This talk regards two-dimensional electron gases that are formed at the STO surface and interfaces. I will actually present a few data regarding different experiments and involving several people at CNR SPIN and University of Napoli with the cooperation of a group at Oak Ridge National Laboratory, mainly involved in TEM measurements.
A 2DEG is basically characterized by a quantum well where electrons coming from some donor state are trapped. One of the still debated issues regarding STO/LAO interfaces is just the nature of the donor states. In the electronic reconstruction models, electrons come from the valence band of the polar layer, that is lifted above the Fermi level by the built-in potential due to the polarization. But one may also consider defects as donors. These can be due to disorder, but in this talk I will focus on the effect of oxygen vacancies.
2DEG at STO interfaces
Polar-non polar heterostructures

A. Brinkman, et al., Nature Mat. 2007

10^{-6} \text{ mbar} \rightarrow \text{Oxygen vacancies dominate!}

Reversing the argument:
Can we demonstrate the formation of a 2DEG in STO as exclusively due to oxygen vacancies?
Can we present interfaces where the role of oxygen vacancies appears as negligible?

Oxygen vacancies can actually dominate the transport properties of samples that are fabricated at too low oxygen partial pressure. In that case we can even get bulk conductivity.
In order to verify whether oxygen vacancies can determine 2DEG formation, we performed an experiment regarding the free surface of STO. The motivation stems from a recent work of ARPES on cleaved STO crystals, which indicated that a robust 2DEG is formed with properties independent on bulk carrier density. I will compare the results with data concerning oxygen vacancies at the interfaces.
2DEG at STO surfaces after low temperature UHV treatments

Single crystal (100) SrTiO$_3$ with TiO$_2$ termination plane
Selective etching procedure
Un. Twente, APL 73, 2920 (1998)

We started with TiO$_2$ terminated STO crystals...
Thermal treatment

Annealing in oxygen at 850°C
Highly insulating
Surface charging: no LEED pattern

Sample A

Annealing in UHV at 250-350°C
Bulk insulating (transparent)
1x1 reconstruction

Sample B

Annealing in UHV at 900°C
Bulk conducting (shiny black)
2x1 reconstruction

$P_0 = 5 \times 10^{-11} \text{ mbar}$

...and performed a series of thermal treatments.
Here is the main result. The $dI/dV$ curves of the different samples show a remarkable difference. I will stay at the phenomenological level, by saying that the red curve is consistent with the idea that a high temperature treatment determines conducting bulk and insulating surfaces, consistently with several previous reports. The blue curve is instead consistent with the idea that the surface itself is conducting, that is, it possesses a finite density of occupied states at the Fermi level.
The photoemission from the Ti3p triplet essentially confirms the existence of occupied Ti3+ states, that constitute the conduction band, and since the experiment is surface-sensitive, it also demonstrate the surface confinement within the nm scale.

Since we have no other contamination, the evolution of oxygen is the only possible source of doping.
The investigation of the VB by photoemission also clarifies the transport mechanism. The left part of the $dI/dV$ plots mainly carry information on the occupied DOS of STO. It is suggestive to compare between XPS spectra and $dI/dV$ of the different samples; the data indicate that the surface defect states (blue curve) are source of enhanced junction conductance.
Oxygen Vacancies at STO surfaces

Out of equilibrium:
flux of vacancies through the surface into the bulk

Equilibrium:
\( c_s > c_b \)

Message
Local doping by Oxygen vacancies CAN determine a 2DEG at STO surface

The results are consistent with a picture where the Gibbs energy of oxygen vacancies at the surface is lower, as also deduced by computation. When we raise the chemical potential of the environment, the vacancies are introduced and at the equilibrium they reach a higher surface concentration. Finally, if we choose the right conditions, we can actually form a 2DEG due to local doping.
Now we turn to the issue of 2DEG formation at interfaces STO interfaces. I will consider on the same foot both STO/LAO and STO/LGO, that in our experience share most relevant physical properties.
If we want to investigate the oxygen content at interfaces we need a tool that is sensitive to chemical properties of samples. We resorted to EELS.
Oxygen vacancy stoichiometry

