Optical Second Harmonic Generation from $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces with different in-plane anisotropies

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Oxide growth with semiconductor-like accuracy allows the fabrication of atomically precise thin films and interfaces displaying a wide range of phases and functionalities that are absent in the corresponding oxide bulk materials. Among the other properties it was found that a two-dimensional electronic gas is formed under some circumstances at the $\text{LaAlO}_3/\text{SrTiO}_3(001)$ interface separating two typical insulating perovskite crystals. The origin of this conducting state has been discussed at length, since different doping mechanisms can act in these material systems. Many experimental results point to the so-called *polar catastrophe* scenario as the principal mechanism driving the formation of the two-dimensional electronic gas. According to this mechanism, the existence of an interfacial polar discontinuity is the key ingredient to drive an electronic reconstruction at the $\text{LaAlO}_3/\text{SrTiO}_3(001)$ interface and the consequent formation of a two-dimensional electron gas. This simple picture has been often questioned by the existence of material systems whose interface are predicted being non-polar according to the simplistic ‘ionic’ limit but that display an electrical behavior analogous to that of $\text{LaAlO}_3/\text{SrTiO}_3(001)$ interfaces. This is the case of the $\text{LaAlO}_3/\text{SrTiO}_3(110)$, i. e., a $\text{LaAlO}_3/\text{SrTiO}_3$ interface with a different in-plane orientation. It is evident that to solve such kind of controversies a detailed investigation of the polar or non-polar state of these interfaces is needed, although this is not simple for the lack of experimental tools that are specifically sensitive to interfacial polarity. Here we apply Optical Second Harmonic Generation to investigate $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces with different in-plane orientations to bridge this gap. By means of a detailed analysis of the symmetries of the Second Harmonic signal generated from these interfaces, we show that the $\text{LaAlO}_3/\text{SrTiO}_3(110)$ interface is strongly polar.

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I. INTRODUCTION

Since the discovery of a two-dimensional electron gas (2DEG) formed at the interface between the two band insulators LaAlO_3 (LAO) and SrTiO_3 (STO),¹ a worldwide research effort has unveiled a surprising array of unexpected phenomena in this system, ranging from tunable conductivity to two-dimensional superconductivity.²

The origin of the interfacial charge carriers in this material system immediately emerged as a highly debated question, since different doping mechanisms can be at play in this oxide heterostructure. A large body of evidence points to the so-called *polar catastrophe* scenario as the mechanism driving the formation of the conducting state.^{3–10} According to this picture, in the ideal ionic limit, the $\text{LAO}/\text{STO}(001)$ interface is formed by an alternate stacking of $[\text{LaO}]^{+1}[\text{AlO}_2]^{-1}$ atomic planes over $[\text{SrO}]^0[\text{TiO}_2]^0$, as displayed in panel (a) of Fig. 1. As shown in the latter panel this leads to planes with an alternating net charge (σ) that in turn, by using a simple electrostatic model, produces a non-negative electric

field (E) and hence an electric potential (V) diverging with LAO thickness. For sufficiently thick LAO films, this potential must be relaxed by an interfacial reconstruction. The latter could be ionic, involving lattice distortions and/or some degree of cationic mixing, but it has been proposed that an electronic reconstruction may instead be the dominating effect, involving a transfer of electrons from LAO to STO (see lower part of Fig. 1(a)), likely into the STO Ti $3d$ conduction band close to the interface, thus giving rise to the interfacial conduction.³

However, many experimental observations have highlighted the presence of point defects, such as cationic intermixing across the interface or oxygen vacancies, able to introduce a chemical doping even in absence of electronic reconstruction.^{3,11–14} Recently the oxygen-vacancy mechanism has attracted a renewed attention because of the observation that a two-dimensional gas is formed at LAO/STO interfaces even when the LAO film is grown in amorphous phase, so as to rule out polar-discontinuity-related mechanisms.^{15,16} However, while oxygen vacancies may explain the formation of a n-type

interface, they can not be used for interpreting the formation of a p-type interface that was predicted since the beginning by the ‘polar catastrophe’ model and whose elusive nature has for long time puzzled the scientific community. However, very recently, evidences of the formation of a p-type interface have been reported that provide a very strong support to the ‘polar catastrophe’ model.¹⁷

Another interesting perspective on the ‘polar catastrophe’ mechanism is represented by a threshold-driven formation of a 2DEG at the LAO/STO(110) interface, that is an interface formed by depositing LAO atomic layers over (110)-oriented STO substrates, as shown in panel (b) of Fig. 1.^{18,19} According to the same ‘ionic’ picture, the LAO/STO(110) interface is formed by a sequence of $[O_2]^{4-}$ – $[LaAlO]^{4+}$ planes over $[O_2]^{4-}$ – $[SrTiO]^{4+}$ planes that displays no polar discontinuity. To complete this picture the LAO/STO(111) interface displays a polar discontinuity too, since it is formed by an alternate sequence of $[Al]^{3+}$ – $[LaO_3]^{3-}$ over $[Ti]^{4+}$ – $[SrO_3]^{4-}$ planes (see panel (c) of Fig. 1). In fact, this interface shows the same threshold insulator-to-metal transition as the other two interfaces. Additionally, (110) interfaces allows changing the electronic subband hierarchy with respect to that of (001) interfaces²⁰ enabling a distinctive electrostatic gate dependence of 2D superconductivity and Rashba spin-orbit fields.²¹

At first sight, this result may appear to challenge the ‘polar catastrophe’ picture. However, recent theoretical studies show that at the LAO/STO(110) interface the STO surface is not an ideal polar stoichiometric surface, but the ground state is characterized by a buckled TiO termination as shown in Fig. 1(e) of Ref. 19. This predicted structural distortion leads again to an interfacial polar discontinuity, that in turn drives the electronic reconstruction through the same ‘polar catastrophe’ mechanism described before for the (001) interface.

In view of all these considerations, an important question arises. Is there an experimental tool suitable to confirm this theoretical prediction, or in other words to probe the existence of an interfacial polarity at the (110) interface?

