

Pulsed laser deposition-induced reduction of SrTiO₃ crystals

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Abstract

We report a generic method for fast and efficient reduction of strontium titanate (SrTiO₃, STO) single crystals by pulsed laser deposition (PLD) of thin-films. The reduction was largely independent of the thin-film material deposited on the crystals. It is shown that thermodynamic conditions (450 °C, 10⁻⁷ torr, 10–60 min), which normally reduce STO (0 0 1) substrates to roughly 5 nm into a crystal substrate, can reduce the same crystals throughout their 500 μm thickness when coupled with the PLD. In situ characterization of the STO substrate resistance during thin-film growth is presented. This process opens up the possibility of employing STO substrates as a back-gate in functional oxide devices.

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1. Introduction

Strontium titanate, SrTiO₃ (STO), is a model oxide system that shows a wide range of interesting properties such as ferroelectricity [1], superconductivity [2], resistive switching [3] and thermoelectricity [4]. The key to the observation of many of these properties has been the wide electronic tunability of STO through doping both with oxygen vacancies and with substitutional elements including (but not limited to) La, Nb, Fe, or Co at the Sr and Ti sites. Specifically, oxygen vacancy doping has been established as a procedure to tailor an enhanced electron effective mass in STO [5,6], which

has great implications in controlling the electrical, thermal and optical properties of this system. Additionally, interfaces of STO with other oxides can yield two-dimensional electronic gases that have been thought to have high mobility and thermoelectric power [7,8]. Due to the extreme stability of STO under reducing conditions owing to the multivalency of Ti, introducing oxygen vacancies can be carried out to high concentrations (up to 10%) and has been conventionally achieved by annealing at very low pressures (<10⁻⁵ torr) for extended periods of time [6]. Oxygen-reduction indeed transforms STO from a wide bandgap (3.2 eV) insulator into a good conductor (<100 mΩ cm), and can be employed to induce a wide range of functionality in the material. In addition, the inadvertent reduction of STO must be accounted for when any low pressure processing is done with or on the surface of single crystals of the material.

It has been both speculated and observed (but never proven) in recent years both by other research groups

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[9–13] as well as by these authors [14,15] that the pulsed laser deposition (PLD) process itself induces oxygen vacancies in substrates of (0 0 1)-oriented STO, especially when oxide films are deposited onto their surfaces at or below oxygen partial pressures of 10^{-6} torr. It is interesting to note that introduction of oxygen vacancies has been observed in STO substrates when oxide thin-films were grown by molecular beam epitaxy (MBE), although the thin-film source was primarily metal atoms alone and the stoichiometric oxide thin-film was formed by the oxygen fed by the substrates [16,17]. The oxygen pressure during growth by PLD plays a crucial role in affecting the overall sample transport properties [18], and possible transport contributions from the STO substrate exposed to reducing conditions during PLD could explain why superconductivity [19] as well as magnetism [20] have been observed at low temperatures in thin-films and interfaces grown on these substrates. The creation of oxygen vacancies during PLD seems ostensibly unlikely due to the usually slow diffusion of oxygen in oxide single crystals [21] and short times under which PLD is performed (typically several minutes to an hour). However, we provide direct evidence that the PLD process coupled with thermodynamically oxygen-reducing conditions facilitates efficient reduction of STO (0 0 1) single-crystal substrates, as well as the first direct observation of the STO substrate reduction process through in situ measurement of the substrate resistance during the PLD growth of thin-films. In addition, STO is widely used as a common substrate for epitaxial growth of various oxide systems like bismuth ferrite (BiFeO_3) [22], lead zirconate titanate (PZT) [23] and yttrium barium copper oxide ($\text{YBa}_2\text{Cu}_3\text{O}_7$) [24], among hundreds of other functional oxide systems. Hence, the procedure herein of the fast reduction of STO substrates shall provide a generic route to build epitaxially grown devices made of oxides on a conducting substrate vis à vis back-gated transistors.

