2DEG and 2DHG in NaTaO₃ polar thin films: thickness and strain dependency

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Abstract
Two-dimensional (2D) carrier gases in perovskite surfaces and interfaces have been intensely studied since their properties are attractive to many functional devices and applications. Here, we demonstrate through ab initio DFT calculations that surface 2D carriers can be found in NaTaO₃ ultrathin films. Furthermore, we show the thickness dependence of such phenomenon and how it can be tuned when biaxial in-plane strain is applied. Tensile does not alter the valence and conduction character of the films but promotes 2D electron and hole gases in the (TaO₂)⁺ and (NaO)⁻ surfaces, respectively. Because of the competition between surface and strain effects to deal with the cleavage-induced polarity, biaxial compression is able to generate 2D hole gases in the (TaO₂)⁺ surface instead. Such carrier-type and layer switching are explained through changes in the electrostatic potential balancing along the [001] direction and (Na,Ta) cations displacements. The presented results concern not only nanoelectronics but also catalytic applications where modulating bandgap and valence/conduction states is desired.

1. Introduction

The combination of two or more semiconductor perovskites in the form of heterojunctions has been essential for several applications due to unique interfacial properties [1]. In one of their main fields, photocatalysis, heterojunctions assist the charge separation in the interface, increasing the lifetime of photo-induced charge carriers, resulting in greater photocatalytic efficiency [2, 3]. Such structures may have their bandgap engineered, better alignment with water redox potentials, and enhanced absorption in the visible spectrum [4, 5]. For instance, sodium tantalate (NaTaO₃) heterojunctions with a range of other materials (such as Ag₃PO₄ [6], CuBi₂O₄ [7], and Sr₂FeTaO₆ [8]) have been recently reported with a significant increase in their photocatalytic performance.

Another application that has been responsible for the increased interest in perovskite heterostructures is nanoelectronics. It is essential to obtain and accurately control high charge densities in nanostructures so that more efficient nanoelectronic devices surpass the standard silicon technology [9, 10]. The production of a two-dimensional electron gas (2DEG) at heterostructure interfaces is quoted as the most promising technology to achieve this goal [11, 12]. After the discovery of a 2DEG in a SrTiO₃/LaAlO₃ junction interface [13], a series of studies have been carried out aiming at other structures with similar conductive properties. The exact reason why a 2DEG emerges in such interfaces is still being discussed. However, it is primarily attributed to the polar catastrophe imposed by the polarity discontinuity in such a region [14, 15], which can also be achieved in clean surfaces and thin films owing to the vacuum exposure [16]. Among the strategies that can be implemented to deal with the resulting polarization and therefore control the 2D carrier gases, biaxial strain (usually introduced by the substrate) and film thickness control have avidly advanced [17–20].

Theoretical investigations have shown that NaTaO₃ (NTO) thin films, when grown in perovskite substrates, have metallic character (2DEG) in both p-type and n-type interfaces [21]. Furthermore, such materials showed...
reduced bandgaps, consistent water band-edge alignment, and hence improved catalytic activity under visible light [22, 23]. Nevertheless, further studies concerning intrinsic properties presented by NaTaO3 thin films that are generally used in such heterostructures are still lacking. Thus, it is essential to investigate the formation of 2D electrons and holes gases on NaTaO3 films. Understanding how the polarity and carrier gases behave with biaxial strain and film thickness is also of fundamental relevance, helping to comprise their properties manipulation and guiding improvements in all their related applications.

Here, we carefully study the effects that thickness and biaxial strain have on the structural and electronic properties of NaTaO3 polar ultrathin films. We show that films with thicknesses greater than 4 nm present 2D carrier gases, which can be handled by in-plane biaxial strain. Even in 5-layers films, despite preserving the insulating bulk character due to strong surface effects, such gases can be achieved if biaxial compression is employed. In addition to the proposed charge carrier gases manipulation, we also reveal the layers inversion and carrier-type switching behavior which happens when strain is applied. The results are relevant for applications where 2D electron and hole gases are desired, as well as where bandgap and valence/conduction states engineering are needed.