In a series of works,^{5,23–31} we have demonstrated that Optical Second Harmonic Generation (SHG) from interfaces is an ideal tool for sensing the interfacial properties of oxide heterostructures. SHG is a nonlinear optical technique based on the detection of doubled-frequency photons in the light reflected or transmitted from the interface. When the illuminated materials are centrosymmetric, SHG is generated with high efficiency only in the thin interfacial regions in which the inversion symmetry is broken. In general, the source of the interfacial SHG is of two types: ‘local’ and ‘non-local’, with the latter strongly dependent on the dielectric and electric-field discontinuity at the interface.³² The ‘non-local’ contribution cannot be affected by the interfacial reconstruction since the latter does not change the macroscopic dielectric properties of the interface. On the contrary the ‘local’ or ‘electric-

FIG. 1. Atomic picture of $LaAlO_3/SrTiO_3$ interface on (001) $SrTiO_3$ (a), (110) $SrTiO_3$ (b), and (111) $SrTiO_3$ (c). In panel (a) it is shown a simple electrostatic model explaining the setting up of an electrostatic potential across the LAO film that diverges by increasing the LAO thickness. This potential increase may be avoided through an interfacial reconstruction, either electronic or structural. In the lower part of panel (a) the hypothesis of an electronic reconstruction is illustrated.

dipole’ term is different from zero because the interface layer has a structure with no inversion symmetry or ‘polar’ that is strongly affected by possible interfacial reconstructions, either structural or electronic in nature. In particular, an inhomogeneous electronic reconstruction leads to the build-up of an electric field across the interface layer that breaks the symmetry.²⁸

This polar asymmetry or ‘polarity’ is then felt by all the electrons present at the interface and is reflected in the SHG signal that can be regarded as a ‘weighted average’ of this degree of polar asymmetry with a weight given approximately by the electron polarizability at optical frequencies. An interesting aspect of SHG is that all interfacial electrons, either mobile or localized, may contribute to it. In our previous works on LAO/STO, we have shown that the interfacial polarity, as sensed by SHG, changes dramatically before the onset of conductivity, thus highlighting the important role of charges which

are injected at the interface but become localized.^{5,23}

In the present work, we have used SHG to analyze the LAO/STO interface in a set of samples with different STO orientations and LAO thicknesses aimed at investigating experimentally the presence or absence of a polar asymmetry at these interfaces, before and/or after the onset of conduction. This is important for a better understanding of the mechanisms acting at these interfaces and leading to their electronic reconstruction. Given the in-plane anisotropy of the LAO/STO(111) and LAO/STO(110) interfaces we measure the SHG signal as a function of the linear input and output light polarization, and as a function of the angle between the incidence plane and the interface principal axis.

II. THEORY

In an SHG experiment, the frequency of the incident light is doubled by the interaction with the material. In general this non-linear interaction can be represented by a non-linear term of the polarization $\mathbf{P} = \mathbf{P}^L + \mathbf{P}^{NL}$ induced in the material. This polarization will then be the source of re-emitted light in the wave-equation, according to the Maxwell's equations. Let us neglect the linear term $\mathbf{P}^L$, which, in the reflection geometry used here, just gives the usual reflected light. The non-linear term of the polarization is, in general, a function of the incoming electro-magnetic field. In most cases, it can be expanded in power series. For SHG, the first non-linear term of this series, the quadratic term, is written under the dipole approximation as:

$$P_i^{NL}(2\omega) = \varepsilon_0 \chi_{ijk}^{(2)}(\omega, 2\omega) E_j(\omega) E_k(\omega). \quad (1)$$

Here ε_0 is the vacuum dielectric constant, $\mathbf{E}(\omega)$ is the incoming electric field oscillating at ω frequency, and $\tilde{\chi}^{(2)}$ is the second-order susceptibility tensor that couples the fundamental and the second harmonic fields. The indices (ijk) assume the values of the system coordinates (xyz) and a sum is assumed over repeated indices. It is easy to show that if the material is inversion symmetric, the $\tilde{\chi}^{(2)}$ tensor vanishes identically. This implies that in an interface between two centro-symmetric materials and under the dipole approximation, the SHG signal can come *only* from the interfacial layer or the upper surface exposed to the air, where the inversion symmetry is naturally broken. Because the LAO film thickness is very small as compared to the optical wavelength, the contribution to SHG of the LAO upper surface would be spatially indistinguishable from the SHG beam generated at the LAO/STO interface and hence this contribution should be taken into account. However, in our past works,²³ we have clearly demonstrated that the source for the SHG signal solely resides in a very thin layer close to the LAO/STO interface. This was ascribed to the much wider LAO bandgap and hence to the larger distance of the SHG photon energy from the material resonance. For

this reason, in the following, we will consider as source of the SHG signal exclusively the LAO/STO interface and the STO upper surface in the case of substrates. In the following we also neglect multipolar contributions to the SHG from the bulk which of course do not depend on the thickness of the LAO layer. The reflection geometry that we use in our experiment is suitable to strongly reduce these contributions. We note that these contributions display an in-plane symmetry that is completely different from that of the dipolar contribution. This symmetry is often exploited to distinguish these two different SHG sources. As we will show our data agree very well with the in-plane symmetry envisaged for the dipolar term only and hence we conclude that the multipolar term is negligibly small. This is probably the consequence of the general finding that crystalline solids have a surface layer structure short of inversion symmetry and hence the electric-dipole contribution dominates.³² For all these reasons we will not consider it further in our analysis.

The $\tilde{\chi}^{(2)}$ tensor has 27 elements. To exploit the crystal symmetries we first write it in the crystal principal axes (abc) coordinate system, where most of the elements are vanishing by symmetry. In absence of structural reconstructions, our three interfaces with (001), (110), and (111) orientations belong to the symmetry groups, $4mm$ (C_{4v} in the Schoenflies notation), $mm2$ (C_{2v}) and $3m$ (C_{3v}), respectively. It is worth noting that structural in-plane reconstructions have been observed at both (110) and (111) interfaces.^{33,34} However these structural reconstructions involve only few atomic cells and hence do not affect the global symmetry of the interface on the macroscopic scale that is probed by SHG.

The non-vanishing terms of $\tilde{\chi}^{(2)}$ for the three symmetry groups are tabulated in literature³⁵ and reported for reader's convenience in Tab. I.

