**TITLE:**

Tuning Oxide Properties by Oxygen Vacancy Control During Growth and Annealing

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Oxides, oxygen vacancies, oxide interfaces, electrical properties, magnetic properties, carrier density, pulsed laser deposition, annealing

**SUMMARY:**

Oxide materials show many exotic properties that can be controlled by tuning the oxygen content. Here, we demonstrate the tuning of oxygen content in oxides by varying the pulsed laser deposition parameters and by performing postannealing. As an example, electronic properties of SrTiO3-based heterostructures are tuned by growth modifications and annealing.

**ABSTRACT:**

Electrical, optical, and magnetic properties of oxide materials can often be controlled by varying the oxygen content. Here we outline two approaches for varying the oxygen content and provide concrete examples for tuning the electrical properties of SrTiO3-based heterostructures. In the first approach, the oxygen content is controlled by varying the deposition parameters during a pulsed laser deposition. In the second approach, the oxygen content is tuned by subjecting the samples to annealing in oxygen at elevated temperatures after the film growth. The approaches can be used for a wide range of oxides and nonoxide materials where the properties are sensitive to a change in the oxidation state.

The approaches differ significantly from electrostatic gating, which is often used to change the electronic properties of confined electronic systems such as those observed in SrTiO3-based heterostructures. By controlling the oxygen vacancy concentration, we are able to control the carrier density over many orders of magnitude, even in nonconfined electronic systems. Moreover, properties can be controlled, which are not sensitive to the density of itinerant electrons.

**INTRODUCTION:**

The oxygen content plays a vital role in the properties of oxide materials. Oxygen has a high electronegativity and, in the fully ionic limit, attracts two electrons from neighboring cations. These electrons are donated to the lattice when an oxygen vacancy is formed. The electrons can be trapped and form a localized state, or they can become delocalized and capable of conducting a charge current. The localized states are typically located in the band gap between the valence and conduction band with a total angular momentum that can be nonzero1–3. The localized states can, thus, form localized magnetic moments and have a large impact on, for instance, the optical and magnetic properties1–3. If the electrons become delocalized, they contribute to the density of itinerant charge carriers. In addition, if an oxygen vacancy or other defects are formed, the lattice adapts to the defect. The presence of defects can, thus, naturally lead to local strain fields, symmetry breaking, and a modified electronic and ionic transport in oxides.

Controlling the oxygen stoichiometry is, therefore, often key to tune, for instance, the optical, magnetic, and transport properties of oxide materials. A prominent example is that of SrTiO3 and SrTiO3-based heterostructures, where the ground state of the material systems is very sensitive to the oxygen content. Undoped SrTiO3 is a nonmagnetic insulator with a band gap of 3.2 eV; however, by introducing oxygen vacancies, SrTiO3 changes the state from insulating to metallic conducting with an electron mobility exceeding 10,000 cm2/Vs at 2 K4. At low temperatures (*T* < 450 mK), superconductivity may even be the favored ground state5,6. Oxygen vacancies in SrTiO3 have also been found to render it ferromagnetic7 and result in an optical transition in the visible spectrum from transparent to opaque2. For more than a decade, there has been a large interest in depositing various oxides, such as LaAlO3, CaZrO3, and γ-Al2O3, on SrTiO3 and examining the properties arising at the interface8–13. In some cases, it turns out that the properties of the interface differ markedly from those observed in the parent materials. An important result of the SrTiO3-based heterostructures is that the electrons can be confined to the interface, which makes it possible to control the properties related to the density of itinerant electrons using electrostatic gating. In this way, it becomes possible to tune, for instance, the electron mobility14,15, superconductivity11, electron pairing16, and magnetic state17 of the interface, using electric fields.

The formation of the interface also enables a control of the SrTiO3 chemistry, where the deposition of the top film on SrTiO3 can be used to induce a redox reaction across the interface18,19. If an oxide film with a high oxygen affinity is deposited on SrTiO3, oxygen can transfer from the near-surface parts of SrTiO3 to the top film, thereby reducing SrTiO3 and oxidizing the top film (see **Figure 1**).

[Place **Figure 1** here]

In this case, oxygen vacancies and electrons are formed near the interface. This process is expected to be the origin of the conductivity formed during the deposition at the interface between SrTiO3 and room-temperature-grown metal films or oxides such as amorphous LaAlO318,20 or γ-Al2O310,21–23. Thus, the properties of these SrTiO3-based interfaces are highly sensitive to the oxygen content at the interface.

