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TITLE:

Tuning Oxide Properties by Oxygen Vacancy Control During Growth and Annealing

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KEYWORDS:

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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 $SrTiO_3$-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 $SrTiO_3$-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 $SrTiO_3$-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 nonzero[1–3]. The localized states can, thus, form localized magnetic moments and have a large impact on, for instance, the optical and magnetic properties[1–3]. 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 $SrTiO_3$ and $SrTiO_3$-based heterostructures, where the ground state of the material systems is very sensitive to the oxygen content. Undoped $SrTiO_3$ is a nonmagnetic insulator with a band gap of 3.2 eV; however, by introducing oxygen vacancies, $SrTiO_3$ changes the state from insulating to metallic conducting with an electron mobility exceeding 10,000 cm^2/Vs at 2 K[4]. At low temperatures ($T <$ 450 mK), superconductivity may even be the favored ground state[5,6]. Oxygen vacancies in $SrTiO_3$ have also been found to render it ferromagnetic[7] and result in an optical transition in the visible spectrum from transparent to opaque[2]. For more than a decade, there has been a large interest in depositing various oxides, such as $LaAlO_3$, $CaZrO_3$, and γ-Al_2O_3, on $SrTiO_3$ and examining the properties arising at the interface[8–13]. 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 $SrTiO_3$-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 mobility[14,15], superconductivity[11], electron pairing[16], and magnetic state[17] of the interface, using electric fields.

The formation of the interface also enables a control of the $SrTiO_3$ chemistry, where the deposition of the top film on $SrTiO_3$ can be used to induce a redox reaction across the interface[18,19]. If an oxide film with a high oxygen affinity is deposited on $SrTiO_3$, oxygen can transfer from the near-surface parts of $SrTiO_3$ to the top film, thereby reducing $SrTiO_3$ 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 $SrTiO_3$ and room-temperature-grown metal films or oxides such as amorphous $LaAlO_3$[18,20] or γ-Al_2O_3[10,21–23]. Thus, the properties of these $SrTiO_3$-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-Al_2O_3 or amorphous $LaAlO_3$ deposited on $SrTiO_3$ 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 electrical[9,11,14], and in some cases the magnetic[15,17], 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 $SrTiO_3$-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 $SrTiO_3$, and nonmagnetic/acid resistant tweezers).

PROTOCOL:

1. Controlling properties by varying growth conditions

1.1. Preparation of high-quality surfaces of $SrTiO_3$

1.1.1. Purchase mixed terminated $SrTiO_3$ 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.

1.1.2. 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.

1.1.3. Ultrasonicate the substrates for 20 min at 70 °C in clean water, which dissolves SrO[24] or form Sr-hydroxide complexes at surface domains terminated with SrO[25], while leaving the chemically stable TiO_2-terminated domains unchanged[26].

1.1.4. Ultrasonicate the substrates in a 3:1:16 $HCl:HNO_3:H_2O$ 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 TiO_2, and the presence of the Sr-hydroxide complexes.

1.1.5. 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: TiO_2-terminated $SrTiO_3$ can be purchased commercially or prepared in various ways based on the selective etching of SrO on the surface[24,27]. The conventional etching in HF also leads to TiO_2-terminated $SrTiO_3$, but this is avoided here due to safety concerns and a risk of the unintentional F-doping of $SrTiO_3$[28].

1.1.6. 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.

1.2. Deposition of the thin film(s) on the substrate

1.2.1. 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.

1.2.2. Connect the four corners of the $SrTiO_3$ 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.

1.2.3. Place the TiO_2-terminated substrate 4.7 cm from the single-crystalline γ-Al_2O_3 target for a typical deposition of γ-Al_2O_3 on $SrTiO_3$.

1.2.4. Start sheet resistance measurements using the Van der Pauw geometry[29], if in situ transport measurements are to be performed.

1.2.5. Heat the substrate to 650 °C at a rate of 15 °C/min or keep the substrate at room temperature.

1.2.6. Prepare for ablating from a single-crystalline γ-Al_2O_3 target in an oxygen pressure of 1×10^{-5} mbar using, for instance, a nanosecond-pulsed KrF laser with a wavelength of 248 nm, a laser fluence of 3.5 J/cm^2, 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.

1.2.7. Deposit the desired thickness of γ-Al_2O_3 (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-Al_2O_3 on the part of the substrate using a physical mask.

1.2.8. Cool down the γ-Al_2O_3/$SrTiO_3$ 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.

1.2.9. Remove the sample from the deposition chamber and stop the electrical measurements.

1.2.10. Store the sample in vacuum, nitrogen or, alternatively, at ambient conditions. The sample degradation is slowest when stored in vacuum or nitrogen[20].

2. Controlling properties by thermal annealing

2.1. Mount the sample with silver paste on a chip carrier.

2.2. Connect the sample electrically to the chip carrier using, for instance, wedge wire bonding of Al wires in the Van der Pauw geometry[29].