It is worth noting that the optical fields in Eq. 1 are written *inside* the material. We should then write them as a function of the external fields, by resorting to the Fresnel tensor $\tilde{L}$, that is a two-indices tensor. This tensor couples the transmitted $\mathbf{E}_t$ and incident $\mathbf{E}_i$ optical fields at the interface according to the following relationship: $\mathbf{E}_t = \tilde{L} \cdot \mathbf{E}_i$. For a cubic crystal, as SrTiO₃, the Fresnel tensor is diagonal and remains so independently of any applied rotation. Therefore we may write it in the laboratory frame. In that system, it is possible to write the diagonal terms of $\tilde{L}$ as a function of the input-output angles and the two indices of refraction across the sample surface exposed to air:

$$\begin{cases} L_{xx} = \frac{2n_1 \cos \beta_2}{n_2 \cos \beta_1 + n_1 \cos \beta_2} \\ L_{yy} = \frac{2n_1 \cos \beta_1}{n_1 \cos \beta_1 + n_2 \cos \beta_2} \\ L_{zz} = \frac{2n_1^2 \cos \beta_1}{n_2(n_2 \cos \beta_1 + n_1 \cos \beta_2)} \end{cases}, \quad (2)$$

where β_1 is the incidence angle set in the experiment. n_1 and n_2 are the indices of refraction of air and STO,

FIG. 2. Experimental geometry. The laboratory reference system has xyz coordinates, with xz incidence plane. The fundamental light has 800 nm wavelength (red line) and the SHG light emitted from the sample has a 400 nm wavelength (blue line). Note that n_1 is the refractive index of air, while n_2 is that of STO and it is assumed to be the same across all the interface and the ultrathin LAO layer (see main text for details on this assumption). The incidence angle is β_1 and the refracted angle into the LAO/STO medium is β_2 . The angle ϕ between the laboratory $\hat{x}$ direction and the crystal principal axis $\hat{a}$ may be varied by rotating the sample around the normal to its surface, while different input and output configurations can be set by using a polarizer and an analyzer (made of a half-waveplate plus a polarizer). Here p is the direction parallel to the incident plane, s is parallel to the sample surface and d is at 45° between the two. The general polarization unit-vector $\hat{e}$ forms an angle α with respect to the p direction in the ps plane.

respectively, the latter depending only on the frequency ω for a given material. In the last sentence an important assumption is implied, i.e., we are treating the interface and the ultrathin LAO layer as being embedded in STO and hence the refractive index of the entire material system is set equal to n_2 (see Refs. 23 and 26 for a more detailed discussion on this point). The angle β_2 of the transmitted ray is a function of β_1 and the refractive indices $n_{1,2}$ through the Snell law. Therefore, the value of a specific tensor element L_{ii} will depend only on the frequency, which is in our case either ω or 2ω . Therefore, in the following we make use of a simplified notation: $L_i(\omega) = L_{1i}$ and $L_{ii}(2\omega) = L_{2i}$.

By resorting to the Fresnel tensor, we may define an effective $\tilde{\chi}^{(2)}$ tensor (in the following we will remove the superscript (2) for simplicity) that links the output SHG

field to the input optical field and contains all the information about the geometry of the incident and emitted fields. Only the amplitude of the latter will be left outside. The effective $\tilde{\chi}^{\text{eff}}$ tensor will be than a function of the frequency and the polarization of the incident and emitted light:

$$\chi_{\alpha_{\text{in}}, \alpha_{\text{out}}}^{\text{eff}} = e_{\alpha_{\text{out}} i}^{(2\omega)} L_{2i} \chi_{ijk}(\omega, 2\omega) L_{1j} L_{1k} e_{\alpha_{\text{in}} j}^{(\omega)} e_{\alpha_{\text{in}} k}^{(\omega)}, \quad (3)$$

where $\hat{e}$ are the unit vectors representing the direction of the incoming and outgoing fields and the angles α_{in} and α_{out} the corresponding angles with respect to the p direction, as depicted in Fig. 2: $\alpha = 0^\circ, 90^\circ, 45^\circ$ correspond to the p , s and d directions, respectively.

The emitted SHG light intensity is proportional to the square modulus of the emitted SHG electric field, and thus it will be in turn proportional to the square modulus of $\tilde{\chi}^{\text{eff}}$. So, for a given choice of the input and output polarization angles, we measure $|\tilde{\chi}^{\text{eff}}|^2$ and hence we may extract the elements of $\tilde{\chi}$. We note that in our measurements we have an arbitrary scaling factor (let us call it A), due to the response of the experimental setup. In general, we can write that the measured SHG intensity, I_{SHG} , is given by:

$$I_{\text{SHG}} = A |\tilde{\chi}^{\text{eff}}|^2. \quad (4)$$

The A factor is the same for all measurements if the experimental geometry, including the beam intensity, is not varied, as we did in our experiment. For this reason, in the following, we will not consider further the parameter A .

According to the geometry sketched in Fig. 2, we have $\hat{e} = \hat{p} \cos \alpha + \hat{s} \sin \alpha$ for both input and output polarizations. Moreover, for the input polarization we have $\hat{p} = \hat{x} \cos \beta_1 + \hat{z} \sin \beta_1$ and $\hat{s} \equiv \hat{y}$. The same holds for the output polarizations, but with a reversed sign for the p_x component. Therefore we have:

$$\hat{e}^{\text{in}} = \begin{pmatrix} \cos \alpha_{\text{in}} \cos \beta_1 \\ \sin \alpha_{\text{in}} \\ \cos \alpha_{\text{in}} \sin \beta_1 \end{pmatrix}; \hat{e}^{\text{out}} = \begin{pmatrix} -\cos \alpha_{\text{out}} \cos \beta_1 \\ \sin \alpha_{\text{out}} \\ \cos \alpha_{\text{out}} \sin \beta_1 \end{pmatrix} \quad (5)$$

Thus, for the input waves we may write:

$$\begin{aligned} \tilde{L}_1 \cdot \hat{e}^{\text{in}} &= \begin{pmatrix} L_{1x} & 0 & 0 \\ 0 & L_{1y} & 0 \\ 0 & 0 & L_{1z} \end{pmatrix} \begin{pmatrix} e_x^{\text{in}} \\ e_y^{\text{in}} \\ e_z^{\text{in}} \end{pmatrix} \\ &= \begin{pmatrix} L_{1x} \cos \alpha_{\text{in}} \cos \beta_1 \\ L_{1y} \sin \alpha_{\text{in}} \\ L_{1z} \cos \alpha_{\text{in}} \sin \beta_1 \end{pmatrix} \end{aligned} \quad (6)$$

For the output waves we obtain an analogous formula by applying the following substitutions $L_1 \rightarrow L_2$, $\alpha_{\text{in}} \rightarrow \alpha_{\text{out}}$, and by changing the sign of the x coordinates.