2. Methods

Density functional theory (DFT) [24, 25] was implemented through the Vienna Ab Initio Simulation Package (VASP) [26, 27] to simulate all cubic NaTaO3 polar films. Projector augmented-wave (PAW) [28] pseudopotentials and the generalized gradient approximation (GGA) within the PBEsol functional [29, 30] have been used to deal with electron-ion and exchange-correlation interactions, respectively. High symmetry k-points in the cubic Brillouin zone were sampled according to the Monkhorst–Pack [31] scheme. The cut-off energy for the plane-wave basis set was set 520 eV, while a 10−2 eV energy difference was adopted for the break condition in ionic relaxations loop (geometry optimizations).

As a starting point, we optimized a Pm 3m cubic NaTaO3 bulk, using a 11 × 11 × 11 k-point grid, and obtained a lattice parameter of a = b = c = 3.95 Å (a0) in excellent agreement with the 3.93 Å experimentally reported [32, 33]. Other bulk-related data can be found in (figure S1 (available online at stacks.iop.org/ NANOX/2/010016/mmedia)). For later strain-related studies, which intrinsically involve atomic displacements, the chosen PBEsol exchange-correlation functional is recommended since it results in a slightly better a0 for the solid bulk phase, as shown in table S1. As for the bandgap, both functionals provide practically the same value (2.24 eV), which are underestimated compared to the experimentally reported 4.10 eV [34], as expected for such kind of GGA implementation, but in agreement with other previous theoretical works [35].

More computationally expensive functionals as HSE06 [36] and PBE0 [37] as well as post-DFT quasi-particle methods (GW) [38] have been successfully used to overcome such underestimation, especially in bulk structures. However, when it comes to their employment in thin films and other nanostructures, particularly in biaxial strain studies, such methods stop being practical. Since our primary goal concerns the observation and formation mechanism of 2D carriers gases on NaTaO3 asymmetric thin films and not a precise description of unoccupied electronic states, standard DFT results shall be reliable enough.

From such bulk crystal, cleavages in the [001] direction were done to model three ultrathin films of different thicknesses: 1.8 nm, with five layers and 25 atoms, named (NTO)5; 3.7 nm, with ten layers and and 50 atoms, called (NTO)10; and 5.6 nm, with fifteen layers and and 75 atoms, labeled (NTO)15. The films were simulated as asymmetric slabs of alternating polar (TaO2)−(NaO)−... (TaO2)−(NaO)− layers in order to have both p-type and n-type surface terminations, as shown in figure 1 (a). To minimize image self-interactions due to periodic boundary conditions, a 17 Å vacuum separated opposite terminations and the k-points integration was realized up to a 5x5x1 grid for all the films. Since dipole corrections have shown little effects in the structural and electronic properties in similar studies [39], we have not implemented it.

Biaxial strain can be employed both by using substrates with varied lattice mismatches and by applying an electric field in the case of piezoelectric substrates [40, 41]. Here, the epitaxial in-plane biaxial strain was simulated by changing the initial a0 in the x-y planes. Being defined as $f = [(a_{film} − a_0) / a_0] × 100\%$, negative and positive values of f indicate biaxial compression and tensile, respectively. The simulated strain range of −5% to 5% is within the experimentally achievable values that can reach up to ±10% [42, 43]. We point out that, starting from the bulk lattice parameter, the three calculated ultrathin films presented the energy minimum when $a_{film} / a_0 = 0.99$. Thus, the new equilibrium lattice parameter of $a_{film} = 3.91$ Å is considered the strain-free case (f = 0%) from which biaxial compressive and tensile strain have been simulated. A complete lattice parameter convergence for all films can be found in figure S2. Despite knowing that the substrate-imposed strain has a profile whose gradient is negative as the distance from the interface increases, the uniform strain model can be considered as a particular case of a non-uniform distribution [44], and therefore describes well the behavior of thin films with only a few layers (ultrathin films), as is the case of our present study.
3. Results and discussion