2. Experimental

We employed $5 \text{ mm} \times 5 \text{ mm} \times 0.5 \text{ mm}$ STO (0 0 1) single-crystal substrates for our study, supplied by either Crystec GmbH or Surfacenet GmbH, which were screened to be single domain and for narrow rocking curve FWHM values (typically $<0.1^\circ$) to ensure high quality and low defect densities. All substrates were cleaned by ultrasonication for 5 min each in trichloroethylene, acetone, and isopropanol successively. Films of various oxide materials (SrTiO_3 , $\text{Sr}_{0.98}\text{La}_{0.02}\text{TiO}_3$, LaAlO_3) were deposited via PLD to various thicknesses at laser energy densities of 1.75 J cm^{-2} and a substrate-target working distance of 4 cm. Growth conditions for the sample data presented here were 8 Hz repetition rates for 8–10 min, with the exact time determined by the deposition rate of each target. The used PLD targets were dense, polycrystalline and polished before each deposition and ablated evenly during the growth process by rotating the target at a constant rate. Samples were grown at either 450°C or 850°C and at

oxygen partial pressures p_{O_2} of 10^{-7} and 10^{-3} torr. The grown films were fully epitaxially oriented on the STO (0 0 1) substrates and nearly single-crystalline as reported by the authors elsewhere [14,15].

For measurement of the sheet resistance R_S of these samples, four platinum-capped titanium contacts (ohmic with n-type STO) were patterned onto the back-side (or front-side) corners of the reduced crystals so that R_S could be measured in a four-corner Van der Pauw geometry. Sheet resistances were calculated from the I - V curves measured with a Keithley precision current source and nanovoltmeter with applied currents anywhere from 0.1 to 100 mA. Back-side sheet resistance measurements were in general taken both before and after light polishing to remove the thin-film from the front-side, where the film removal effectively eliminated the other parallel resistor contribution to conduction.

For in situ sheet resistance measurements, gold-capped chromium contacts were patterned in a four-corner Van der Pauw geometry on the top-side of an STO (0 0 1) substrate and a large platinum-capped titanium contact (both of which are ohmic with n-type STO) was patterned on the back-side. The contacted STO substrate was inserted into a chip carrier on a heater fixture specially designed for this experiment inside the PLD vacuum chamber. The edges of the substrate and all chip carrier contacts were masked from PLD growth so that the thin-film could only grow on the inner portion of the substrate, while still contacting all top-side metal contacts and positioned directly above the back-side contact across the substrate. Measurements were made using a Keithley 2000 multimeter through an electrical feedthrough connecting the chip carrier under vacuum.

3. Results and discussion

Reduction of strontium titanate is well-known to induce n-type carriers for electrical conduction [6,25,26]. An oxygen vacancy frees two electrons, which dopes the insulator to a semiconductor, and the multivalency of titanium (in moving from the +4 to +3 oxidation state) allows the accommodation of several atomic percent oxygen vacancies and resulting carrier concentrations greater than 10^{22} cm^{-3} [6]. The redox chemistry of such a process in standard Kröger–Vink notation is given by,



It has been observed previously that “short circuit” dislocation paths in (0 0 1)-oriented strontium titanate crystals – which are formed during the Verneuil crystal growth process (also known as the “flame fusion process”) – can act as fast diffusion pathways for oxygen, and that these c -axis “pipelines” can be resistively switched individually [27]. In addition, it is possible that oxygen vacancies cluster to form short-circuit paths of percolating reduced areas, increasing the overall conductivity of the material,

albeit with local inhomogeneity [28]. These studies have typically relied on highly reducing thermodynamic conditions ($<10^{-6}$ torr) to induce oxygen vacancies, which are also used in the growth of oxide thin-films via PLD. In highly reduced thin-films of STO, an oxygen vacancy results in a local tetragonal distortion [5,15,29] due to the greater length of the Ti–Ti bond over that of Ti–O–Ti [30]. No evidence for this has been reported in bulk reduced STO – which cannot typically achieve as high levels of reduction as thin-films – and X-ray diffraction of our reduced crystals (either through vacuum annealing or PLD-induced reduction) indicates that they are structurally identical to those that have not been reduced, and also that there are no second phases present after reduction (Fig. 1).