$\delta = 0 \text{ at } 1 \times 10^{-3} \text{ mbar}$

*but* 2% maximum error $\rightarrow 0.12 \text{ e}^-/\text{cell}$

C. Cantoni, et al. ADV. MAT. 2012

Here are some results. In the upright panel, the integrated O K scan profile confirms the sensitivity of EELS to determine oxygen stoichiometry with spatial resolution at the atomic level. However, to get the quantitative information it is necessary to consider with due care the O-K ELNES spectra, since not all the components are directly connected to oxygen stoichiometry. Here I show the depth profile of the “c” line intensity, which is constant across the sampled region within STO.

By quantitatively analyzing the data, we get the best estimation of vacancies stoichiometry $d = 0$. This fact is a support to the idea that in a conductive sample grown at $1 \times 10^{-3}$ mbar the 2DEG is not populated by electrons provided by oxygen vacancies. However, the experimental maximum error is 2%. This means that the required information is very close to the experimental sensitivity.

We then need further confirmation to conclude that the 2DEG at interfaces can be populated even in absence of oxygen vacancies.
Further limiting the role of oxygen vacancies

Deposition at high oxygen pressure

**Drawback**
The plasma plume is stopped by the buffer gas
The energy of impinging species is reduced
The surface mobility of adatoms drops

Energetic particles can favor 2D growth of oxide thin films through an island break-up mechanism with prompt insertion, at very low coverage, and enhanced surface diffusion, above 50% monolayer coverage.

growth conditions may be bad!

To this aim we considered growth at very high oxygen pressure, in spite of the possible drawbacks.
In our previous work we demonstrated that 2D growth of LAO and of LGO can be achieved even at 10-1 mbar, but samples were insulating.
We decided to analyze the growth dynamics by resorting to plume diagnostics such as fast photography and time resolved spectroscopy. Here are some results.

At 10-1 mbar the plume propagates in a shock wave regime and it halts after travelling about 35 mm away from the target. Effects of the buffer gas are: the species loose energy by collisions and reach the substrate with low kinetic energy; instead, they possess high internal energy; moreover, the oxygen supersaturation is increased by the strong compression of the gas on the plume front edge. However, care must be paid to the target-substrate distance.
By optimizing the distance, conductive samples can be realized. At the given conditions, it is generally agreed that the content of oxygen vacancies in samples is marginal.
In conclusion, our measurement demonstrate that oxygen vacancies can be collected at the free surface of STO crystals and there determine the formation of a 2DEG. In the case of interfaces, on one hand we know that oxygen vacancies can affect the conductivity; but on the others, we proved that at standard deposition conditions they don’t accumulate at the interface; and that it is possible to grow conducting interfaces in extremely oxidizing conditions. In other words, observation of a 2DEG doesn’t seem to imply the presence of oxygen vacancies.
Conclusions

1. **Oxygen vacancies can determine the formation of a 2DEG at the STO free surface**

\[ \text{Local } V(O) \rightarrow 2\text{DEG} \]

2. **STO interfaces**

- \(10^{-3} \text{ mbar} : \) \(V(O) = 0 \) (EELS)
- \(10^{1} \text{ mbar} : \) conductive interfaces

\[ 2\text{DEG} \not\rightarrow \text{Local } V(O) \]

Our measurement demonstrate that oxygen vacancies can be collected at the free surface of STO crystals and there determine the formation of a 2DEG. In the case of interfaces, on one hand we know that oxygen vacancies can affect the conductivity; but on the others, we proved that at standard deposition conditions they don’t accumulate at the interface; and that it is possible to grow conducting interfaces in extremely oxidizing conditions. In other words, observation of a 2DEG doesn’t seem to imply the presence of oxygen vacancies.

In conclusion, it is apparent that different forms of electron confinement (even in terms of different donor states) at the surface of SrTiO\(_3\) lead to essentially the same 2DEG.
MODA LAB: an integrated laboratory for fabrication of oxide films and for surface analyses