3.1. Surface 2D carriers gases

As a result of the slab design along the [001] direction, the stacking of (TaO$_2$)$_n$ (NaO)$^-$ … (TaO$_2$)$_n$ (NaO)$^-$ layers leads to polar terminations, as shown by the (NTO)$_{10}$ optimized structure in figure 1(a). In heterostructures where there is an ionic polar discontinuity in the interface, the resulting electrostatic potential diverges and an unexpected electronic reconstruction takes place to compensate such discontinuity, which characterizes the polar catastrophe [45, 46]. Hence, there is an accumulation of charge carriers in the interface (two-dimensional gases) to balance such divergence. Despite not having a two materials interface, the vacuum also leads to a polar discontinuity that may well promote electronic reconstruction and induce the formation of 2D carrier gases on the surface. However, it was not the case for (NTO)$_{10}$ that shows an insulating band structure when $f = 0\%$, as presented in figure 1(b), with a bulk-like indirect $\Gamma - R$ bandgap of $E_g = 0.46$ eV. The valence band (VB) is coming from O atoms on the top layers, in green, whereas the conduction (CB) is attributed to Ta atoms on the bottom layers, in blue. Such distinctive band-edges spatial location when the film is semiconductor is expected to benefit charge carrier separation, increasing their lifetime and enhancing the film’s photocatalytic activity [47, 48].

When biaxial compressive strain is applied, figure 1(b) shows an increase in the film bandgap value until $f = -2\%$, reaching a maximum of 1.55 eV. At such a point, there is an inversion in the valence and conduction band description. From $f = -2\%$ on, VB and CB are on the bottom and top layers, respectively. This character is maintained in further compression, with the bandgap decreasing until $f = -4\%$, where the VB presents filled states that characterize a two-dimensional hole gas (2DHG) on the bottom layer. Conversely, when the film is under biaxial tensile strain, the bandgap vanishes as soon as $f = 1\%$. Sequentially at $f = 2$ and $3\%$, the VB presents filled states (2DHG) on the top layer due to further tensile increase. Finally, besides the previous 2DHG, a 2DEG can also be found on the bottom layer at $f = 4\%$, yet no inversion of bottom to top bands has taken place. The 2D gases here observed are comparable to those found in studies with similar perovskites such as in KTaO$_3$ [39], LaTaO$_3$ [49], and other oxide thin films and interfaces [50–52]. For the present material, analogous 2D electron gases have already been theoretically predicted for NaTaO$_3$/SrTiO$_3$ interfaces [12, 21]. Experimentally, although NaTaO$_3$–Fe$_2$O$_3$ composites presented enhanced Seebeck coefficient attributed to the formation of a 2DEG in the heterogeneous interface [53], it lacks experimental data for both for NaTaO$_3$ interfaces and thin films, as here reported, to confirm and understand such carrier gases.

The layer resolved projected density of states (pDOS), shown in figure 2, confirms the VB/CB surface character and depicts the layer inversion phenomenon indicated in figure 1. In the strain-free (NTO)$_{10}$ film (central panel), the VB is definitely from top end O atoms of the X (NaO)$^-$ layer while the CB is coming from the
Ta atoms of the bottom subsurface layer II. Tensile strain up to 4% (right panel), induces a 2DEG on the subsurface layer II, and the DOS profile is kept. On the other hand, a −4% biaxial compression (left panel) leads to an inversion in the DOS profile and the VB is found on the bottom surface layer, I (TaO$_2$)$_2^+$, whereas the CB has changed to the top X (NaO)$^-$ layer. Furthermore, a 2DHG is clearly seen on the bottom surface layer, I (TaO$_2$)$_2^+$. The partial charge density of the bands corresponding to the charge carrier gases (figure 3) reveals their orbital nature. We note that both 2DHG and 2DEG arising after biaxial strain is applied, figures 3(a) and (c), are concentrated in the O 2p$_{xy}$ and Ta 5d$_{xy}$ orbitals, respectively, of (TaO$_2$)$_2^+$ bottommost layers. In contrast, the 2DHG coming from the film’s spontaneous polarization that can be recovered with small tensile values is

**Figure 2.** Layer resolved pDOS of the (NTO)$_{10}$ film when it is strain-free (central panel) and under the biaxial strain limits of $f = -4\%$ (left panel) and $f = 4\%$ (right panel). Red and blue lines refer to O 2p and Ta 5d orbitals, respectively. The Fermi level has been set to zero in all cases and is represented by black dashed lines. Compressive strain clearly inverts the DOS profile and leads to a 2DHG on the bottom layers, whereas tensile strain barely changes the DOS but induces a 2DEG on the bottom subsurface layer.