The characterization of the reduction of the STO single crystals was carried out using sheet resistance measurements from contacts on the back-side and/or front-side (thin-film-side) of the crystals. We report the back-side sheet resistance as a gauge for oxygen reduction because it, rather than the nominal concentration of oxygen vacancies or carriers, is the relevant quantity in deconvoluting transport measurements of films grown on STO or in establishing a functional back-gate. The film–substrate system may be modeled as resistors in parallel (Fig. 2), and as such the determination of film resistivity (or carrier concentration from Hall measurements) at a given film thickness requires that the measured sheet resistance comes from current flowing predominantly in the film. We also present resistance measurements through the cross-plane direction

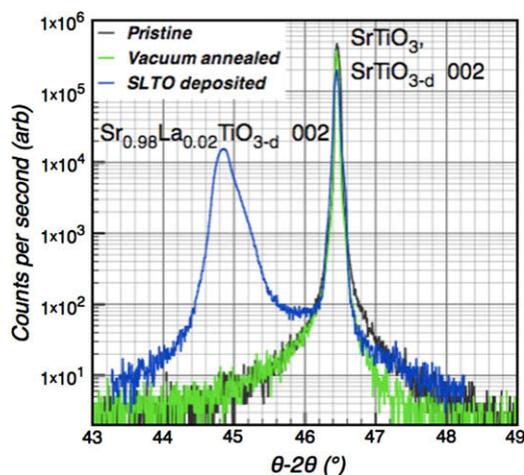


Fig. 1. Out-of-plane (*c*-axis) 002 X-ray diffraction peaks in θ – 2θ for STO (0 0 1) single-crystal substrates in pristine form (black), vacuum annealed for 60 min at 450 °C (green), and fully reduced through PLD deposition of a 1000 nm SLTO thin-film (blue). The SLTO thin-film 002 peak appears below 45° due to a tetragonal distortion induced by a high oxygen vacancy concentration (~ 1 –10%); the STO peak does not change after reduction, indicating that the structure remains cubic and with a similar lattice parameter, and is not reduced to the extent that the film is. No other peaks became apparent upon reduction, nor did in-plane lattice parameter shifts occur in reciprocal space mapping, indicating no new phases or structural change occurred upon removal of small amounts of oxygen from STO single crystals. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

of the entire substrate and in some instances on the front-side of the film–substrate system. Because the distribution of oxygen vacancies in the reduced crystals is likely non-uniform, it is difficult to relate the measured sheet resistances to bulk resistivity.

To account for any possible reduction due merely to the high temperature vacuum environment present during PLD, we annealed STO substrates in the PLD chamber without any thin-film growth as control experiments. When an STO substrate was heated to 450 °C in the PLD system (on the same heater, using the same silver adhesive as used when PLD is performed) at $p_{O_2} = 10^{-7}$ torr for 60 min, a very slight discoloration of the STO crystal from its stoichiometrically translucent white color to a bluish gray could be observed, well-known to occur when STO is doped with oxygen vacancies [31,32]. However, upon removing these samples after cooling in vacuum, no appreciable conduction could be measured in four-point Van der Pauw geometry on the front-side, back-side, or through the cross-plane of the substrate. This implies that the diffusion length of oxygen vacancies during the 60 min anneal at 450 °C and 10^{-7} torr was extremely short, and that the slight discoloration comes from only a small fraction of the total substrate thickness (likely a thin surface layer <10 nm thick, for which resistances are too high to measure on our instrumentation). This was confirmed by performing an in situ re-oxygenation with oxygen gas isotopically enriched to 10% O^{18} . After a new sample was annealed for 60 min in the same vacuum conditions, the O^{18} mixture was introduced into the chamber to ~ 400 torr while still at a temperature of 450 °C and held for 5 min before cooling in the same pressure. It could be noticed clearly that re-oxygenation of the STO substrate occurred quickly (within several seconds) as the color returned to a white, translucent appearance in the oxygen environment (as visible through the vacuum chamber window with illumination). Fig. 3 shows the diffusion profile of O^{18} in this substrate as measured by secondary ion mass spectroscopy (SIMS), and indicates that for 60 min ($t = 3600$ s) under high vacuum conditions at 450 °C, appreciable reduction only occurred within the first 5 nm of the substrate's top surface. This indicates (from $x = (Dt)^{1/2}$, where x is the diffusion length) a bulk diffusion coefficient D of $1.3 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$, concomitant with diffusion rates of oxygen in bulk STO found in previous studies extrapolated to lower temperatures [21,33,34].