Here, we report the use of postdeposition annealing and variations in the pulsed laser deposition parameters to control the properties in oxide materials by tuning the oxygen content. We use γ-Al2O3 or amorphous LaAlO3 deposited on SrTiO3 at room temperature as examples on how the carrier density, electron mobility, and sheet resistance can be changed by orders of magnitude by controlling the number of oxygen vacancies. The methods offer some benefits beyond those obtained with electrostatic gating, which is typically used to tune the electrical9,11,14, and in some cases the magnetic15, 17, properties. These benefits include forming a (quasi-)stable final state and avoiding the use of electric fields, which requires electrical contact to the sample and may cause side effects.

In the following, we review general approaches for tuning the properties of oxides by controlling the oxygen content. This is done in two ways, namely, 1) by varying the growth conditions when synthesizing the oxide materials, and 2) by annealing the oxide materials in oxygen. The approaches can be applied to tune a range of properties in many oxide and some monoxide materials. We provide a concrete example on how to tune the carrier density at the interface of SrTiO3-based heterostructures. Ensure that a high level of cleanliness is exercised to avoid contamination of the samples (e.g., by using gloves, tube furnaces dedicated to SrTiO3, and nonmagnetic/acid resistant tweezers).

**PROTOCOL:**

1. **Controlling properties by varying growth conditions**
   1. **Preparation of high-quality surfaces of SrTiO3**
      1. Purchase mixed terminated SrTiO3 substrates (e.g., of 5 mm x 5 mm x 0.5 mm in size) with a typical surface angle of 0.05°–0.2° with respect to the (001) crystal planes.

NOTE: The miscut angle determines the flatness of the surface, which is important for epitaxial growth on the substrate, as well as for the resulting properties at the interface.

* + 1. Clean the desired number of substrates by ultrasonication in acetone for 5 min and ethanol for 5 min at room temperature in a standard ultrasonicator.
    2. Ultrasonicate the substrates for 20 min at 70 °C in clean water, which dissolves SrO24 or form Sr-hydroxide complexes at surface domains terminated with SrO25, while leaving the chemically stable TiO2-terminated domains unchanged26.
    3. Ultrasonicate the substrates in a 3:1:16 HCl:HNO3:H2O acidic solution (e.g., 9:3:48 mL) at 70 °C for 20 min in a fume hood to selectively etch SrO due to the basic nature of SrO surface domains, the acidity of TiO2, and the presence of the Sr-hydroxide complexes.
    4. Remove the residual acid from the substrates by ultrasonication in 100 mL of clean water for 5 min at room temperature in a fume hood.

NOTE: TiO2-terminated SrTiO3 can be purchased commercially or prepared in various ways based on the selective etching of SrO on the surface24,27. The conventional etching in HF also leads to TiO2-terminated SrTiO3, but this is avoided here due to safety concerns and a risk of the unintentional F-doping of SrTiO328.

* + 1. Bake the substrates in an atmosphere of 1 bar of oxygen for 1 h at 1,000 °C with a heating and cooling rate of 100 °C/h in a ceramic tube furnace, to relax the substrate surface into a state with low energy.
  1. **Deposition of the thin film(s) on the substrate**
     1. Mount the substrates on the heater or a chip carrier, depending on whether in situ transport measurements during the deposition are to be performed.

NOTE: A silver paste that cures at room temperature can be conveniently used for substrate mounting.

* + 1. Connect the four corners of the SrTiO3 surface to a chip carrier electrically using, for instance, standard wedge wire bonding with 20 µm-thick Al wires, if in situ transport measurements are desired. Mount the chip carrier onto a chip carrier holder where wires connect the sample to an electrical measurement setup through a vacuum-compatible connector.
    2. Place the TiO2-terminated substrate 4.7 cm from the single-crystalline γ-Al2O3 target for a typical deposition of γ-Al2O3 on SrTiO3.
    3. Start sheet resistance measurements using the Van der Pauw geometry29, if in situ transport measurements are to be performed.
    4. Heat the substrate to 650 °C at a rate of 15 °C/min or keep the substrate at room temperature.
    5. Prepare for ablating from a single-crystalline γ-Al2O3 target in an oxygen pressure of 1 x 10-5 mbar using, for instance, a nanosecond-pulsed KrF laser with a wavelength of 248 nm, a laser fluence of 3.5 J/cm2, and a frequency of 1 Hz. Tune the properties using the oxygen content by using an oxygen deposition pressure in the range of 10-6 to 10-1 mbar or by varying other deposition parameters.
    6. Deposit the desired thickness of γ-Al2O3 (typically 0–5 unit cells).