TABLE I. Non-vanishing $\tilde{\chi}^{(2)}$ elements in different symmetries

Symmetry	Non-vanishing elements
$4mm (C_{4v})$	$xxz = xzx = yzy = yzz$ $zxx = zyy$ zzz
$mm2 (C_{2v})$	$xxz = xzx$ $yzy = yzz$ zxx zyy zzz
$3m (C_{3v})$	$xxz = xzx = yzy = yzz$ $zxx = zyy$ zzz $yyy = -yxx = -xxy = -xyx$

The elements $\chi_{\alpha_{in}, \alpha_{out}}^{\text{eff}}$ can be more easily calculated in the crystal reference system. Therefore we rotate the vectors $\tilde{L}_1 \cdot \hat{e}^{\text{in}}$ and $\tilde{L}_2 \cdot \hat{e}^{\text{out}}$ in the crystal reference frame and indicate them with $\mathbf{R}^{\text{in}}$ and $\mathbf{R}^{\text{out}}$, respectively. It is worth noting that in doing this we can leave unchanged the expressions for the Fresnel factors since they are invariant under any rotation. By using the rotated vectors, Eq. 3 may be rewritten as:

$$\chi_{\alpha_{in}, \alpha_{out}}^{\text{eff}} = R_{\alpha_{out}i}^{\text{out}} \chi_{ijk}(\omega, 2\omega) R_{\alpha_{in}j}^{\text{in}} R_{\alpha_{in}k}^{\text{in}} \quad (7)$$

In the case of an incidence angle $\beta_1 = 45^\circ$ we may calculate the $\mathbf{R}^{\text{in}, \text{out}}$ elements and obtain the Tabs. II and III.

TABLE II. INPUT ELEMENTS

$\mathbf{R}^{\text{in}}$	p	s	d
x	$\frac{1}{\sqrt{2}} L_{1x} \cos \phi$	$-L_{1y} \sin \phi$	$\frac{1}{2} L_{1x} \cos \phi - \frac{1}{\sqrt{2}} L_{1y} \sin \phi$
y	$\frac{1}{\sqrt{2}} L_{1x} \sin \phi$	$L_{1y} \cos \phi$	$\frac{1}{2} L_{1x} \sin \phi + \frac{1}{\sqrt{2}} L_{1y} \cos \phi$
z	$\frac{1}{\sqrt{2}} L_{1z}$	0	$\frac{1}{2} L_{1z}$

By substituting the elements of Tabs. II and III in Eq. 7 we may find the expression of $\chi_{\alpha_{in}, \alpha_{out}}^{\text{eff}}$ for different polarization combinations. By exploiting the equality of some components, as reported in Tab. I, we obtain the following expressions for all the non-vanishing polarization combinations. Some of them are redundant regarding the information they carry on the elements of the $\tilde{\chi}$ tensor. Therefore, we may choose a set of special polarization

TABLE III. OUTPUT ELEMENTS

$\mathbf{R}^{\text{out}}$	p	s	d
x	$-\frac{1}{\sqrt{2}} L_{2x} \cos \phi$	$-L_{2y} \sin \phi$	$-\frac{1}{2} L_{2x} \cos \phi - \frac{1}{\sqrt{2}} L_{2y} \sin \phi$
y	$-\frac{1}{\sqrt{2}} L_{2x} \sin \phi$	$L_{2y} \cos \phi$	$-\frac{1}{2} L_{2x} \sin \phi + \frac{1}{\sqrt{2}} L_{2y} \cos \phi$
z	$\frac{1}{\sqrt{2}} L_{2z}$	0	$\frac{1}{2} L_{2z}$

combinations that allow to extract all the independent components of $\tilde{\chi}$. In the Sec.IV all the sets of chosen combinations for the different symmetries are explicitly reported.

A. 4mm symmetry

$$\begin{aligned}
\chi_{ss}^{\text{eff}} &= \chi_{ps}^{\text{eff}} = 0 \\
\chi_{sp}^{\text{eff}} &= \frac{1}{\sqrt{2}} L_{2z} L_{1y}^2 \chi_{zxx} \\
\chi_{ds}^{\text{eff}} &= \frac{1}{\sqrt{2}} L_{2y} L_{1y} L_{1z} \chi_{xxz} \\
\chi_{pp}^{\text{eff}} &= \frac{1}{2\sqrt{2}} L_{2z} L_{1x}^2 \chi_{zxx} - \frac{1}{\sqrt{2}} L_{2x} L_{1x} L_{1z} \chi_{xxz} + \frac{1}{2\sqrt{2}} L_{2z} L_{1z}^2 \chi_{zzz}
\end{aligned} \quad (8)$$

B. mm2 symmetry

$$\begin{aligned}
\chi_{ss}^{\text{eff}} &= 0 \\
\chi_{sp}^{\text{eff}} &= \frac{1}{\sqrt{2}} L_{2z} L_{1y}^2 (\chi_{zxx} \sin^2 \phi + \chi_{zyy} \cos^2 \phi) \\
\chi_{ps}^{\text{eff}} &= \frac{1}{2} L_{2y} L_{1x} L_{1z} \sin 2\phi (\chi_{yyz} - \chi_{xxz}) \\
\chi_{ds}^{\text{eff}} &= \frac{1}{2} L_{2y} L_{1z} \left[\frac{1}{2} L_{1x} (\chi_{yyz} - \chi_{xxz}) \sin 2\phi + \sqrt{2} L_{1y} (\chi_{xxz} \sin^2 \phi + \chi_{yyz} \cos^2 \phi) \right] \\
\chi_{pp}^{\text{eff}} &= -\frac{1}{\sqrt{2}} L_{2x} L_{1x} L_{1z} (\chi_{xxz} \cos^2 \phi + \chi_{yyz} \sin^2 \phi) + \frac{1}{2\sqrt{2}} L_{2z} L_{1x}^2 (\chi_{zxx} \cos^2 \phi + \chi_{zyy} \sin^2 \phi) + \frac{1}{2\sqrt{2}} L_{2z} L_{1z}^2 \chi_{zzz}
\end{aligned} \tag{9}$$

C. 3m symmetry

$$\begin{aligned}
\chi_{ss}^{\text{eff}} &= L_{2y} L_{1y}^2 \cos 3\phi \chi_{yyy} \\
\chi_{sp}^{\text{eff}} &= \frac{1}{2} L_{2z} L_{1y}^2 \chi_{zxx} - \frac{1}{\sqrt{2}} L_{2x} L_{1y}^2 \sin 3\phi \chi_{yyy} \\
\chi_{ps}^{\text{eff}} &= -\frac{1}{2} L_{2y} L_{1x}^2 \cos 3\phi \chi_{yyy} \\
\chi_{ds}^{\text{eff}} &= \frac{1}{\sqrt{2}} L_{2y} L_{1z} L_{1y} \chi_{xxz} + \left[(L_{1y}^2 - \frac{1}{2} L_{1x}^2) \frac{\cos 3\phi}{2} + \frac{1}{\sqrt{2}} L_{1x} L_{1y} \frac{\sin 3\phi}{\sqrt{2}} \right] L_{2y} \chi_{yyy} \\
\chi_{pp}^{\text{eff}} &= \frac{1}{2\sqrt{2}} L_{2x} L_{1x}^2 \sin 3\phi \chi_{yyy} + \frac{1}{2\sqrt{2}} L_{2z} L_{1z}^2 \chi_{zzz} + \frac{1}{2\sqrt{2}} L_{2z} L_{1x}^2 \chi_{zxx} - \frac{1}{\sqrt{2}} L_{2x} L_{1x} L_{1z} \chi_{xxz}
\end{aligned} \tag{10}$$