However, when substrates were subjected to precisely the same environment but with PLD, oxygen reduction in the substrate occurred with orders of magnitude more severity. It should first be noted that for the thinnest films grown – 8 nm of $\text{Sr}_{0.98}\text{La}_{0.02}\text{TiO}_3$ (SLTO) – no appreciable reduction occurred in the STO substrate as the back-side sheet resistance was $>10^9 \Omega \text{ SQ}^{-1}$ after growth, with or without the film remaining on the top-side of the substrate. However, for SLTO films of thickness 90–150 nm, sheet resistance values were in the range of 7.4–7.8 $\Omega \text{ SQ}^{-1}$ on the back-side of the STO substrates (Fig. 4) after growth

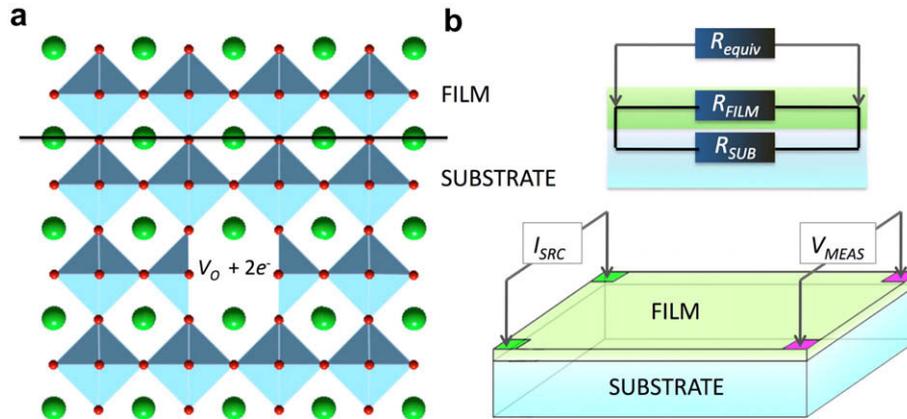


Fig. 2. (a) The cubic perovskite structures of both the (001) STO single-crystal structure and that of an epitaxial perovskite thin-film such as SrTiO₃, LaAlO₃, or Sr_{1-x}La_xTiO₃, including an oxygen vacancy. (b) An electrical transport model (equivalent resistor circuit) for the thin-film/substrate system for a conductive thin-film or interface and a reduced STO single-crystal substrate. Contacts here are located in a four-corner Van der Pauw geometry and the same parallel-resistor consideration can be made for Hall bar contacts as well.

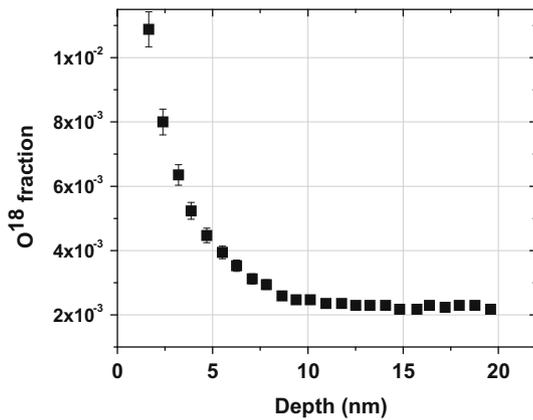


Fig. 3. Depth profile of 10% enriched O¹⁸ gas inside a re-oxygenated annealed STO (001) single-crystal substrate as measured by SIMS. The 2×10^{-3} baseline at 10% O¹⁸ represents the 0.2% natural abundance of the isotope.

with or without the film still present on the top-side; these substrates also turned visually dark and bluish. This resistance decreased even further to $2.7 \Omega \text{ SQ}^{-1}$ when an SLTO film of 750 nm was grown. Oxygen diffusion through the entire 500 μm -thick substrate implies a diffusion coefficient of $2.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ with PLD, 10 orders of magnitude faster than that without, and five orders of magnitude faster than that for oxygen diffusion along dislocation paths in similar *c*-axis oriented STO crystals [34].