2.3. Connect the chip carrier electrically to the measurement equipment, using a connector and wires with a thermally resistant insulation.

2.4. Start the sheet resistance measurements.

2.5. Place the chip carrier equipped with the sample in a closed furnace.

2.6. Flush thoroughly with the gas used for the annealing while checking whether the sample resistance is sensitive to a change in the atmosphere.

2.7. Anneal the sample using the desired annealing profile. Typical annealing temperatures are 50–250 °C and 100–350 °C for a-$LaAlO_3$/$SrTiO_3$ and γ-Al_2O_3/$SrTiO_3$ 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.

2.8. Abort the annealing when a desired change in the sheet resistance has occurred.

2.9. Cool down the sample by ramping down the temperature, or take out the sample.

2.10. 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 $SrTiO_3$-based heterostructures, as shown in **Figure 2**.

[Place **Figure 2** here]

Here, the thickness of γ-Al_2O_3 is varied and the resulting sheet resistance is measured after the γ-Al_2O_3/$SrTiO_3$ heterostructure is removed from the deposition chamber. This results in a large variation in the transport behavior of the γ-Al_2O_3/$SrTiO_3$ 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 distance[30] and the oxygen partial pressure[31].

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-Al_2O_3 thickness or deposition pressure is varied (see **Figure 3**).

[Place **Figure 3** here]

Here, the electron mobility of the γ-Al_2O_3/$SrTiO_3$ heterostructure reaches a value exceeding 100,000 cm^2/Vs at 2 K when the γ-Al_2O_3 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-Al_2O_3 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-Al_2O_3/$SrTiO_3$ and amorphous-$LaAlO_3$/$SrTiO_3$ 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-$LaAlO_3$/$SrTiO_3$ heterostructures, and it is found that the annihilation of vacancies in $SrTiO_3$ occurs through the 16 nm-thick amorphous $LaAlO_3$ layer[23]. The γ-Al_2O_3 film is, however, found to serve as a blocking layer for oxygen diffusion, and the oxygen vacancies at the $SrTiO_3$ side are annihilated through oxygen diffusion through $SrTiO_3$, leading to a more thermally resilient interface conductivity[23]. 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-Al_2O_3/$SrTiO_3$ 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-Al_2O_3/$SrTiO_3$ heterostructure can be used to enable different properties[23]. **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-Al_2O_3, 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-Al_2O_3 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 previously[32,33]. 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 $SrTiO_3$. Schematic illustration of how oxygen vacancies and electrons are formed in the interface-near region of $SrTiO_3$ 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-Al_2O_3/$SrTiO_3$ heterostructures. (**b**) Sheet resistance (R_s) of the γ-Al_2O_3/$SrTiO_3$ interface as a function of the thickness of the γ-Al_2O_3 layer. (**c**) Sheet carrier density (n_s) as a function of the γ-Al_2O_3 layer thickness. (**d**) Carrier mobility (μ) as a function of the γ-Al_2O_3 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-Al_2O_3/$SrTiO_3$ as a function of the carrier density (n_s), tuned by varying the thickness of γ-Al_2O_3 (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 (G_s) of the (**a**) γ-Al_2O_3/$SrTiO_3$ and (**b**) a-$LaAlO_3$/$SrTiO_3$ heterostructures as a function of the time during which the samples are annealed in 1 bar of oxygen. (**c**) The sheet carrier density (n_s) as a function of sheet conductance (G_s) measured at room temperature after two γ-Al_2O_3/$SrTiO_3$ 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-Al_2O_3 on $SrTiO_3$ 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-Al_2O_3/$SrTiO_3$ interface by applying a positive bias on the c-AFM tip and scanning on the γ-Al_2O_3 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 pO_2 at high temperature), the changes can be reversible. However, for the case of $SrTiO_3$-based heterostructures, interfacial oxygen vacancies are typically formed using pulsed laser deposition, which may capture the oxidation state in a nonequilibrium state[34]. In this case, the temperature profile and oxygen partial pressure at and after the deposition are crucial for the resulting properties. Oxygen vacancies in $SrTiO_3$ are typically unstable under ambient conditions[22], 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 $SrTiO_3$[10,35,36]. 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 $SrTiO_3$ occurs by interactions with the surrounding atmosphere at elevated temperatures[37].