**Figure 3.** (NTO)$_{10}$ partial charge density plots. The compression-induced 2DHG (a) takes place in O 2p$_{xy}$ orbitals from the bottom (TaO$_2$)$_2^+$ layer. Small tensile values can resume the spontaneous polarization 2DHG (b) that mostly happens in O 2p$_{xy}$ orbitals from the top (NaO)$^-$ layer. Further tensile (c) promotes a 2DEG located in Ta 5d$_{xy}$ orbitals from the bottom (TaO$_2$)$_2^+$ subsurface layer. The cross-sectional view shows the slightly more delocalized character of tensile carrier gases, which have wider contour lines than the compression gas, in agreement with their band structures. An isosurface value of 0.005 e/Bohr$^3$ was used for all plots.
located mainly in the O 2p₂ orbitals of the top (NaO)⁻ surface layer, parallel to the initial polarization (figure 3(b)). We conclude that the strain polarization changes the layer in which the 2D gases are located, in addition to changing their character to orbitals lying in the biaxial strain plane. Besides that, the greater delocalization of tensile gases can also be seen in the cross-sectional panels, which reveal wider contour lines than the compression gas, reflecting the band structure character.

Facing such a surprising behavior, we remember that surface 2D carriers gases can be viewed as a consequence of the competition between antiparallel surface and residual strain effects [39, 44]. Below a certain critical thickness $C_{th}$, surface effects are great enough to prevail over strain ones and compensate the polarity simultaneously, providing an insulating bulk-like character to the film. Near $C_{th}$, the polarity is still compensated, though some indicative of it might be apparent. Above $C_{th}$, although surface effects are still predominant, strain polarization is great enough to counteract. The remaining polarization can not compensate for the polarity, and the charge transfer occurs [39, 44].

We believe that our (NTO)$_{10}$ film is below, yet around, the system’s $C_{th}$. Initially, at $f = 0\%$, the film is insulating with a small bandgap, which means surface effects are predominant and strong enough to deal with the polarity. Nevertheless, compressive biaxial strain assists the strain polarization until a point ($f = -4\%$) where it effectively counterbalances the surface one. As a consequence, a 2DHG appears and the DOS has an inverted profile. Tensile strain, on the other hand, seems to be in favor of the initial polarity and allows the charge transfer to take place right at $f = 2\%$ with the DOS profile kept.

To confirm our results and further understand how biaxial strain is moving the cations, changing the physical and electronic structure of our films, we have calculated the layer-resolved electrostatic potential together with the relative displacements of Na and Ta atoms along the [001] axis, which are both discussed in the following section.

### 3.2. Electrostatic potential and atomic displacements

In order to follow the variation trend of the (NTO)$_{10}$ electronic structure with biaxial strain, figure 4(a) shows the [001] (z-axis) electrostatic potential plot for chosen strain values. Note that there is only a slight unbalance in the electrostatic potential in the strain-free case, pointing towards the bottom (TaO$_2$)$^{3-}$ layers. The (Na, Ta) cations, on the other hand, move towards the top (NaO)$^-$ layer to stabilize the structure, explaining the relative displacements between anions and cations observed for the strain-free film in figure 1. However, such strain effects are still secondary and not strong enough to compete with surface polarization. Thus, even though the strain-free film is insulating, its small bandgap and the fact that a weak polarization is apparent indicate that surface effects are in their limit ($\sim C_{th}$).