In order to control for any possible doping of the substrate by the thin-film's constituent elements through inter-diffusion at elevated temperatures, we grew homoepitaxial films of STO onto the STO crystals. The STO thin-films showed identical behavior to the SLTO thin-films in reducing the STO substrates. Additionally, films of LaAlO₃ (LAO) were grown and also yielded similar results. We have listed the back-side resistance of the thin-film-substrate combination and the substrate alone after grinding

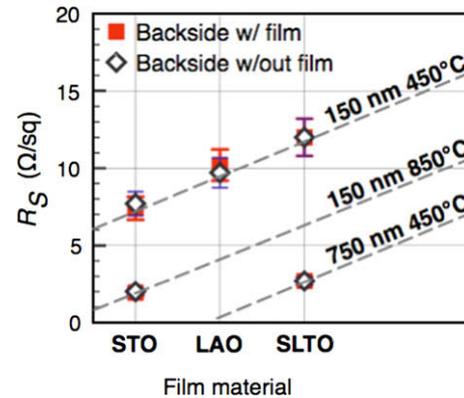


Fig. 4. Sheet resistances measured from Van der Pauw contacts placed on the back-side of (001)-oriented STO substrates after PLD for various thin-films – SrTiO₃ (STO), LaAlO₃ (LAO) and Sr_{0.98}La_{0.02}TiO₃ (SLTO) – grown on the top surface of the substrates at 10^{-7} torr. Films grown at 10^{-3} torr showed back-side R_S values in the range of $1 \text{ M} \Omega \text{ SQ}^{-1}$. Measurements were made after the back-side had been polished clean of any silver adhesive and washed both with the thin-film remaining intact on the top surface (“with film”), and with the film polished off to account for any shorting through the film due to *c*-axis short-circuit paths through the substrate (“without film”). Both measurements were nearly identical for every sample, indicating that the large majority of transport occurred in the substrate itself.

off the thin-film on top for different thin-film materials in Table 1. With a grown film of LAO or STO, the cross-plane resistance through the STO substrate was typically in the range of 5–10 Ω , crudely giving a value of resistivity for the 500 μm -thick reduced crystals on the order of 10 $\Omega \text{ cm}$, a value similar to that reported for crystals reduced for 10 days at 1200 °C and 5×10^{-6} torr [6]. When the growth temperature was increased to 850 °C (with $p_{\text{O}_2} = 10^{-7}$) for a 150 nm grown STO film, the back-side sheet resistance of the STO substrate dropped to $2 \Omega \text{ SQ}^{-1}$. In contrast, an oxygen pressure of only 10^{-3} torr (at 450 °C) during growth of a 150 nm STO film resulted in a back-side sheet resistance of $4 \text{ M} \Omega \text{ SQ}^{-1}$, indicating that at higher oxygen

Table 1

Back-side resistance for the thin-film-substrate combination for different materials deposited by PLD before and after the removal of the thin-film.

S. No.	Thin-film material	Growth temperature (°C)	Thickness of film (nm)	Back-side resistance with film (Ω)	Back-side resistance without film (Ω)
1	STO	450	100	7.4	7.7
2	STO	850	150	1.93	2.01
3	LAO	450	150	10.2	9.7
4	SLTO	450	150	12	12
5	SLTO	850	750	2.7	2.7

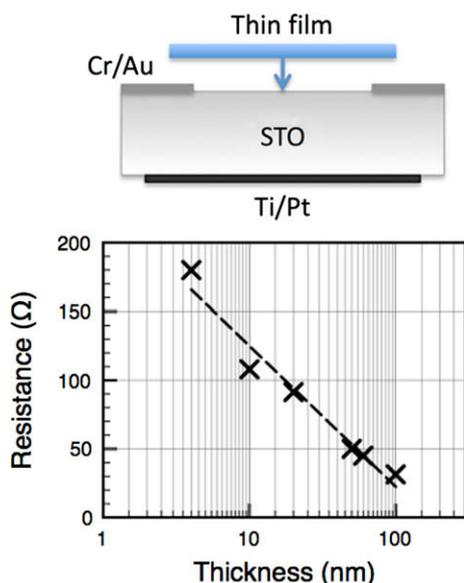


Fig. 5. Top: schematic of the thin-film growth process during in situ measurement of resistance during PLD. Cross-plane resistance of the STO substrate (bottom) during thin-film growth of $\text{Sr}_{0.98}\text{La}_{0.02}\text{TiO}_3$ on it, as measured in situ between a single top-side Cr/Au contact and a back-side Ti/Pt contact as described in the text.

growth pressures some reduction may still occur, but is greatly diminished. When re-exposed to an oxygen environment at elevated temperatures, crystals reduced under any conditions (and with or without films still present) returned to a translucent white color and their resistances increased beyond $1 \text{ G}\Omega \text{ SQ}^{-1}$, showing clearly that the conductivity resulting from PLD was in fact due to oxygen reduction.

