Independent Tuning of Optical Transparency Window and Electrical Properties of Epitaxial SrVO$_3$ Thin Films by Substrate Mismatch

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Transparent metallic oxides are pivotal materials in information technology, photovoltaics, or even in architecture. They display the rare combination of metallicity and transparency in the visible range because of weak interband photon absorption and weak screening of free carriers to impinging light. However, the workhorse of current technology, indium tin oxide (ITO), is facing severe limitations and alternative approaches are needed. AMO$_3$ perovskites, M being a nd$^1$ transition metal, and A an alkaline earth, have a genuine metallic character and, in contrast to conventional metals, the electron–electron correlations within the nd$^1$ band enhance the carriers effective mass ($m^*$) and bring the transparency window limit (marked by the plasma frequency, $\omega_p^*$) down to the infrared. Here, it is shown that epitaxial strain and carrier concentration allow fine tuning of optical properties ($\omega_p^*$) of SrVO$_3$ films by modulating $m^*$ due to strain-induced selective symmetry breaking of 3d-t$_{2g}$(xy, yz, xz) orbitals. Interestingly, the DC electrical properties can be varied by a large extent depending on growth conditions whereas the optical transparency window in the visible is basically preserved. These observations suggest that the harsh conditions required to grow optimal SrVO$_3$ films may not be a bottleneck for their future application.

1. Introduction

Transition metal oxides are among the most studied materials due to the tremendous variety of properties they may display, such as superconductivity, metal–insulator transition, or multiferroicity.$^{[1]}$ High electrical conductivity and carrier mobility are critical requirements for the implementation of these materials in some advanced electronic components.$^{[2]}$ However, the room-temperature carrier mobility ($\mu$) of the much explored SrTiO$_3$ n-type semiconductor, for instance, in which the conduction band derives from rather localized 3d orbitals, is only $\approx 10$ cm$^2$ V$^{-1}$ s$^{-1}$. Similarly, the much larger carrier mobility discovered in LaAlO$_3$/SrTiO$_3$ and related interfaces, is limited to low temperatures.$^{[3]}$ In a different approach, focus was directed toward semiconductors made out of late transition metals, such as BaSnO$_3$ (BSO). In BSO, the relatively broad conduction band derived from Sn-5s orbitals anticipates a larger carrier mobility. Indeed, this has been experimentally observed by the breakthrough report of $\mu \approx 320$ cm$^2$ V$^{-1}$ s$^{-1}$ in La-doped BaSnO$_3$ (La-BSO) single crystals.$^{[4]}$ Unfortunately, in La-BSO thin films the carrier mobility was found to be substantially reduced,$^{[5,6]}$ although molecular beam epitaxy (MBE) growth technique and proper substrate selection$^{[7]}$ have allowed to partially recover ($\approx 150$ cm$^2$ V$^{-1}$ s$^{-1}$) the single-crystal mobility value. Anyhow, in these semiconducting materials, metallicity is obtained via doping and, in consequence, optimal conductivity can only be achieved via the subtle balance between the doping concentration and mobility, that typically vary in the opposite direction.
upon doping. In an essentially different approach, the attention has recently shifted toward intrinsically conducting oxides made of early transition metal elements such as: V, Nb, Mo, etc. In the case of SrVO$_3$ (SVO), for example, the partial occupation of the V-3d band (3d$^1$ electronic configuration) is responsible of the metallic conductivity. In this material the valence band is made out of O-2p orbitals lies well below the 3d band and a large optical band gap exists ($\approx 3$ eV) which guarantees no photon absorption in the visible range. Moreover, the intrinsically narrow V-3d band should lead to relatively strong electron–electron correlations and consequently to an enhanced effective mass. The large carrier concentration ($\approx 1$ electron per unit cell) and large effective mass combine to produce a plasma frequency ($\omega_p^*\approx 2.3$ eV) near infrared and thus SVO is found to be metallic and transparent in the visible optical range.

In recent years, SVO thin films have been grown by a number of techniques, including hybrid-MBE and pulsed laser deposition (PLD) and room-temperature resistivity (respectively mobility) values have been found to be ranging from 200 $\mu\Omega$ cm (resp. 0.8 cm$^2$ V$^{-1}$ s$^{-1}$) to 28 $\mu\Omega$ cm (resp. 10 cm$^2$ V$^{-1}$ s$^{-1}$) in best films.