Biaxial strain induces additional structural changes. In figure 4(b), the layer resolved displacement of (Na,Ta) cations in relation to their O neighbors along z has been plot taking the strain-free case as the reference. Compressive strain moves the cations even further towards the top (NaO)$^-$ surface layer. At $f = -2\%$, the

![Figure 4](image-url)
The electrostatic potential is perfectly balanced, which means that the slight remaining polarization has been dealt with by atomic movements towards the top (NaO)\(^{-}\) layer triggered when strain is applied. The (Na, Ta) cations present a positive relative displacement (figure 4(b), cyan triangular line), and the film has the most pronounced insulating character (\(E_g = 1.55\ \text{eV}\)). This is the inversion point above which the electrostatic potential slope becomes negative and the VB (CB) switches from the top (bottom) to the bottom (top) layers. When further compression takes place, the relative displacement increases significantly (blue triangular line) and the strain polarization prevents surface effects from totally canceling the polarity. Thus, the critical thickness is shifted downwards, and the charge transfer leads to a 2DHG. We see in figure 4(a) that, at \(f = -4\%\) there is a downward slope in the electrostatic potential, which indicates the strain-induced polarization.

On the other hand, there is no such inversion when biaxial tensile strain is exerted, as previously revealed in figure 1. For \(f = 2\%\), it can be seen that there is surely an upward slope in the electrostatic potential. Tensile stretches the film, moving (Na,Ta) cations towards the bottom (\(\text{TaO}_2\)\(^{+}\)) layer, in favor of the initial polarization (figure 4(b), cyan dotted line). Therefore, surface effects can not compensate for the polarity any longer, and the film presents a 2DHG at \(f = 2\%\) and \(3\%\). Thereafter, at \(f = 4\%\), the electrostatic slope is boosted since (Na,Ta) cations move further towards the bottom layer (blue dotted line). In such case, tensile-induced polarization overwhelms and, besides the previous 2DHG, a 2DEG can also be observed. At last, we point that the measured cation displacement when \(f = 4\%\) is comparable to those found in classic ferroelectric materials such as BaTiO\(_3\). Nonetheless, NaTaO\(_3\) is considered an incipient ferroelectric [54, 55] and much have yet to be studied and reported about the exact conditions needed to induce bulk ferroelectricity.

We report here two types of switches that in-plane biaxial strain is capable of performing. Compression is able to resume the 2DHG that would initially exist on the top (NaO)\(^{-}\) layer, were it not for surface effects that cancel the polarity. However, the compression-induced polarization changes the VB/CB description. Thus, the 2DHG is resumed but now on the bottom (\(\text{TaO}_2\)\(^{+}\)) surface. Tensile, in turn, first favors the initial polarization and the 2DHG on the top surface. When increased, the cations displacement polarization changes the type of gas to a 2DEG. It also changes the surface on which the gas is found to the bottom one. To investigate how the observed polarization behavior and the biaxial strain effect vary with the film thickness, we discuss in detail the results for (NTO)\(_{5}\) and (NTO)\(_{10}\) ultrathin films within the next section.

### 3.3. Thickness dependence

The results for the (NTO)\(_{5}\) and (NTO)\(_{15}\) films reaffirm our conclusions drawn from the intermediate film. Furthermore, it helps to elucidate some previously discussed concepts once some phenomena are a little clearer for such cases. The electrostatic potential and the band structure plots for the above-mentioned films are shown in figures S4 and S5, respectively. The bulk-like indirect bandgap character as well as the orbital character of 2D carrier gases observed for the ultrathin films discussed herein is the same as previously exposed for (NTO)\(_{10}\) in figure 3.

We believe that if (NTO)\(_{15}\) is below but close to the critical thickness \(C_{th}\) the ultrathin (NTO)\(_{10}\) film will certainly be below. Due to its reduced thickness, surface effects are unquestionably sufficient to deal with polarity. Thus, even facing positive cations relative displacements, surface effects balance the electrostatic potential of the film (figure S4(a)). Accordingly, the strain–free film has a very insulating character, as shown in the bandgap versus strain plot in figure 5, with both VB and CB coming from bottom layers (figure S5(a)). Biaxial compression changes the CB character to the top layer. Furthermore, it favors the constraint effects, which effectively start to compete with surface ones, reducing the bandgap of the film. When \(f = -5\%\), the latter is no longer sufficient to deal with polarity, and therefore the charge transfer occurs promoting a 2DHG on the bottom surface layer, I (\(\text{TaO}_2\)\(^{+}\)). The electrostatic potential presents a negative slope and there is again an inversion in the VB/CB layer character. Biaxial tensile, on the other hand, changes the VB character to the top layer and triggers movements that favor the initial polarity. However, although the film’s bandgap decreases, even 5% of tensile is not enough to overcome surface effects, which keeps the electrostatic potential balanced, with no VB/CB inversion, and the film remains insulating.

