then to room temperature at 2 K/s until heat dissipation was too low to follow the setpoint. These experiments were carried out at a constant O₂ pressure of 0.005 hPa. Control experiments performed with a constant O₂ pressure of 0.075 hPa produced the same results. The heating curve in chamber 1 to 1293 °C [1533 °C] dwell temperature is shown in Fig. 15(h), and the
The corresponding topographic images at different lateral resolutions in Figs. 15(b), 15(c), and 15(f) show uniform terraces separated by steps of equal height. Al$_2$O$_3$ has a hexagonal crystal structure with a c-axis lattice parameter of $c = 1.2993$ nm at room temperature. In this direction, normal to the substrate surface in this case, it consists of six oxygen planes with alternating incomplete filling of Al. Six steps in the black height profile in Fig. 15(e) add up to about 1.37 nm, identifying the steps as single such steps with a height of $c/6$. The phase image in Fig. 15(d) shows a uniform signal on the terraces, consistent with a uniform surface reconstruction. The step edges show a weak, but spatially well-defined positive signal.

Similar to our study of DyScO$_3$, we performed a systematic study of the thermal preparation process as a function of dwell temperature. All other parameters in the process remained unchanged. The results are shown in Figs. 16–18. Again, the left panel in each row shows the topology of the surface, with height profiles recorded along the blue and black lines shown in the diagram on the right in the same color. The topmost row [Figs. 16(a) and 16(b)] was measured on a surface prepared by ex situ oven annealing for 5 h at 1050 °C. This is the highest temperature achievable by our ambient-pressure, molecular oxygen flow tube furnace. This measurement serves to make the connection to the oven annealing substrate preparation we used previously. Terrace patches have formed but are not yet connected into contiguous stripes. There are numerous holes and islands, and steps have not aligned in a direction perpendicular to the miscut.

The in situ annealing at 1300 °C [1356 °C] [Figs. 16(c) and 16(d)] produces a terrace structure, but with holes, islands, and strongly meandering edges. The terraces differ in height by single steps ($c/6 = 0.22$ nm). However, patches with smaller step heights are visible on the terraces, most probably due to the presence of hydroxyl adsorbates from the exposure of the surface to atmospheric moisture before being loaded into the system. At 1400 °C [1460 °C] [Figs. 16(e) and 16(f)], these patches on the terraces still exist, preferentially covering protruding triangles at the terrace edges. Finally, at 1450 °C [1512 °C] [Figs. 16(g) and 16(h)], the patches vanish and the terraces show a uniform height throughout. However, islands of full monolayer height persist, and the terrace edges still meander significantly. The islands and terrace edges have become rounded, and the triangular protrusions have disappeared.

Further heating to 1293 °C [1533 °C] (this sample was prepared in chamber 1) produces terraces without islands and a fairly uniform width as shown in Figs. 17(a) and 17(b). This represents the optimal conditions for uniform terraces separated by single ($c/6$) steps. Although the temperature window for this surface morphology is rather narrow ($\pm 10$ °C), this morphology is reproducibly obtained, as demonstrated by the result of a different sample prepared with nominally identical conditions shown in Figs. 17(c) and 17(d). Another substrate prepared in chamber 2 at 1470 °C [1533 °C] confirms the temperature calibration between the two chambers based on the melting point. The very similar terrace structure, shown in Figs. 17(e) and 17(f), demonstrates the reproducibility of the process within the rather narrow temperature window of 20–30 K between Figs. 16(g) and 16(h) and Figs. 17(e) and 17(f). Again, terraces with uniform height and fairly uniform width are obtained, although over larger distances, step edges touch occasionally. Sapphire requires little laser power to maintain this temperature: For [1533 °C], only 89 W and 95 W were needed in chambers 1 and 2, respectively.

The step-bunching tendency rapidly increases with higher annealing temperatures. As shown in Figs. 17(g) and 17(h), the surface locally separates at 1480 °C [1544 °C] into alternating wavy and straight steps until the amplitude of the wavy steps becomes large enough to touch the neighboring straight steps to form double steps with a height of $c/3$ (0.43 nm).

This process is mostly completed at 1500 °C [1565 °C], shown in Figs. 18(a) and 18(b). When descending a train of steps, e.g., the black profile in Fig. 18(b), one predominantly finds double steps on the surface. However, this structure is not uniform over large distances because all $c/6$ steps are equivalent, and the double-step bunching instability starts at several lateral positions independently. Different patches of double steps are therefore separated by single or triple steps, or by twinning or merging step edges laterally, representing antiphase boundaries between domains of the surface morphology.