III. EXPERIMENT

LAO/STO interfaces of varying thicknesses and substrate orientations were fabricated by pulsed laser deposition (PLD) according to the recipes given in Refs. 18 and 36. Two STO substrates, (110) and (111) oriented, were used simultaneously for each deposition. The film thickness was monitored by mean of high-pressure Reflection High-Energy Electron Diffraction (RHEED) on the (110) sample. Films with $n = 4$ and 8 LAO monolayers (MLs) were prepared on STO(110). At the same time, the simultaneous deposition on STO(111) leads to ≈ 5 and ≈ 10 LAO(111) MLs. Control samples were also grown in a different deposition run, consisting of 2 and 5 LAO(001) MLs on STO(001). The STO(001) substrates were chemically and thermally treated to have TiO_2 termination.¹⁸ After deposition the samples were cooled down in oxygen rich atmosphere to minimize the formation of oxygen vacancies according to the recipes of Refs. 4 and 37. To compare the LAO/STO interfaces and the bare (110) and (111) substrates under the same conditions, the latter were exposed to the same temperature and pressure of the deposition process for 1000 s, but without LAO deposition. These samples, and the STO(001) substrate, are labeled here as $n = 0$ MLs films.

Atomic force microscopy topographic images showed

surface morphology of terraces and steps 1 monolayer high, with low root-mean-square roughness of around 1 Å. The transport properties of (110) and (111) interfaces were previously characterized by using six-contact arrangement in Hall geometry, from which the sheet resistance and mobility could be extracted, with values similar to those found in (001) interfaces.¹⁸ Similarly to what happens in (001) interfaces, these experiments also indicated the existence of a critical value thickness for a insulator-to-metal transition, with an abrupt jump to a metallic state above a thickness of 7 MLs and 9 MLs for (110) and (111) interfaces, respectively. This observation may suggest that an interface polarity should be associated to both (110) and (111) interfaces, which is further elucidated by our SHG experiments discussed below.

For the optical investigation, the experimental geometry is depicted in Fig. 2. In particular, the incidence angle, β_1 , is set at 45° . Laser pulses of ≈ 35 fs and average energy-per-pulse of $200 \mu\text{J}$ were generated at 1 kHz by a Ti:sapphire laser system. The laser wavelength was 800 nm, corresponding to a photon-energy of the fundamental beam of about 1.55 eV and of the second-harmonic of about 3.10 eV, which is far from any optical resonance of both LAO and STO. Both the input fundamental and the output SHG beams were linearly polarized and the polarization direction controlled and analyzed by means

FIG. 3. Panel (a) shows the total SHG Yield (integral over all ϕ angles and all polarization combinations) as a function of the LAO coverage. The values are normalized to those measured from the surface of the (100) substrate. Panel (b) shows the $|\chi_{ijk}|$ components for the (001) samples, normalized to their value in the substrate, as a function of the LAO coverage. The inset shows an example of SHG vs azimuthal angle ϕ in the case of a $n = 5$ sample for different polarization combinations: *pp*, black triangles; *ds*, blue squares; *sp*, red circles. As this polar plots do not contain additional information, the data are not shown for all samples.

of half-waveplates and polarizers. For each sample the experimental conditions were the same. The laser spot size was about $300 \mu\text{m}$. The I_{SHG} at different azimuthal angles ϕ was filtered by optical filters and a monochromator from the fundamental light and measured with a photomultiplier. As the photomultiplier saturated by increasing the laser power, the response of our phototube was measured at several signal levels, and a correction curve was derived, so to correct all our data-sets accord-

ingly. All SHG measurements were performed in air.

IV. RESULTS AND DISCUSSION

Let's first observe the total SHG yield as reported in Fig. 3(a). The total SHG yield is obtained by integrating the signal over ϕ and averaging on all different polarization configurations. It provides an approximate measure of the interface dipolar asymmetry or 'polarity'. We remark here that the latter may be set up or enhanced by an interfacial reconstruction, either structural or electronic. First, we compare the SHG yield for the different substrates. We observe that the signal from the (110) surface is about four and eight times higher than the signal from the (001)- and (111)-STO, respectively. This indicates a strong polarity already present at the (110) surface. Intriguingly, this strong polarity is present in the 4 MLs LAO/STO(110) sample too and its magnitude is comparable with the above-threshold signals of the other two samples, although, as stated above, from a stoichiometric LAO/STO interface with parallel atomic planes we expect an interface with no-polar discontinuity. On the contrary this result strongly supports the theoretical findings that at the LAO/STO(110) interface the STO surface is not an ideal polar stoichiometric surface, but the ground state is characterized by a buckled TiO termination which leads again to an interfacial polar discontinuity.¹⁹ We notice that according to our results this structural distortion is already present on the surface of the bare STO(110) and that, given the intensity of the SHG signal, the induced polar discontinuity is larger than those occurring at the other insulating interfaces. To explain this observation it would be desirable to perform theoretical calculations which link the $\tilde{\chi}$ elements to the actual microscopic structure of the interface.

Let's now discuss the behavior of the SHG yield going from an insulating to a conductive interface. Coherently with the findings of our previous works,^{5,23} the SHG from bare STO(001) and the 2 MLs LAO/STO(001) interface is approximately constant while it has an abrupt enhancement in the conductive sample ($n = 5$ MLs). A similar behavior may be observed for the samples grown on (111) substrates, although there is a significant increase of the signal already in the insulating sample with 5 MLs of LAO. However, in the case of the (110) substrates, the SHG yield stays high over all the range. As already discussed in the Sec. I, the absence of this correlation between the SHG signal and the onset of conductivity is not surprising since SHG probes something different, i.e., the interfacial polarity and its variations. Besides, in (110) interfaces, the structural component may be dominant in most of the $\tilde{\chi}$ elements as compared to the contribution to SHG related with the charge injection. For this reason the latter may be hidden when averaging over all the elements of the $\tilde{\chi}$ tensor. Yet, it is possible that a specific element of the $\tilde{\chi}$ tensor is more sensitive to the polarity component due to the injected charges than that related

FIG. 4. SHG signal as a function of the azimuthal angle ϕ and polarization combinations for (111) samples. Open symbols are the data and the solid lines are best fit curves according to Eqs. 10.

to the structural symmetry-breaking. To scrutinize this hypothesis it is important to extract the different $\tilde{\chi}$ elements.