To characterize the reduction process in detail electronically and as a function of thickness, we built a system to allow the in situ measurement of either four-point Van der Pauw (VDP) sheet resistance or cross-plane two-wire resistance during the PLD growth process of our thin-films. Resistance was monitored on the top-side of the substrate (in the film) in VDP geometry as well as across the substrate from a single top-side corner contact to the back-side contact (Fig. 5). The sample within the chip carrier was brought to 450°C at 10^{-7} torr, where a resistance of several $\text{k}\Omega$ could be measured in either configuration (cross-plane or VDP) before the PLD process. Once the growth of SLTO began, resistances decreased to several hundred ohms after several nanometers of film were grown. When the deposition was stopped and held for anywhere from 5

to 30 min at a given thickness, no change in resistance was observed. However, as the film was grown thicker, the cross-plane resistance decreased monotonically, fully confirming that the thin-film growth – rather than the time spent at elevated temperature under vacuum – was responsible for oxygen reduction. When the oxygen pressure was increased inside the chamber beyond 10^{-3} torr, resistances grew too large to be measured. At high vacuum, in-plane measurements attempted via the Van der Pauw configuration could not be made since the top-side contacts were shorted to the metal chip carrier out-of-plane through the conducting STO substrate.

To directly observe the difference between an STO crystal exposed to thin-film growth at both elevated temperature and low pressure and one under the same conditions but masked from the PLD plume and thin-film growth on its surface, we patterned a ~ 300 nm thick platinum shadow mask on the edges of an STO substrate (leaving the center of the substrate clean) and grew 150 nm of SLTO on top of the partially masked substrate at 10^{-7} torr and 450°C . It can clearly be seen optically after the Pt mask and SLTO thin-film were polished off that the masked area retained a far lighter color (Fig. 6); additionally, we performed conducting-AFM measurements locally on both the PLD-exposed and masked areas to measure the cross-plane through-substrate current, and found considerably more conduction – a factor of four times as much – in the area where the SLTO thin-film had been grown.

These data may imply that the hot laser plume actively reduces STO during growth regardless of the film material. Samples grown at room temperature showed no reduction of the substrate; in addition, as mentioned, substrates annealed at 450°C and 10^{-7} torr showed no appreciable reduction, with the back-side sheet resistance in both cases greater than $1 \text{ G}\Omega \text{ SQ}^{-1}$. However, substrates which were subject to the deposition of STO at room temperature and 10^{-7} torr and then subsequently annealed at 450°C for 30 min in 10^{-7} torr of oxygen did become quite reduced, with a back-side substrate sheet resistance of $45 \Omega \text{ SQ}^{-1}$. These data indicate that it is the combination of both the PLD oxide growth process and low pressure anneal which act to remove oxygen from STO single-crystal substrates; they also indicate that the reduction is likely not a function of the PLD plume during growth, but rather an activation for diffusion induced by the film which enables fast reduction in the presence of elevated temperature and high vacuum.