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 species[37]. This may influence the level of cation interdiffusion as the effective temperature at the $SrTiO_3$ 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 mixture[37]. 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 $SrTiO_3$-based heterostructures annealed at 100–350 °C considered here[23,36]. 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 state[34]. 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} /cm^2 for back-gating with ~100 V through 0.5 mm-thick $SrTiO_3$)[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 density[10,23] 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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Figure 1

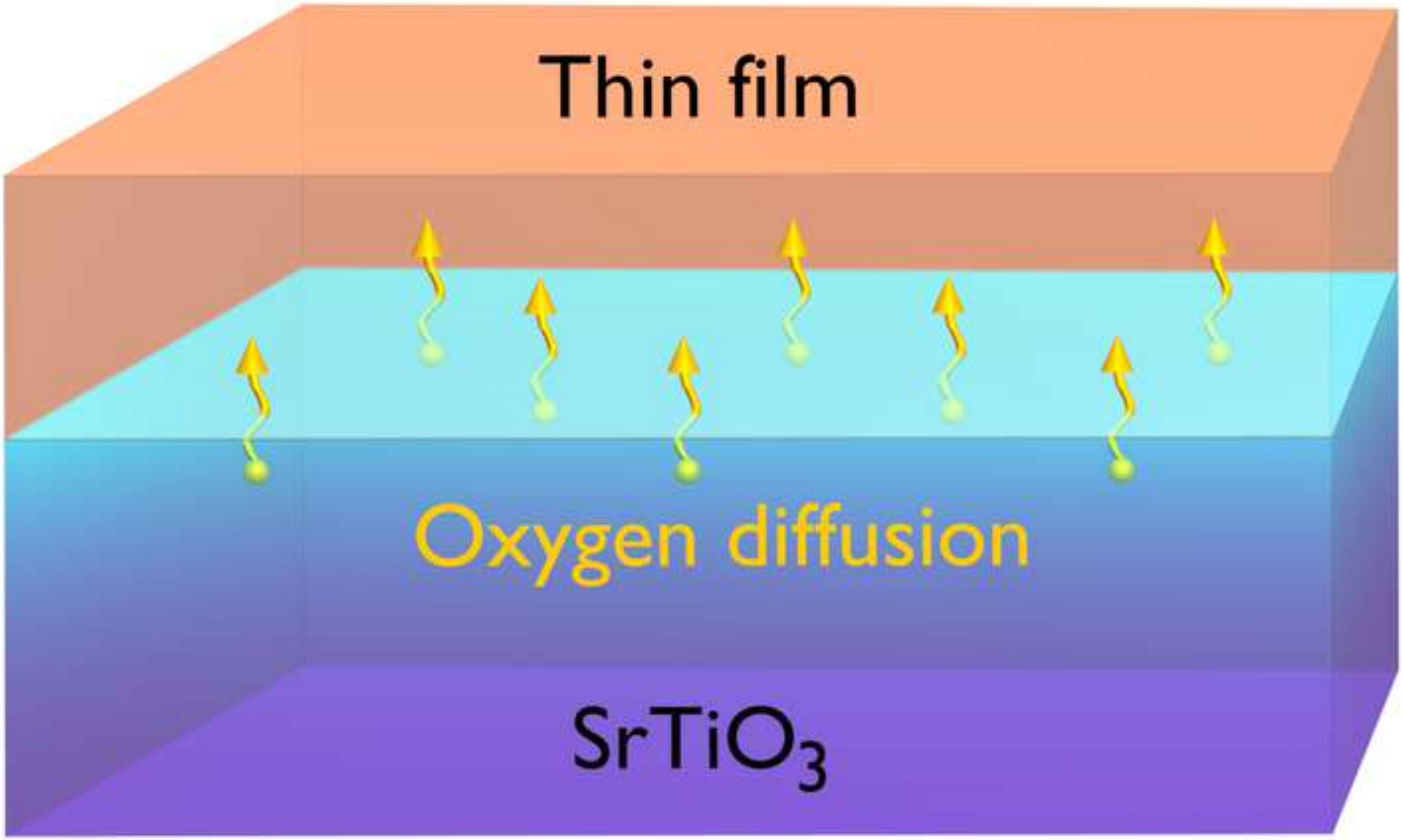


Figure 2

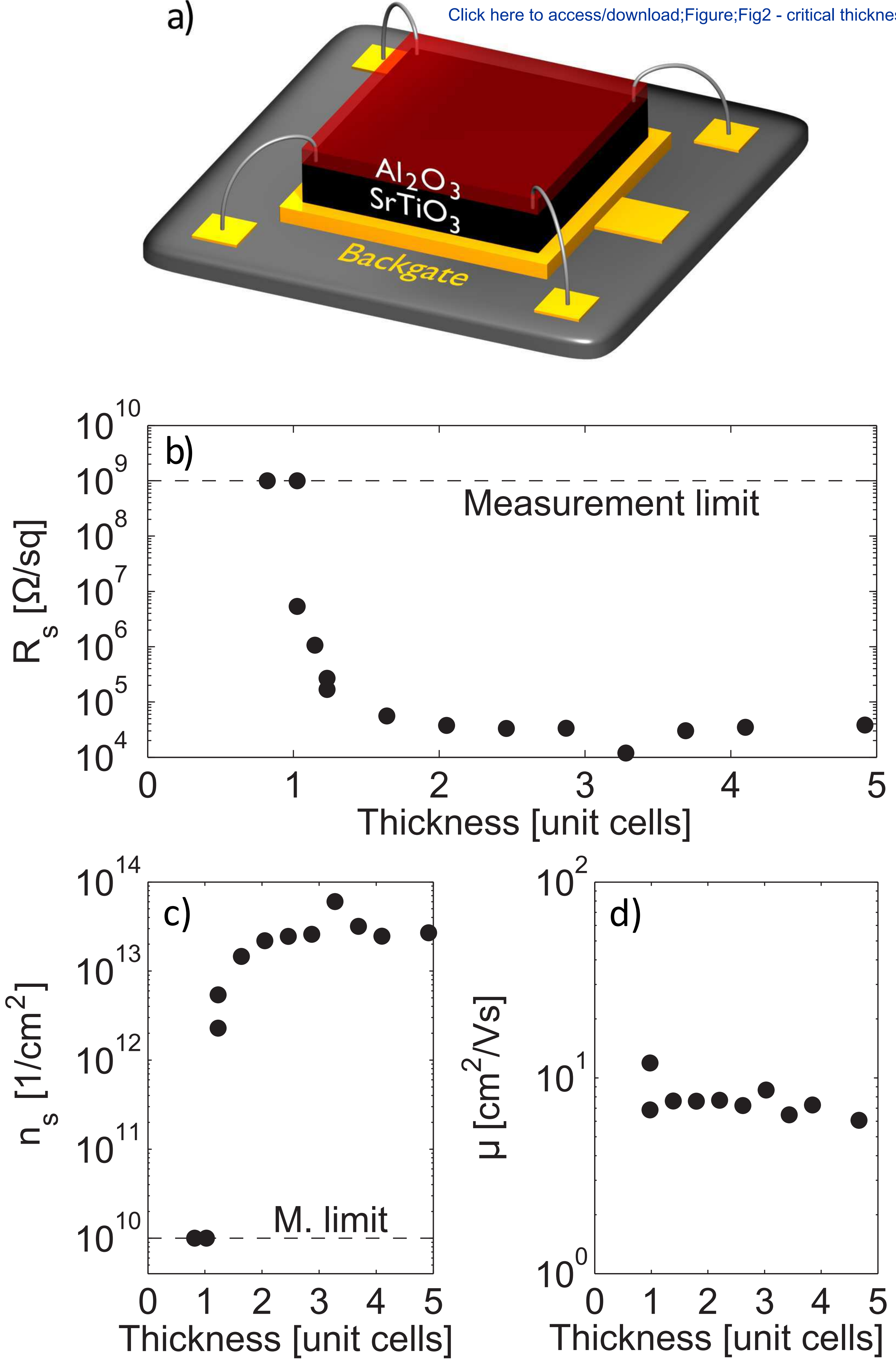

a)
Al2O3
SrTiO3
Backgate
b)
Measurement limit
Rs [Ω/sq]
Thickness [unit cells]
c)
M. limit
ns [1/cm2]
Thickness [unit cells]
d)
μ [cm2/Vs]
Thickness [unit cells]