Similarly, the (NTO)\(_{15}\) film is certainly above the critical thickness \(C_{th}\), where the competition between surface and strain effects prevents the polarity from being completely resolved and charge transfer is allowed right in the strain-free case. At \(f = 0\%\), a 2DHG is observed on the top surface (NaO)\(^{-}\) layer (figure S5(b)), together with a clear upward slope in the electrostatic potential (figure 4S(b)) that indicates the polarity-induced imbalance. (NTO)\(_{15}\) responds to in-plane biaxial strain exactly as the (NTO)\(_{10}\) does, as shown in figure 5. As biaxial compression is applied, strain effects are able to counterbalance the electrostatic potential and provide an insulating character to the film for \(-3\% \leq f \leq -1\%\). A maximum bandgap occurs for \(f = -2\%\), which is again the layer inversion point where the electrostatic potential is fully balanced. When \(f = -4\%\), strain effects owing to (Na,Ta) cations displacements are so dominant as to induce a significant strain polarization. The electrostatic potential slope becomes considerably negative, and a 2DHG is again observed, but now on the
bottom surface layer I (TaO$_2$)$^+$ On the other hand, tensile leads to strain effects that favor the initial polarization, accentuating the upward slop in its electrostatic potential to such an extent that at $f = 4\%$, besides the 2DHG on the top surface layer, a 2DEG is also found on the bottom one.

Interestingly, previous results have shown critical thicknesses of $\sim 2.4$–4 nm for other perovskite thin films [18, 44, 56], which are in agreement with our thicknesses. However, there had been no such reports for NaTaO$_3$ films hitherto. Besides that, the presence of ultrathin epitaxial overlayers or substrates has little effect upon the discussed behavior provided that they impose the same polarity discontinuity as the vacuum does [39].

4. Conclusions

We have systematically explored the structural and electronic properties of NaTaO$_3$ ultrathin films and their variation according to biaxial in-plane strain and thickness. The (5,10)-layers films (1.8 and 3.7 nm, respectively) proved to be insulating when strain-free, although the 15-layers film (5.6 nm) presents a 2DHG on its top (NaO$^-$) surface layer. The (NTO)$_3$ electronic character indicates that the critical thickness $C_{th}$ for NaTaO$_3$ films is around 4 nm. Smaller thicknesses allow surface effects to be predominant over constraint ones and effectively cancel the polarity. The electrostatic potential is balanced, and the film takes on an insulating character. Larger thicknesses allow strain effects to be relevant in the competition with surface effects, which are no longer sufficient to cancel the polarity. In such cases, the charge transfer occurs leading to 2D carrier gases.

Biaxial in-plane compression moves the cations towards the top (NaO$^-$) surface and the strain-induced polarization promotes a switched 2DHG on the bottom (TaO$_2$)$^+$ layers even for film thicknesses as small as 1.8 nm. Tensile, in turn, moves the cations towards the top (TaO$_2$)$^+$ surface, quickly allowing a 2DHG to appear for (NTO)$_{10}$ and to be reinforced for the (NTO)$_{15}$ film. Further tensile induces a new 2DEG on the bottom (TaO$_2$)$^+$ layers. Nevertheless, (NTO)$_3$ maintains its insulating character due to the strong surface effects therein. In addition to being an effective method of controlling and manipulating the electronic properties of NaTaO$_3$ films, such as the bandgap, biaxial strain can also induce conductivity through 2D carrier gases. In-plane biaxial strain can also switch both the layer character of the gases from top negative layers to bottom positive ones and the gas type itself from 2DHG or 2DEG. Such results can be attractive in a range of applications, such as nanoelectronics, which have not been the focus of NaTaO$_3$ films thus far.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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