The combination of large electrical conductivity and optical transparency in the visible range is a bonus of strong interest in photovoltaics, plasmonics, or information technologies and not surprisingly, correlated transparent oxides are attracting much attention. A question then arises: which are the factors limiting the carrier mobility and the transparency window of SVO thin films? In epitaxial films, several factors may come into play. First, epitaxial strain may break the degeneracy of the cubic environment of the metallic vanadium cation in SVO by splitting the V-3d-$t_{2g}$ triplet (Figure 1a). As a consequence, the conduction band width ($W$) and the electron orbital occupancy of the $t_{2g}$ orbitals can be modified, affecting electron–electron correlations and carrier mobility. Interestingly, it was reported that chemical pressure in Ca$_{1-x}$SrVO$_3$ induces a gradual deformation of the unit cell that tunes $W$ and, subsequently, the electronic and optical properties. It is understood that shorter V–O–V bonds in CaVO$_3$ compared to those of SrVO$_3$ are established via bending of the V–O–V bond angle $\theta$ away from the $\theta = 180^\circ$ observed in SVO. This bending reduces $W$ and increases the electron–electron correlations with a subsequent increase of the carrier effective mass ($m^*$) and reduction of the plasma frequency. However, a recent report on SVO films epitaxially grown on substrates having different structural mismatch suggests that the electrical and optical properties of the SVO films vary depending on the substrate used although the variation does not correlate with epitaxial strain.

Intriguingly, the reported plasma frequency $\omega_p^*$ ($\hbar\omega_p^* = 2.3$ eV) is substantially larger than that early measured in bulk and epitaxial films ($\approx 1.3$ eV). Second, during growth, point defects, associated to nonstoichiometry or others, may arise compromising $\mu$ (Figure 1b). Third, structural mismatch between film and substrate produces a mechanical stress that can induce plastic deformations by strain relaxation in the film structure, which should also affect $\mu$ (Figure 1c). These latter effects have been found to be of relevance in La-BSO films and related materials. Finally, in ultrathin SVO films, only few unit cells thick, quantum confinement may also give rise to selective orbital occupancy within the $t_{2g}$ manifold but this range of film thicknesses is beyond the present scope.

In this work, we aim at disentangling the role of these potential contributions to the electronic and optical properties of SVO thin films grown by PLD. Due to their outmost relevance for electro-optic applications, we shall focus on carrier density and mobility, as well as the plasma frequency, and their dependence on structural mismatch with the substrates and growth conditions, namely the oxygen partial pressure and temperature. It turns out that, under optimized growth conditions and for SVO films tens of nanometer thick, the structural mismatch governs the carrier mobility and film conductivity, both decreasing in films grown on mismatched substrates. It is observed that SVO films grown on substrates imposing a tensile strain are epitaxially stressed but films grown on substrates imposing a compressive strain of similar magnitude, are relaxed. In any event, misfit-related defects are observed by electron microscopy, blurring to some extent genuine epitaxial strain effects on electronic transport properties. Interestingly, we have observed that this detrimental effect can however be partially mitigated by increasing the carrier concentration favoring the appearance of charge-screened defects (Figure 1c). Spectroscopic ellipsometry and infrared reflectivity have been used to derive the plasma frequency $\omega_p^*$ and its dependence on structural mismatch and growth conditions. Two conclusions emerge. First, for all films, $\hbar\omega_p^*$ ($= 1.2–1.3$ eV) is found to scale with the carrier concentration. Second, the above observation suggests that electron bandwidth and orbital occupancy of the $t_{2g}$ states are sensitive to strain (Figure 1a), as we have confirmed by X-ray absorption and X-ray linear dichroism measurements at vanadium L$_{2,3}$ edges. It thus follows that carrier mobility in SVO films can be modulated by suitable choice of substrate and growth conditions.

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**Figure 1.** a) Sketch of the impact of (tensile) strain on the VO$_6$ polyhedron deformation and breaking of degeneracy of 3$d^1$-$t_{2g}(x\_y, x\_z, y\_z)$ orbitals. Electron occupancy is indicated by a vertical arrow. b) Carrier scattering (curved arrows) caused by point defects. c) Carrier scattering caused by extended defects, such as dislocations and cracks. Charge-screened defects are indicated by circles.
conditions while preserving a large transparency and the cutoff plasma energy below the visible spectrum.

2. Experimental Results

2.1. Growth Window

We first determined the growth window of SVO thin films in the PO2 (4 × 10^{-7} to 1 × 10^{-4} mbar) and T (700 °C to 800 °C) ranges on (001) STO and (001) LSAT. The room-temperature resistivity (ρ) and crystalline phases (pure SrVO3 films or coexistence of SrVO3 and Sr3V2O8 phases were obtained) are summarized in the (ρ, T, PO2) diagram shown in Figure 2, where we include the room-temperature resistivity of the films on LSAT and STO versus the (T, PO2) growth parameters. It can be appreciated that the main trends are common to both LSAT and STO substrates.