Figure 3

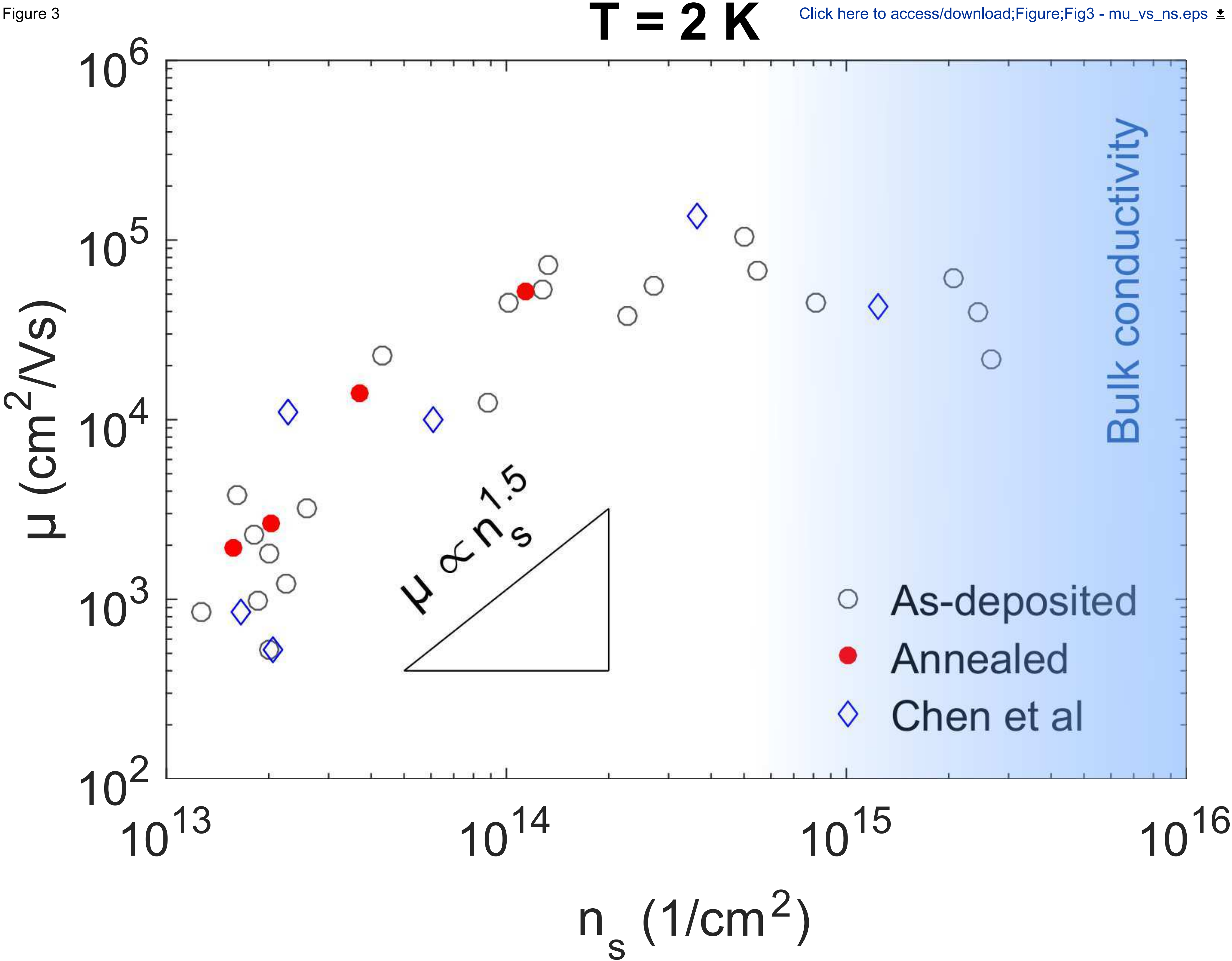

T = 2 K
10^6
10^5
10^4
10^3
10^2
μ (cm^2/Vs)
10^{13}
10^{14}
10^{15}
10^{16}
n_s (1/cm^2)
$\mu \propto n_s^{1.5}$
Bulk conductivity
As-deposited
Annealed
Chen et al