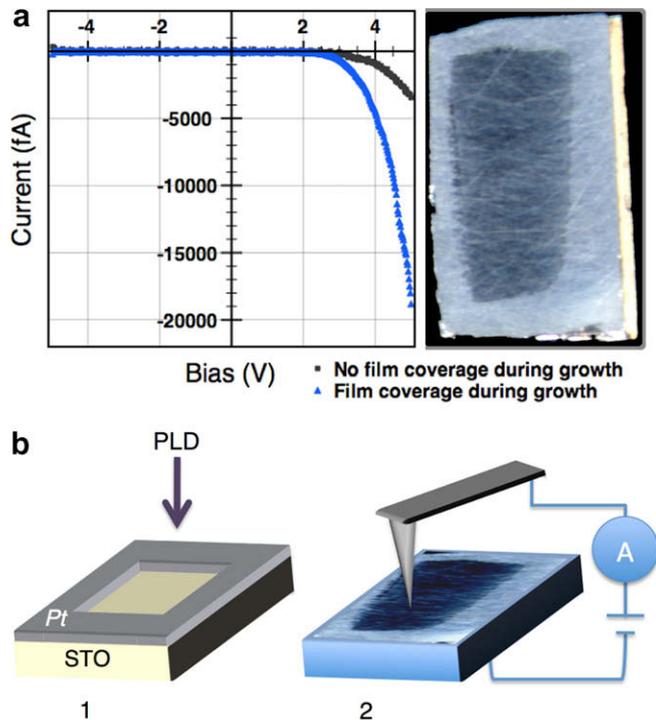


Fig. 6. Conducting-AFM data for an STO (001) single crystal with an SLTO film grown over the center of the substrate after placement of a Pt shadow mask around the top edges. Film and mask were removed prior to AFM. (a) Left: I - V curves to ± 5 V for inside (SLTO film coverage) and outside (no film coverage) the masked regions indicating Schottky transport and a much higher current through the area exposed to PLD at +5 V. Right: optical photograph of the substrate subsequent to both film growth and removal of the Pt mask and SLTO thin-film by polishing (including ~ 10 – 50 μm polishing of the substrate as well). (b) Schematic of the masked substrate prior to PLD film growth (1) and of the substrate after mask/film removal during conductive-AFM measurements (2). Dimensions of the substrate are $5\text{ mm} \times 2.5\text{ mm} \times 0.5\text{ mm}$.

From these results it is clear that the PLD process induces oxygen vacancies in STO substrates when coupled with low ($<10^6$ torr) growth pressures. Strontium titanate can in fact become significantly reduced with only a fraction of a percent of donors: if all were active, a mere 0.01% oxygen vacancy concentration would result in $5 \times 10^{18}\text{ cm}^{-3}$ electrons; 2% would yield 10^{21} cm^{-3} . The low mobility (1 – $6\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$) at room temperature limits the conductivity, though. However, because the thickness of typical substrates is 0.5 mm – or 5×10^3 times the thickness of a 100 nm thin-film – the absolute resistance of the substrate is easily as low as that of the film, despite potentially large differences in resistivity between substrate and a metallic thin-film. Since typical thin-film sheet resistances for metallic oxides with $\sim 100\text{ nm}$ or less thickness can be in the range of 10 – $10,000\ \Omega\text{ SQ}^{-1}$ or greater, a substrate resistance on the order of $10\ \Omega\text{ SQ}^{-1}$ or less will convolute measurements of even highly conducting films. With the system represented by two resistors in parallel, the total measured resistance is given by:

$$\frac{1}{R_{\text{measured}}} = \frac{1}{R_{\text{substrate}}} + \frac{1}{R_{\text{film}}} \quad (2)$$

If both substrate and film resistances are equal, then half the current will flow through the substrate and the interpreted resistivity of the film will lower by 50%. This error will be very significant ($>10\%$) for thin-film materials whose sheet resistances are not an order of magnitude lower than the sheet resistance of the substrate. There will still clearly be a large amount of error even for films grown at 10^{-3} torr if R_S values for the film are megaohms or greater. It is thus imperative to consider the effects of the substrate conduction on any measurement of a thin-film on STO; however, such in situ reduction can prove extremely useful in creating back-gated devices such as ferroelectrics, spintronics [35] and transistors by precluding the need to find another epitaxial thin-film conductive layer. In addition, the efficient creation oxygen vacancy pathways in the reduced crystals may see applications as membrane materials for proton exchange.

4. Conclusions

Our results clearly demonstrate the remarkable efficiency with which the PLD process removes oxygen from this material – over 10 orders of magnitude faster than that of a high vacuum anneal and reported values of bulk diffusion. Surprisingly, this rate is also orders of magnitude faster than that for diffusion along dislocations in STO; a microscopic mechanism for this phenomenon is still not fully understood. As the paradigmatic single crystal for oxide thin-film growth due to its cubic crystal structure and ideal lattice parameter of $3.905\ \text{\AA}$, the widespread use of STO must be questioned with respect to growth of functional conducting oxides or other nanomaterials – especially at low oxygen pressures and high temperatures – but may be employed to create back-gated devices for dielectric oxides grown at low oxygen pressures. In addition, reduced STO can show resistive switching behavior, especially when lightly doped with an element such as cobalt [36,37], and can also show functionality as a thermoelectric material when co-doped with lanthanum; the practical use of PLD to efficiently reduce strontium titanate, then, can see use in creating reduced single crystals with interesting functionality.

Acknowledgements

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