NOTE: This can be determined using, for instance, reflective high-energy electron diffraction (RHEED) oscillations or atomic force microscopy measurements, where the latter is measured as the height difference produced by preventing the deposition of γ-Al2O3 on the part of the substrate using a physical mask.

* + 1. Cool down the γ-Al2O3/SrTiO3 heterostructure at a rate of 15 °C/min at the deposition pressure without performing an additional annealing step if a high-temperature deposition is done.
    2. Remove the sample from the deposition chamber and stop the electrical measurements.
    3. Store the sample in vacuum, nitrogen or, alternatively, at ambient conditions. The sample degradation is slowest when stored in vacuum or nitrogen20.

1. **Controlling properties by thermal annealing**
   1. Mount the sample with silver paste on a chip carrier.
   2. Connect the sample electrically to the chip carrier using, for instance, wedge wire bonding of Al wires in the Van der Pauw geometry29.
   3. Connect the chip carrier electrically to the measurement equipment, using a connector and wires with a thermally resistant insulation.
   4. Start the sheet resistance measurements.
   5. Place the chip carrier equipped with the sample in a closed furnace.
   6. Flush thoroughly with the gas used for the annealing while checking whether the sample resistance is sensitive to a change in the atmosphere.
   7. Anneal the sample using the desired annealing profile. Typical annealing temperatures are 50–250 °C and 100–350 °C for a-LaAlO3/SrTiO3 and γ-Al2O3/SrTiO3 heterostructures, respectively, depending on the thickness of the top film and the desired rate of oxygen incorporation.

NOTE: Use more heat-compatible options than Al wires and standard ceramic chip carriers if temperatures above 350–400 °C are needed.

* 1. Abort the annealing when a desired change in the sheet resistance has occurred.
  2. Cool down the sample by ramping down the temperature, or take out the sample.
  3. Stop the electrical measurements.

NOTE: The resistance is generally temperature dependent, which must be taken into account if specific transport properties at a certain temperature are the goal.

**REPRESENTATIVE RESULTS:**

**Controlling properties by varying growth conditions**

Varying the deposition parameters during the deposition of oxides can lead to a large change in the properties, in particular for SrTiO3-based heterostructures, as shown in **Figure 2**.

[Place **Figure 2** here]

Here, the thickness of γ-Al2O3 is varied and the resulting sheet resistance is measured after the γ-Al2O3/SrTiO3 heterostructure is removed from the deposition chamber. This results in a large variation in the transport behavior of the γ-Al2O3/SrTiO3 interface, ranging from highly insulating to metallic conducting around a critical thickness of 1-unit cell (0.8 nm). If the thickness is carefully controlled close to the critical thickness, the sheet conductance and carrier density can be tuned by several orders of magnitude. However, at room temperature, the electron mobility stays largely unchanged. A similar tuning can be found when other deposition parameters are varied, such as the substrate-to-target distance30 and the oxygen partial pressure31.

Whereas the electron mobility stays largely unchanged at room temperature, it changes dramatically when we cool the sample to 2 K and when the γ-Al2O3 thickness or deposition pressure is varied (see **Figure 3**).

[Place **Figure 3** here]

Here, the electron mobility of the γ-Al2O3/SrTiO3 heterostructure reaches a value exceeding 100,000 cm2/Vs at 2 K when the γ-Al2O3 is deposited with a thickness of 3.5 unit cells in an oxygen partial pressure of approximately 10-5 mbar. Raising the partial pressure or deviating from the γ-Al2O3 thickness results in both a decrease in the carrier density and electron mobility by two orders of magnitude.

**Controlling properties by thermal annealing**

The oxygen content can also be controlled using *ex situ* thermal annealing in oxidizing or reducing conditions. Here, the final state after annealing is determined by three parameters: the annealing time, the temperature, and the atmosphere. An example is provided in **Figure 4a,b**.