Figure 4

Click here to access/download;Figure;Fig4 - annealing.eps

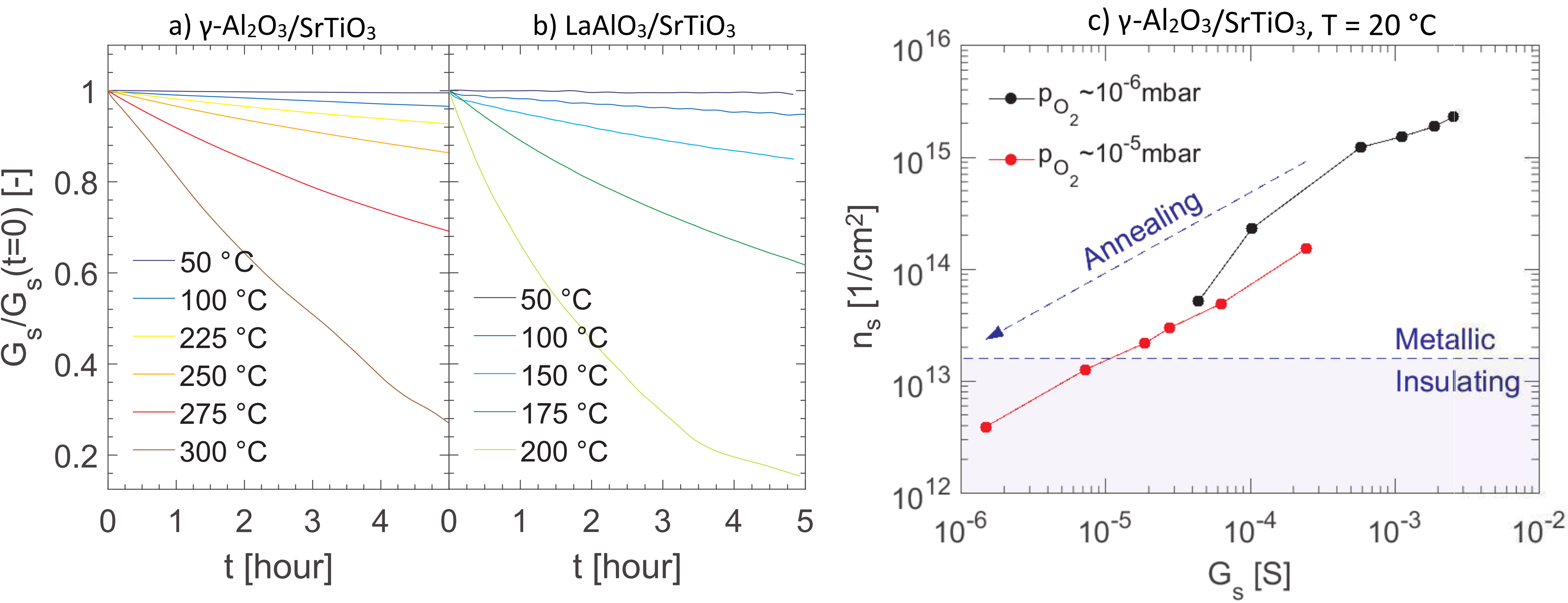
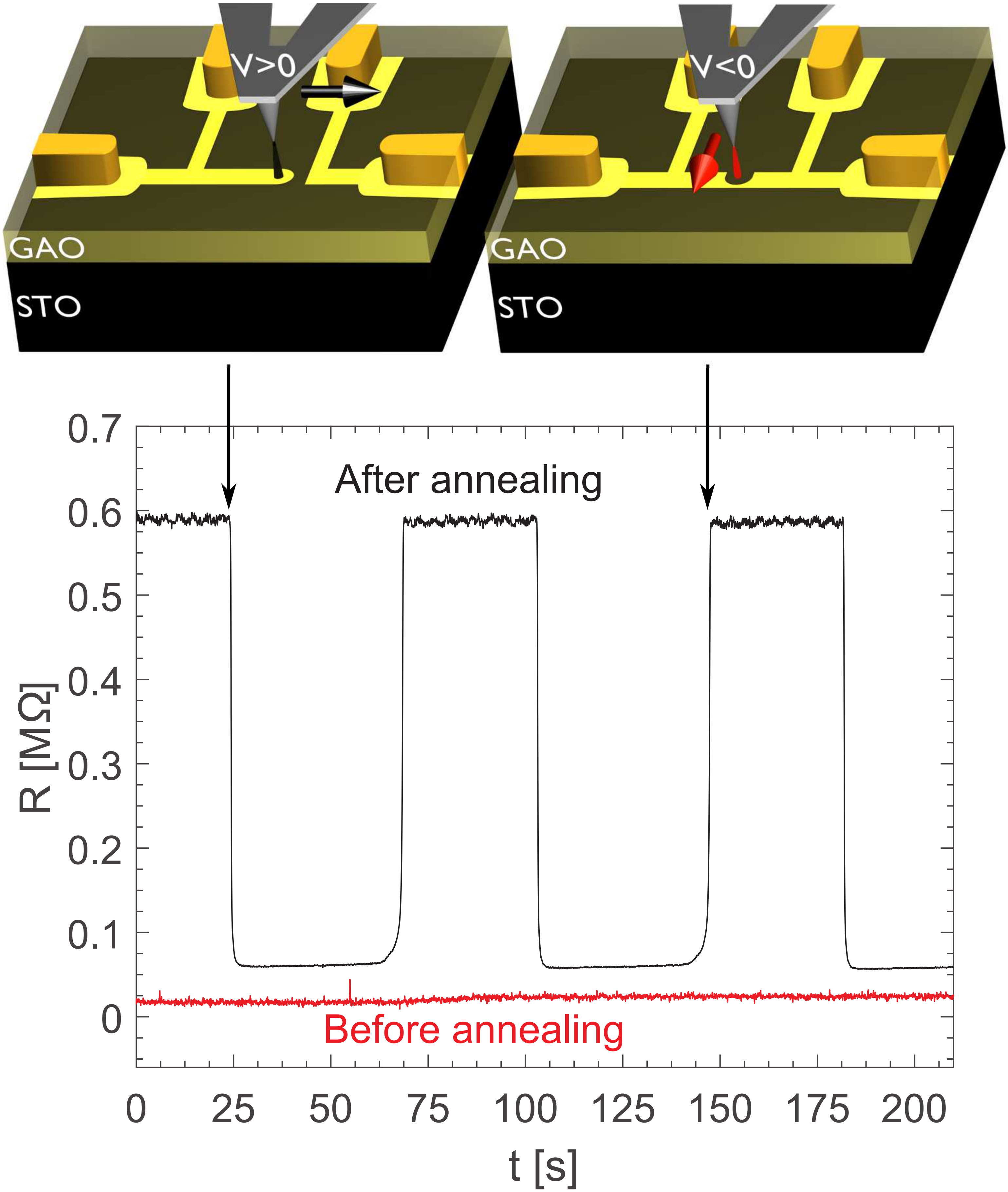


Figure 5

Click here to access/download;Figure;Fig5 - cAFM.eps



Name of Material/ Equipment	Company
$SrTiO_3$	Crystec
$LaAlO_3$	Shanghai Daheng Optics and Fine Mechanics Co.Ltd.
Al_2O_3	Shanghai Daheng Optics and Fine Mechanics Co.Ltd.
Chemicals and gases	Standard suppliers
Silver paste	SPI Supplies, Structure Probe Inc
Ultrasonicator	VWR
Wedge wire bonder	Shenzhen Baixiangyuan Science & Technology Co.,Ltd.
Pulsed laser deposition	Twente Solid State Technologies (TSST)
Resistance measurement setup	Custom made
Hall measurements	Cryogenics
Furnace	Custom made