For this reason now we focus our attention on the SHG signal as a function of polarization and azimuthal angle in order to single out all the elements of the $\tilde{\chi}$ tensor for each interface. As predicted by Eqs. 8, the SHG signal from the (001) interfaces does not depend on the azimuthal angle for all the polarization combinations. This is nicely confirmed by the inset of Fig. 3(b) which shows exemplarily a measurement for the $n=5$ MLs sample at different polarization combinations. As obvious from the second and third of Eqs. 8, we may extract the amplitude of χ_{xxz} and χ_{zxx} by measuring the SHG signal for the *ds* and *sp* polarization combinations, respectively. These two quantities may be used in the last of Eqs. 8 for extracting χ_{zzz} , once the relative phase of these elements is known. This has been done in Ref. 23, where we found that χ_{xxz} , χ_{zxx} , χ_{zzz} are always real, with the notable exception of the $n = 1$ MLs sample, and that the χ_{xxz} component has opposite sign (-1) compared to χ_{zxx} and χ_{zzz} . Based on the same assumptions here, we extract the $\tilde{\chi}$ elements shown in Fig. 3(b).

FIG. 5. Behavior of the $|\chi_{ijk}|$ elements as a function of LAO coverage for (111) samples (a) and for (110) samples (b). The values of χ_{yyy} in panel (a) and of χ_{zzz} in panel (b) are reduced by a factor 10 and 2, respectively. The values are obtained by means of the fitting procedure as described in the text. The insets show the phase Δ of each element. The color code used here for the polarization combinations corresponds to that of Figs. 4 and 6

We observe that all the $\tilde{\chi}$ elements display a strong variation of the SHG signal across the insulator-to-metal transition, going from the under to the above threshold samples, coherently with our previous works.

Let us now discuss the (111) samples. Fig. 4 shows all the measurements for *pp*, *sp*, *ss*, and *ds* polarization combinations for $n = 0, 5, 10$ samples. Beside the technical details, let us remark some qualitative evidence. First of all, the average SHG signal is definitely changing a lot with the LAO coverage for the (111) samples, as already observed. Second, the *ss* curves are not much different at $n = 0, 5, 10$, although they have a completely

FIG. 6. SHG signal as a function of the azimuthal angle ϕ and polarization combinations for (110) samples. Open symbols are the data and the solid lines are best fit curves according to Eqs. 9.

different amplitude as shown below. They all have the same shape, with six equivalent lobes. The other curves, on the contrary, show dramatic changes in the shape by varying the film thickness. In Fig. 4 the solid lines represent the results of a fitting procedure based on Eqs. 10. The fitting procedure we use is quite straightforward and provide results that are robust against a change in the initial parameters. However, contrary to the (001) samples, there is no way to fit our data by using real quantities for the elements of the $\tilde{\chi}$ tensor, that hence we assume complex. We first recognize that the ss combination depends on χ_{yyy} only, thus it is possible to obtain directly χ_{yyy} up to an unknown phase factor. Then we fix the so obtained value of χ_{yyy} in the Eqs. 10 for sp and ds , where only χ_{zxx} and χ_{xxz} , respectively, are left as adjustable parameters.

As said it is not possible to measure the phase of the χ_{yyy} component, as it only appears in square modulus. Therefore the phases of χ_{zxx} and χ_{xxz} may be obtained only as relative values with respect to the χ_{yyy} phase. Finally, all components are participating in the last of Eqs. 10 describing the pp combination, so that we can extract the χ_{zzz} component by fixing all the others to the previously extracted values.

In Fig. 5(a) the results of the fitting procedure are summarized as a function of the LAO coverage. We notice that all components are changing, but the χ_{yyy} has the largest change of all: it becomes about 30 times higher

above threshold than its value below threshold. It is interesting to note that the χ_{zzz} value of the substrate is larger than that of χ_{yyy} , but above threshold the latter becomes huge compared to χ_{zzz} . This is surprising since in (001) samples χ_{zzz} is usually the largest component. Moreover the χ_{zzz} element decreases quite a lot with the LAO coverage, a reduction of about 70%, and the same happens to χ_{zxx} and χ_{xxz} . As a final remark, the phases shown in the inset of Fig. 5(a) also changes dramatically, undergoing a rotation of more than π in the 10 MLs sample.

An analogous fitting procedure has been applied to the data from (110) samples. Fig. 6 shows all the measurements for pp , sp , and ds combinations on $n = 0, 4, 8$ LAO/STO samples, and the best-fit curves obtained by means of Eqs. 9. We note that these polarization combinations carry all the information on the $\tilde{\chi}$ tensor elements, although, for completeness, we report in the Eqs. 9 all the non-vanishing polarization combinations for the (110) interfaces. The fit results are summarized in Fig. 5(b) as a function of the LAO coverage. In Fig 6, despite the insulator-to-metal transition, no qualitative change is immediately visible in the measurements. Beside some numerical change, the overall shape of the curves is quite unchanged. On the contrary, the behavior of the $\tilde{\chi}$ -components as a function of the LAO coverage shows interesting trends. In particular, while all the other components are approximately constant over the entire range of thicknesses, the χ_{zzz} component increases by about 50% across the insulator-to-metal transition. The phases reported in the inset of Fig. 5(b) show a pretty irregular behavior, for which, at the moment, we do not have a good explanation.

By gathering together the results on the SHG yield (Fig. 3(a)) and the χ_{zzz} -component of the (110) samples, it is clear that these samples display a strong interfacial polarity already below the conduction threshold, thus confirming the theoretical results reported in Ref. 19. Moreover, the behavior of the χ_{zzz} -component shows that this polarity is also affected somehow by the charge injection. Why charge injection modifies only this component is an interesting issue as well as the irregular behavior of the phase factor observed in Fig. 5(b) and the large SHG observed already at the STO(110) surface. All these experimental observations deserve a more detailed theoretical investigation suitable to link the $\tilde{\chi}$ -components to the interface microscopic structure. However, this investigation is beyond the scope of the present work.

V. CONCLUSIONS

In summary we have investigated LAO/STO interfaces with different STO orientations and LAO thicknesses by means of optical second harmonic generation that once more has revealed being an invaluable tool for probing the interface polarity of LAO/STO heterostructures. De-

spite the ionic model with a stoichiometric structure that foresees a polar discontinuity only in (001) and (111) samples, we measure a strong polar discontinuity at the (110) interfaces too, already large at the surface of bare STO(110). This confirms recent theoretical results that report the formation of a buckled TiO termination, energetically favored against a polar stoichiometric STO interface. This structural distortion of the interface is already present in the bare substrate and it is reflected in our observation of a strong SHG signal from these interfaces. Moreover, by analyzing in detail the elements of the $\tilde{\chi}$ tensor, we find that while in LAO/STO(001) samples all the $\tilde{\chi}$ -components are influenced by the charge injection occurring above threshold, for the other orientations, only some components show a strong variation across the insulator-to-metal transition. For a better un-

derstanding of the latter findings a detailed theoretical work is needed that is suitable to link the microscopic structure of the interface to the elements of the $\tilde{\chi}$ tensor. This is a very difficult task that goes beyond the scope of the present work.