[Place **Figure 4** here]

Here, the sheet conductance of γ-Al2O3/SrTiO3 and amorphous-LaAlO3/SrTiO3 heterostructures is measured while the samples are annealed in 1 bar of oxygen at various temperatures. The fastest decrease in the conductance is observed for amorphous-LaAlO3/SrTiO3 heterostructures, and it is found that the annihilation of vacancies in SrTiO3 occurs through the 16 nm-thick amorphous LaAlO3 layer23. The γ-Al2O3 film is, however, found to serve as a blocking layer for oxygen diffusion, and the oxygen vacancies at the SrTiO3 side are annihilated through oxygen diffusion through SrTiO3, leading to a more thermally resilient interface conductivity23. The carrier density of the heterostructures can be controlled by stopping the annealing in oxygen, as shown in **Figure 4c** for the case of the γ-Al2O3/SrTiO3 heterostructure. In this case, the heterostructure is annealed in several steps at approximately 200 °C. After each step, the heterostructure is cooled down to room temperature, where the carrier density is measured. The annealing results in a controlled decrease of the carrier density, as well as in a transition from a metallic conducting to an insulating interface.

The change in the conducting state of the γ-Al2O3/SrTiO3 heterostructure can be used to enable different properties23. **Figure 5** shows an example.

[Place **Figure 5** here]

Here, conducting nanolines can be drawn using conductive Atomic Forced Microscopy (c-AFM) only in a high resistive state. After the deposition of γ-Al2O3, the heterostructure is in a low resistive state, and no observable change occurs when a c-AFM tip with a positive bias scans on the γ-Al2O3 surface from one electrode to another. However, after annealing the heterostructure at 150 °C in air for 3 h, a high resistive state can be obtained at the interface. When the positively biased tip is scanned between the electrodes, a conducting line with a width of approximately 50 nm can be formed at the high resistive interface. When the nanoline connects the two electrodes, a sharp decrease in the resistance is observed, as reported previously32,33. The nanoline can be subsequently erased by applying a negative bias on the tip and scanning across the nanoline.

**FIGURE AND TABLE LEGENDS:**

**Figure 1: Oxygen vacancy formation in SrTiO3.** Schematic illustration of how oxygen vacancies and electrons are formed in the interface-near region of SrTiO3 during the deposition of a thin film with a high oxygen affinity. Reprinted figure with permission from a study by Chen et al.18. Copyright 2011 by the American Chemical Society.

**Figure 2: Controlling the transport properties by tuning the top layer thickness.** (**a**) Schematic illustration of the γ-Al2O3/SrTiO3 heterostructures. (**b**) Sheet resistance (*Rs*) of the γ-Al2O3/SrTiO3 interface as a function of the thickness of the γ-Al2O3 layer. (**c**) Sheet carrier density (*ns*) as a function of the γ-Al2O3 layer thickness. (**d**) Carrier mobility (*µ*) as a function of the γ-Al2O3 layer thickness. Reprinted figure with permission from a study by Christensen et al.12. Copyright 2016 by AIP Publishing.

**Figure 3: Controlling the electron mobility by varying the deposition parameters**. The electron mobility (*µ*) of γ-Al2O3/SrTiO3 as a function of the carrier density (*ns*), tuned by varying the thickness of γ-Al2O3 (blue diamonds), primarily varying the oxygen partial pressure during the pulsed laser deposition (grey circles) or by performing postannealing in 1 bar of oxygen at approximately 200 °C (red circles). Reprinted figure with permission from a study by Christensen et al.31. Copyright 2018 by the American Physical Society.

**Figure 4: Controlling the transport properties by annealing in oxygen.** Normalized sheet conductance (*Gs*) of the (**a**) γ-Al2O3/SrTiO3 and (**b**) a-LaAlO3/SrTiO3 heterostructures as a function of the time during which the samples are annealed in 1 bar of oxygen. (**c**) The sheet carrier density (*ns*) as a function of sheet conductance (*Gs*) measured at room temperature after two γ-Al2O3/SrTiO3 samples have been annealed in 1 bar of oxygen at approximately 200 °C. The two samples have been synthesized using a pulsed laser deposition of γ-Al2O3 on SrTiO3 using an oxygen background pressure of 10-6 mbar and 10-5 mbar, which leads to different initial carrier densities after the deposition. Reprinted figure with permission from a study by Christensen et al.23. Copyright 2017 by the American Physical Society.