Comments/Description

Single crystalline (001) oriented, 0.05-0.2 degree miscut angle

Single crystalline

Single crystalline

05001-AB, High purity silver paint
USC500D HF45kHz/100W

HS-853A Aluminum wire bonder
PLD from TSST with software version V3.0.29, equipped with a 248 nm KrF nanosecond laser (Compex Pro 205 F) from Coherent
Based on the following electrical instruments and custom written software:
Keithley 6221 DC and AC current source
Keithley 2182A nanovoltmeter
Keithley 7001 switch system with a matrix card
Keithley 6487 picoammeter
Based on the following electrical instruments and custom written software:
Keithley 2400 DC current source
Keithley 2182A nanovoltmeter
Keithley 7001 switch system with a matrix card
Custom written software control of a FTTF 500/70 tube furnace from Scandia Ovnen AS and a eurotherm 2216e temperature controller

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Title of Article: Tuning oxide properties by oxygen vacancy control during growth and annealing – the case of SrTiO3-based heterostructures

Author(s): Dennis V Christensen, Felix Trier, Merlin von Soosten, Yulin Gan, Yu Zhang, Simone Sanna, Yunzhong Chen, and Nini Pryds

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09 Nov 2018

Title: Tuning oxide properties by oxygen vacancy control during growth and annealing
Authors: Dennis V Christensen, Felix Trier, Merlin von Soosten, Yulin Gan, Yu Zhang, Simone Sanna, Yunzhong Chen, and Nini Pryds

Dear editor

Thank you for your recent communication regarding our submission JoVE58737. We greatly appreciate the overall positive comments received from the two reviewers, and we have modified the manuscript according to your as well as their suggestions. Point-by-point comments are found later in this document marked with blue.

Please do not hesitate to contact us for further clarification.

On behalf of all the co-authors,
sincerely,

Dennis Christensen

Editorial comments:

Changes to be made by the Author(s) regarding the written manuscript:

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3. Figure 4: Please use °C for temperature unit. Please include a space between all numbers and their corresponding units (i.e., 20 °C, 37 °C, etc.).

Author: Revised accordingly.

4. Please provide figures with higher resolution if possible.

Author: All figures are now provided in high quality.

5. Please revise the title to be more concise.

Author: The title has been shortened to "Tuning oxide properties by oxygen vacancy control during growth and annealing"

6. Please provide an email address for each author.

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Author: Revised accordingly.

8. Please revise the protocol text to avoid the use of any personal pronouns (e.g., "we", "you", "our" etc.).

Author: Revised accordingly.

9. Please revise the protocol to contain only action items that direct the reader to do something (e.g., "Do this," "Ensure that," etc.). The actions should be described in the imperative tense in complete sentences wherever possible. Avoid usage of phrases such as "could be," "should be," and "would be" throughout the Protocol. Any text that cannot be written in the imperative tense may be added as a "Note." Please include all safety procedures and use of hoods, etc. However, notes should be used sparingly and actions should be described in the imperative tense wherever possible.

Author: Revised accordingly.

10. Lines 100-105: The Protocol should contain only action items that direct the reader to do something. Please move the introduction about the protocol to the end of Introduction section.

Author: Revised accordingly.

11. Please simplify the Protocol so that individual steps contain only 2-3 actions per step and a maximum of 4

sentences per step. Use sub-steps as necessary.
Author: Revised accordingly.

12. Please add more details to your protocol steps. There should be enough detail in each step to supplement the actions seen in the video so that viewers can easily replicate the protocol. Please ensure you answer the "how" question, i.e., how is the step performed? Alternatively, add references to published material specifying how to perform the protocol action. Some examples:
Lines 119-123: Please specify the mass of substrates and volume of water/acidic solution added.
Author: Example of acid volume is added. The mass of the substrate (less important) follows directly from its size (more important), which is stated above.

Lines 125-126: Please specify again the volume of water used to wash.
Author: Revised accordingly

1.1.3: What type of device is used for thermal treatment?
Author: Revised accordingly

2.1: Please describe how this is done.
Author: Revised accordingly

13. Please include single-line spaces between all paragraphs, headings, steps, etc.
Author: Revised accordingly

14. After you have made all the recommended changes to your protocol (listed above), please highlight 2.75 pages or less of the Protocol (including headings and spacing) that identifies the essential steps of the protocol for the video, i.e., the steps that should be visualized to tell the most cohesive story of the Protocol.
Author: Highlighted in yellow

15. Please highlight complete sentences (not parts of sentences). Please ensure that the highlighted part of the step includes at least one action that is written in imperative tense.
Author: Highlighted accordingly

16. Please include all relevant details that are required to perform the step in the highlighting. For example: If step 2.5 is highlighted for filming and the details of how to perform the step are given in steps 2.5.1 and 2.5.2, then the sub-steps where the details are provided must be highlighted.
Author: Highlighted accordingly

17. Discussion: Please also discuss critical steps within the protocol.
Author: The most critical parts of the protocol are to get the temperature profiles and oxygen partial pressures right. This has been merged into the discussion.