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- ¹ A. Ohtomo, H. Y. Hwang, A high-mobility electron gas at the $\text{LaAlO}_3/\text{SrTiO}_3$ heterointerface, *Nature* **427**, 423 (2004).
- ² F. M. Granozio, G. Koster, and G. Rijnders, Functional Oxide Interfaces, *MRS Bulletin* **38**, 1017-1023 (2013).
- ³ N. Nakagawa, H. Y. Hwang, and D. A. Muller, *Nature Mat.* **5**, 204 (2006).
- ⁴ S. Thiel, G. Hammerl, A. Schmehl, C. W. Schneider, J. Mannhart, Tunable quasi-two-dimensional electron gases in oxide heterostructures, *Science* **313**, 1942 (2006).
- ⁵ A. Savoia, D. Paparo, P. Perna, Z. Ristic, M. Salluzzo, F. M. Granozio, U. S. di Uccio, C. Richter, S. Thiel, J. Mannhart, L. Marrucci, Polar catastrophe and electronic reconstructions at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface: Evidence from optical second harmonic generation, *Phys. Rev. B* **80**, 075110 (2009).
- ⁶ M. L. Reinle-Schmitt, C. Cancellieri, D. Li, D. Fontaine, M. Medarde, E. Pomjakushina, C. W. Schneider, S. Gariglio, P. Ghosez, J. M. Triscone, and P. R. Willmott, Tunable conductivity threshold at polar oxide interfaces, *Nat. Comm.* **3**, 932 (2012).
- ⁷ C. Cancellieri, D. Fontaine, S. Gariglio, N. Reyren, A. D. Caviglia, A. Fete, S. J. Leake, S. A. Pauli, P. R. Willmott, M. Stengel, P. Ghosez, and J. M. Triscone, Electrostriction at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface, *Phys. Rev. Lett.* **107**, 056102 (2011).
- ⁸ C. Cantoni, J. Gazquez, F. Miletto Granozio, M. P. Oxley, M. Varela, A. R. Lupini, S. J. Pennycook, C. Aruta, U. Scotti di Uccio, P. Perna, and D. Maccariello, Electron Transfer and Ionic Displacements at the Origin of the 2D Electron Gas at the LAO/STO Interface: Direct Measurements with Atomic-Column Spatial Resolution, *Adv. Mater.* **24**, 3952 (2012).
- ⁹ Z. Q. Liu, C. J. Li, W. M. Lü, X. H. Huang, Z. Huang, S. W. Zeng, X. P. Qiu, L. S. Huang, A. Annadi, J. S. Chen, J. M. D. Coey, T. Venkatesan, and Ariando, Origin of the Two-Dimensional Electron Gas at $\text{LaAlO}_3/\text{SrTiO}_3$ Interfaces: The Role of Oxygen Vacancies and Electronic Reconstruction *Phys. Rev. X* **3**, 021010 (2013).
- ¹⁰ J. Gazquez, M. Stengel, R. Mishra, M. Scigaj, M. Varela, M. A. Roldan, J. Fontcuberta, F. Sanchez, G. Herranz, Competition between Polar and Nonpolar Lattice Distortions in Oxide Quantum Wells: New Critical Thickness at Polar Interfaces, *Phys. Rev. Lett.* **119**, 106102 (2017).
- ¹¹ S. A. Pauli and P. R. Willmott, Conducting interfaces between polar and non-polar insulating perovskites, *J. Phys.: Condens. Matter.* **20**, 264012 (2008).
- ¹² K. Yoshimatsu, R. Yasuhara, H. Kumigashira, and M. Oshima, Origin of Metallic States at the Heterointerface between the Band Insulators LaAlO_3 and SrTiO_3 , *Phys. Rev. Lett.* **101**, 026802 (2008).
- ¹³ A. S. Kalabukhov, Y. A. Boikov, I. T. Serenkov, V. I. Sakharov, V. N. Popok, R. Gunnarsson, J. Borjesson, N. Ljustina, E. Olsson, D. Winkler, and T. Claeson, Cationic Disorder and Phase Segregation in $\text{LaAlO}_3/\text{SrTiO}_3$ Heterointerfaces Evidenced by Medium-Energy Ion Spectroscopy, *Phys. Rev. Lett.* **103**, 146101 (2009).
- ¹⁴ S. A. Chambers, M. H. Engelhard, V. Shutthanandan, Z. Zhu, T. C. Droubay, L. Qiao, P. V. Sushko, T. Feng, H. D. Lee, T. Gustafsson, E. Garfunkel, A. B. Shah, J.-M. Zuo, and Q.M. Ramasse, Instability, intermixing and electronic structure at the epitaxial $\text{LaAlO}_3/\text{SrTiO}_3$ (001) heterojunction, *Surf. Sci. Rep.* **65**, 317 (2010).
- ¹⁵ Y. Z. Chen, N. Pryds, J. E. Kleibeuker, G. Koster, J. R. Sun, E. Stamate, B. G. Shen, G. Rijnders, and S. Linderöth, Metallic and Insulating Interfaces of Amorphous SrTiO_3 -Based Oxide Heterostructures, *Nano Lett.* **11**, 3774-3778 (2011).
- ¹⁶ S. W. Lee, Y. Q. Liu, J. Heo, and R. G. Gordon, Creation and Control of Two-Dimensional Electron Gas Using Al-Based Amorphous Oxides/ SrTiO_3 Heterostructures Grown by Atomic Layer Deposition, *Nano Lett.* **12**, 4775-4783 (2012).
- ¹⁷ H. Lee, N. Campbell, J. Lee, T. J. Asel, T. R. Paudel, H. Zhou, J. W. Lee, B. Noesges, J. Seo, B. Park, L. J. Brillson, S. H. Oh, E. Y. Tsymbal, M. S. Rzchowski, and C. B. Eom, Direct observation of a two-dimensional hole gas at oxide interfaces, *Nature Mat.* **17**, 231-236 (2018).
- ¹⁸ F. Sánchez, C. Ocal, J. Fontcuberta, Tailored surfaces of perovskite oxide substrates for conducted growth of thin