**Figure 5: Enabling the writing of conducting polymer** Four-probe resistance as a function of time as conducting polymer are attempted to be written using a conducting atomic force microscopy (c-AFM) tip. After annealing at approximately 150 °C for 3 h, conducting lines can be written at the γ-Al2O3/SrTiO3 interface by applying a positive bias on the c-AFM tip and scanning on the γ-Al2O3 surface. When the conducting line contacts two electrodes, the resistance drops sharply. Applying a negative bias and scanning across the conducting line leads to the erasure of the polymer. Reprinted figure with permission from a study by Christensen et al.23. Copyright 2017 by the American Physical Society.

**DISCUSSION:**

The methods described here rely on using the oxygen content to control oxide properties, and the oxygen partial pressure and operating temperature are, thus, critical parameters. If the total oxidation state of the system is tuned in a way where the system remains in a thermodynamic equilibrium with the surrounding atmosphere (i.e., changed pO2 at high temperature), the changes can be reversible. However, for the case of SrTiO3-based heterostructures, interfacial oxygen vacancies are typically formed using pulsed laser deposition, which may capture the oxidation state in a nonequilibrium state34. In this case, the temperature profile and oxygen partial pressure at and after the deposition are crucial for the resulting properties. Oxygen vacancies in SrTiO3 are typically unstable under ambient conditions22, and changes in the oxygen content induced by annealing will generally be irreversible.

Other disadvantages are the side effects from the elevated temperature or modified deposition. During elevated temperature, cation diffusion, for instance, can occur. A significant cation interdiffusion has been reported during the pulsed laser deposition of various oxides on SrTiO310,35,36. Controlling the oxygen content is typically done by changing the oxygen deposition pressure. Below a pressure of approximately 10-3 mbar, the plasma plume in the pulsed laser deposition is hardly affected by the background pressure, and a change in the oxidation state of SrTiO3 occurs by interactions with the surrounding atmosphere at elevated temperatures37. When the pressure is increased from 10-3 to 10-1 mbar, the background gas interacts with the plasma plume, which results in oxidizing the plume, as well as lowering the kinetic energy of the plasma species37. This may influence the level of cation interdiffusion as the effective temperature at the SrTiO3 surface is lowered and plasma species arrive with lower velocities. Argon stops the plasma species approximately as efficiently as oxygen, and hence, the side effects of changing the kinetic energy can be circumvented by fixing the total deposition pressure but varying the oxygen partial pressure, using an argon/oxygen mixture37. When performing annealing, cation diffusion can be avoided by annealing at temperatures high enough to allow oxygen diffusion but low enough to prevent significant cation diffusion. This is the case for the SrTiO3-based heterostructures annealed at 100–350 °C considered here23,36. It should, however, be noted that in some cases, cation diffusion and variations in the defect configuration induced by the deposition or postannealing can also be a desirable way to tune the oxide properties.

The two different approaches for changing the oxygen content differ from each other in several ways. Using the growth approach where the pulsed laser deposition parameters are varied, it is possible to obtain states that are either thermodynamically stable or thermally quenched in a nonequilibrium state34. The annealing approach drives the sample toward thermal equilibrium at the given annealing conditions, but intermediate nonequilibrium states can also be obtained. The annealing approach, moreover, minimizes sample-to-sample variations as the properties can be tuned in a single sample, whereas different samples with varying properties are prepared according to the growth approach. On the other hand, the initial state might be lost after the annealing process.

The two approaches also differ from electrostatic gating, which is usually used to tune, in particular, the carrier density of confined electronic systems. Electrostatic gating benefits from a fast and versatile change in the electrical properties, which can often be done in situ while measuring other properties. However, the obtaining state is not permanent, a significant hysteresis may be observed, and the range in which the carrier density can be tuned is limited (typically on the order of less than 10-12­ /cm­2 for back-gating with ~100 V through 0.5 mm-thick SrTiO3)12,23,38,39. Controlling the properties by tuning the oxygen vacancy content leads to a (quasi-)permanent state with large changes in the carrier density10,23 and the possibility to change properties that are not necessarily affected by a change in the density of itinerant electrons. Furthermore, a combination of the gating and annealing processes can utilize their respective advantages for a precise control of the interface properties.

The annealing approach is particularly compatible with a range of additional measurements besides the resistance measurements described here. These measurements can include Hall, gate, optical, and magnetic measurements, which can be used to probe the tuning of various properties. The measurements also include those where wire access or electrostatic gating is challenging, such as photoemission experiments.

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**DISCLOSURES:**

The authors have nothing to disclose.

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