18. References: Please do not abbreviate journal titles.

Author: Revised accordingly.

Reviewers' comments:

Reviewer #1:

Manuscript Summary:
The manuscript "Tuning oxide properties by oxygen vacancy control during growth and annealing - the case of SrTiO3-based heterostructures" by Christensen et al. describes experimental means to control and characterize the oxygen vacancy concentration and profile in SrTiO3-based 2DEG electron gases. The contribution is very interesting and suitable to be illustrated by video. The accompanying manuscript reads well and explains all experimental procedure clearly and in sufficient detail. Therefore, I am happy to recommend its publication.
Author: We thank the reviewer for the positive evaluation of the manuscript.

Minor Concerns:
While reading, I had a few minor issues that may be addressed by the authors:

End of first paragraph (lines 56, 57): I think it may be useful to generalize the first section also to defects beyond oxygen vacancies. They are of course the most prominent species, also the most relevant to this contribution, however, other defects such as cation vacancies, anti-site, extended defects, etc. can all cause strain fields, break symmetry and modify transport. Therefore, I think it is important to note that oxygen vacancy defects are not the only engineering tool available in oxides.
Author: The reviewer is certainly correct that other defects than oxygen vacancies may also play a very important role in determining the properties of oxides. Controlling these defects can therefore also be used to tune the properties. We have extended the sentences in question in the introduction to cover both oxygen vacancies as well as other defects. In addition, we have added the following sentence to the discussion: "It should, however, be noted that in some cases cation diffusion and variations in the defect configuration induced by the deposition or post-annealing can also be a desirable way to tune the oxide properties."

Line 67: Reference for opaqueness of SrTIO3 after reduction: Ref.2 refers to a 2017-paper - however, this phenomenon was of course observed already much earlier. I feel a proper reference to original literature should be added here.
Author: The change in color when introducing oxygen vacancies in SrTiO3 has been known for more than half a century, however, we have not been able to find the original reference. We therefore simply use one of the references already used in the manuscript, which also happens to show this change in the optical properties very clearly.

Protocol step 1.1.3.: Is it really to relax surface tension or to allow formation of smooth step terraces? Or is this what the authors mean?
Author: The annealing process is to bring the substrate surface into a low energy state. We have rephrased the sentence to "(..) to relax the substrate surface into a state with low energy"

Line 232-234: Do I understand correctly that if side-diffusion is determining the conduction state, this implies that the lateral distribution of defect may vary over the sample? Hence, while the edges will be more oxidized than the center of the sample?
Author: The oxidation in the case of GAO/STO can occur from the bottom and from the sides. This will depend on the boundary conditions of the sample, i.e. whether is it exposed air from the sides and bottom or are there some parts covered such as when mounted on a chip carrier. Therefore, the relative contributions of oxidation from the sides and the bottom may vary, and a systematic study on this under various conditions is missing. We have observed earlier some gradient in the sheet resistance along the interface pointing towards the outer parts are

being somewhat more oxidized as the reviewer correctly mention.

In the same section, I would also recommend to add a clearer statement that the actual state controlled via annealing depend on three parameters, i.e. temperature, annealing time and atmosphere (I assume).
Author: The reviewer is correct, and we have now added the following sentence to the manuscript: "Here, the final state after annealing is determined by three parameters: annealing time, temperature and atmosphere".

Figures: Please check if GAO (used in the figures instead of g-Al2O3) is properly defined in the main text (figure captions).
Author: Excellent point. We have added the abbreviation GAO in the caption for figure 5.

Reviewer #2:

Manuscript Summary:
The authors deal with the problem of oxygen content fine tuning in strontium titanate based heterostructure, proposing two different (but not alternative) approaches based on controlling the growth conditions and on oxygen thermal annealing respectively. The paper, mainly based on already published results (suitably cited), is clear and well-written and of some interest for the community. For such reason, I recommend it for publication in JOVE.
Author: We thank the reviewer for the positive evaluation of the manuscript.

Figure 1:

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Title: Metallic and Insulating Interfaces of Amorphous SrTiO3-Based Oxide Heterostructures

Author: Yunzhong Chen, Nini Pryds, Josée E. Kleibeuker, et al

Publication: Nano Letters

Publisher: American Chemical Society

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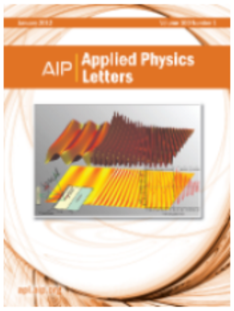

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Author(s):	Dennis V Christensen, dechr@dtu.dk Felix Trier, fetri@dtu.dk Merlin von Soosten, mervso@dtu.dk Yulin Gan, yuga@dtu.dk Yu Zhang, yuazha@dtu.dk Simone Sanna, sime@dtu.dk Yunzhong Chen, yunc@dtu.d

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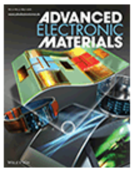

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