At higher temperatures, the step bunches increase in height, exposing larger and larger terraces between the steps. This process can be followed in Figs. 18(c)–18(h). At 1700 °C [1773 °C], regions of regular double-step trains still coexist with bunched areas. At
1800 °C [1877 °C], the bunched regions already dominate the surface, with individual terraces reaching widths of a few micrometers. Close to the melting point at 1950 °C [2034 °C], steps as high as several nanometers are observed, probably forming nanofacets. Between the bunched steps, the terraces may reach widths of 10 μm and lengths of several times the distance, as demonstrated in Fig. 19(c). This makes it feasible to fabricate entire prototype devices from epitaxial films grown on a single, atomically flat terrace.
As shown in Fig. 15(g), the surface reconstructs in the $(\sqrt{3} \times \sqrt{3})R \pm 9^\circ$ reconstruction shown at room temperature in Fig. 19(a). On some samples, we observe this reconstruction already at room temperature. Otherwise, it forms at 1200°C–1250°C and vanishes at temperatures above 1550°C [1617°C], reappearing again during cooling. This reconstruction is rich in Al, possibly providing a good template for subsequent growth because a higher reactivity may be beneficial for heteroepitaxy.
particularly for metal layers. Compared to the hydroxyl-terminated surface [Figs. 16(e) vs 16(g)], it appears to yield better surface mobility with a smoother morphology and therefore possibly sharper interfaces. The similar intensities of fractional and integer-order reflections indicate a surface reconstruction domain size similar to the terrace size or the RHEED transfer width, whichever is smaller. This is remarkable for such a large surface unit cell and demonstrates the very high surface mobility on these
surfaces at the preparation temperature, indicating that an epitaxial template with a very small point defect density has been obtained.

Figure 19(b) shows the image of an entire $5 \times 5$ mm$^2$ substrate taken after the back surface was heated to the melting point. When local melting occurs, the strong contrast of the melting droplets with the ground back surface of the substrate can easily be discerned by using a camera on the front of the substrate because Al$_2$O$_3$ remains transparent in the visible range up to the melting point. Owing to (1)
the temperature gradient between the back and front surfaces, (2) small temperature variations along the surface, and (3) good control accuracy at high temperatures, the melting process can be well controlled, thus avoiding a catastrophic melting of the entire substrate crystal. As discussed in the Introduction, the melting point is reproducibly reached within ±5 K, which is the same reproducibility we find in preparing the surface step systems, and may be used to calibrate the absolute temperature of the crystal back surface. Such a calibration is only possible with simple oxides at sufficiently high oxygen pressures because complex oxides usually decompose well below the melting point.

IV. CONCLUSIONS

The discovery of wet chemical etching and ex situ annealing for substrate preparation marked a breakthrough that has enabled the fabrication of high-quality oxide heterostructures. On the other hand, the usual procedures of the wet chemical methods can require quite complex pre-deposition processing, the use of hydrofluoric acid, and long anneals. These steps may impose limits on the purity and on throughput.

In the thermal annealing procedure presented in this work, we demonstrate the mitigation of these limitations. For example, for SrRuO$_3$ epitaxy, we show a clear improvement of the layer properties when growing on thermally prepared SrTiO$_3$ substrates vs optimized chemically prepared SrTiO$_3$ substrates.

Our results demonstrate that in situ annealing preparation of substrates at sufficiently high temperatures just prior to growth is a generally applicable method that works for all simple and binary perovskite oxides we have tried. This procedure yields a high throughput because the precleaning and thermal preparation each take only about 30 min. It is highly reproducible and allows the selective preparation of different step systems from the same starting surface, as the main parameters are the oxygen background pressure, the temperature, and the duration of the anneal, the latter two being largely interchangeable as with any thermally activated process. In a single heating step, both the preparation of atomically smooth, evenly spaced terraces and the termination of the surface with a single surface reconstruction are achieved in situ with high structural quality and purity. The latter is based on the desorption of the most volatile species of the compound near its decomposition boundary, a process that is irreversible as long as this species is not continuously supplied.

These results suggest working in an environment with a constant supply of the volatile species, similar to the molecular beam epitaxy of III–V compounds. With a constant overpressure of the volatile species in oxide epitaxy, one may study and prepare the equilibrium configurations of surface reconstructions and then proceed to the adsorption-limited growth of oxides. This method has enabled the fabrication of III–V heterostructures of extreme structural quality and purity.

Such processes, which may even extend beyond the growth of oxides to include almost any element of the periodic table, may indeed become possible with thermal laser epitaxy. During thermal laser deposition, both the substrate and the elemental or compound sources are continuously heated by laser beams compatible with low-pressure atmospheres of almost any composition.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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