- films, *Chem. Soc. Rev.* **43**, 2272-2285 (2014).
- ¹⁹ A. Annadi, Q. Zhang, X. R. Wang, N. Tuzla, K. Gopinadhan, W. M. Lü, A. R. Barman, Z. Q. Liu, A. Srivastava, S. Saha, Y. L. Zhao, S. W. Zeng, S. Dhar, E. Olsson, B. Gu, S. Yunoki, S. Maekawa, H. Hilgenkamp, T. Venkatesan, & Ariando, Anisotropic two-dimensional electron gas at the $\text{LaAlO}_3/\text{SrTiO}_3$ (110) interface, *Nat. Comm.* **4**, 1838 (2013).
 - ²⁰ D. Pesquera, M. Scigaj, P. Gargiani, A. Barla, J. Herrero-Martin, E. Pellegrin, S. M. Valvidares, J. Gazquez, M. Varela, N. Dix, J. Fontcuberta, F. Sánchez, G. Herranz, Two-Dimensional Electron Gases at $\text{LaAlO}_3/\text{SrTiO}_3$ Interfaces: Orbital Symmetry and Hierarchy Engineered by Crystal Orientation, *Phys. Rev. Lett.* **113**, 156802 (2014).
 - ²¹ G. Herranz, G. Singh, N. Bergeal, A. Jouan, J. Lesueur, J. Gazquez, M. Varela, M. Scigaj, N. Dix, F. Sánchez, J. Fontcuberta, Engineering two-dimensional superconductivity and Rashba spin-orbit coupling in $\text{LaAlO}_3/\text{SrTiO}_3$ quantum wells by selective orbital occupancy, *Nat. Comm.* **6**, 6028 (2015).
 - ²² F. Trier, S. Amoruso, D. V. Christensen, A. Sambri, Y. Z. Chen, X. Wang, E. Stamate, R. Bruzzese, and N. Pryds, Controlling the conductivity of amorphous $\text{LaAlO}_3/\text{SrTiO}_3$ interfaces by in-situ application of an electric field during fabrication, *Appl. Phys. Lett.* **103**, 031607 (2013).
 - ²³ A. Rubano, M. Fiebig, D. Paparo, A. Marino, D. Maccarriello, U. Scotti di Uccio, F. Miletto Granozio, L. Marrucci, C. Richter, S. Paetel, and J. Mannhart, Spectral and spatial distribution of polarization at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface, *Phys. Rev. B* **83**, 155405 (2011).
 - ²⁴ T. Günter, A. Rubano, D. Paparo, M. Lilienblum, L. Marrucci, F. Miletto Granozio, U. Scotti di Uccio, R. Jany, C. Richter, J. Mannhart, and M. Fiebig, Spatial inhomogeneities at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface: Evidence from second harmonic generation, *Phys. Rev. B* **86**, 235418 (2012).
 - ²⁵ A. Rubano, T. Günter, T. Fink, D. Paparo, L. Marrucci, C. Cancellieri, S. Gariglio, J.-M. Triscone, and M. Fiebig, Influence of atomic termination on the $\text{LaAlO}_3/\text{SrTiO}_3$ interfacial polar rearrangement, *Phys. Rev. B* **88**, 035405 (2013).
 - ²⁶ D. Paparo, A. Rubano, L. Marrucci, Optical second-harmonic generation selection rules and resonances in buried oxide interfaces: the case of $\text{LaAlO}_3/\text{SrTiO}_3$, *J. Opt. Soc. Am. B* **30**, 2452 (2013).
 - ²⁷ A. Rubano, C. Aruta, U. S. di Uccio, F. M. Granozio, L. Marrucci, T. Günter, T. Fink, M. Fiebig, D. Paparo, Electronic states at polar/nonpolar interfaces grown on SrTiO_3 studied by optical second harmonic generation, *Phys. Rev. B* **88**, 245434 (2013).
 - ²⁸ G. De Luca, A. Rubano, E. di Gennaro, A. Khare, F. M. Granozio, U. S. di Uccio, L. Marrucci, D. Paparo, Potential-well depth at amorphous- LaAlO_3 /crystalline- SrTiO_3 interfaces measured by optical second harmonic generation, *Appl. Phys. Lett.* **104**, 261603 (2014).
 - ²⁹ A. Rubano, T. Günter, M. Lilienblum, C. Aruta, F. Miletto Granozio, U. Scotti di Uccio, L. Marrucci, D. Paparo, and M. Fiebig, Optical Second Harmonic Imaging as a diagnostic tool for monitoring oxides thin-film epitaxial growth, *App. Surf. Sci.* **327**, 413417 (2015).
 - ³⁰ A. Rubano, G. De Luca, J. Schubert, Z. Wang, S. Zhu, D.G. Schlom, L. Marrucci, and D. Paparo, Polar asymmetry of $\text{La}_{(1-\delta)}\text{Al}_{(1+\delta)}\text{O}_3/\text{SrTiO}_3$ heterostructures probed by optical second harmonic generation, *Appl. Phys. Lett.* **107**, 101603 (2015).
 - ³¹ A. Rubano, T. Günter, M. Fiebig, F. M. Granozio, L. Marrucci, D. Paparo, Ultrafast Modification of the Polarity at $\text{LaAlO}_3/\text{SrTiO}_3$ Interfaces, *Phys. Rev. B* **97**, 035438 (2018).
 - ³² P. Guyot-Sionnest Y. R. Shen, Local and nonlocal surface nonlinearities for surface optical second-harmonic generation, *Phys. Rev. B* **35**, 4420-4426 (2018).
 - ³³ B. C. Russell Martin R. Castell, Reconstructions on the polar SrTiO_3 (110) surface: Analysis using STM, LEED, and AES, *Phys. Rev. B* **77**, 245414 (2008).
 - ³⁴ X. Torrelles, G. Cantele, G. M. De Luca, R. Di Capua, J. Drnec, R. Felici, D. Ninno, G. Herranz, M. Salluzzo, Electronic and structural reconstructions of the polar (111) SrTiO_3 surface, *Phys. Rev. B* **99**, 205421 (2019).
 - ³⁵ R.W. Boyd, *Nonlinear optics*, Academic Press, 1992, pag. 44.
 - ³⁶ R. Bachelet, F. Valle, I. C. Infante, F. Snchez, J. Fontcuberta, Step formation, faceting and bunching in atomically flat SrTiO_3 (110) surfaces, *Appl. Phys. Lett.* **91**, 251904 (2007).
 - ³⁷ Sing, M. et al. Profiling the Interface Electron Gas of $\text{LaAlO}_3/\text{SrTiO}_3$ Heterostructures with Hard X-Ray Photoelectron Spectroscopy, *Phys. Rev. Lett.* **102**, 176805 (2009).