Data in Figure 2 show that single-phase and highly conducting SVO films are obtained at the lowest oxygen partial pressure (PO2 = 4 × 10^{-7} mbar which corresponds to the base pressure of the growth chamber) whereas when increasing PO2, films are multiphase (SrVO3, Sr3V2O8) and less conducting. Films grown at PO2 = 4 × 10^{-4} mbar show only the (001) reflections of the SVO perovskite indicating that the films are (001) textured, without traces (within the experimental sensitivity) of the PO2 (4 × 10^{-4} mbar) and STO versus the (T, PO2) growth parameters. It can be appreciated in Figure 2 that films grown around 750–800 °C present the lowest resistivities. The roughness of the films increases with PO2. AFM images are shown in Figure S1 in the Supporting Information. Illustrative values of resistivity and roughness (rms) of films grown at 750 °C, are: ρ = 82 μΩ cm and rms = 0.41 nm for the film deposited on LSAT and ρ = 200 μΩ cm and rms = 0.52 nm for the film deposited on STO. The resistivity values compare well with those early reported for thin films grown either by PLD (30–200 μΩ cm)\[14,15,17,29\] or hybrid-MBE (≈30–40 μΩ cm)\[5,12\] as we shall analyze in detail below.

Interestingly, in Figure 2 it can be appreciated that in all cases, the resistivity values of SVO//LSAT films are significantly smaller than those of the SVO//STO films. As the structural mismatch of SVO on STO, f(STO) = +1.59%, is larger than that of SVO on LSAT, f(LSAT) = +0.65%, it may be hypothesized that f, and the associated elastic or plastic responses of the SVO lattice, may play an important role on carrier transport in SVO films. In the following, we shall use the optimal growth conditions determined above (PO2 = 4 × 10^{-7} mbar, T = 750 °C) to explore in a systematic manner the role of structural mismatch between SVO and the substrates (STO, LSAT, NGO, and LAO), on the electrical, optical, spectroscopic properties and the microstructure of the films. Surface morphology analysis (topographic images are in Figure S2 in the Supporting Information) shows that, irrespectively of the substrate, films grown under these conditions are remarkably flat, with rms = 0.52 nm (STO), 0.41 nm (LSAT), 0.46 nm (NGO), and 0.48 nm (LAO). In agreement with earlier findings,\[13\] when increasing PO2, SVO films display the gradual formation of outgrowths at their surface, related to the formation of spurious Sr3V2O8 phase as evidenced by X-ray diffraction (XRD) data shown below.

2.2. Structural Properties

The XRD θ–2θ scans of films deposited under the optimal conditions (750 °C, 4 × 10^{-7} mbar) on all substrates, zoomed around the (002) reflection of the corresponding substrates, are shown in Figure 3a.

We first focus on the SVO film on STO which has the largest tensile structural mismatch (f(STO) = +1.59%). The (002) reflection of the SVO film (Figure 3a (green curve)), is located at the right of the (002) STO reflection, and attentive inspection reveals Laue fringes (Figure S3, Supporting Information). Interestingly, the (002) SVO reflection occurs at lower angle than that expected for bulk SVO (indicated by a vertical dashed line in Figure 3a), implying an expanded c-axis (c(SVO//STO) ≈ 3.873 Å). Therefore, the observed expansion of c-axis is not due to the stress (tensile) imposed by the substrate but is likely related to growth-induced defects, including nonstoichiometry, as commonly found in SVO films.\[11,12,16,17\] The reciprocal space maps (Figure S4, Supporting Information) show that the (002) SVO and (002) STO reflections are well aligned along [100] indicating that the in-plane cell parameter of SVO and STO are closely coincident and thus SVO is in-plane strained (a = 3.905 Å). Therefore, the VO3 coordination polyhedron in SVO//STO has c/a < 1.

In the opposite limit, for SVO//LAO films where a large compressive mismatch exists (f(LAO) = –1.37%), two broad (002) SVO reflections can be observed in the XRD pattern (top violet curve). One occurring at (2θ)1 = 46.94°, indicates an out-of-plane
cell parameter $c(SVO/\text{LAO}) \approx 3.868 \text{ Å}$ and the other, located at $(2\theta) \approx 46.3^\circ$, indicates a larger $c$-axis: $c(SVO/\text{LAO}) \approx 3.919 \text{ Å}$. These reflections occur at smaller $2\theta$ angles than bulk (002) SVO (vertical dashed line); hence both peaks correspond to larger $c$-axis than bulk SVO. Although this behavior could be expected if the negative mismatch of the LAO substrate on the film would induce a compressive epitaxial strain on the basal plane of SVO, the reciprocal space maps (Figure S4, Supporting Information) indicate that the cell parameters of SVO are not clamped to those of the substrate but relaxed. Therefore, for SVO//LAO, the VO$_6$ coordination polyhedron has an enhanced tetragonality $c/a > 1$.

The X-ray reflections of SVO films on LSAT and NGO are hardly discernible from those of the substrate due to the close structural matching and a noticeable SVO line-broadening that, in accordance with topographic images (Figure S2, Supporting Information), can be attributed to the limited size (grain size $\leq 50 \text{ nm}$) of the coherently-diffracting volume, shrunk by the presence of strain-induced defects (see Section 2.4). From the $\theta$–2$\theta$ and reciprocal space maps (Figure S4, Supporting Information) we determine that the corresponding $c$-axis parameters are $c(SVO/\text{LSAT}) \approx 3.87 \text{ Å}$ and $c(SVO/\text{NGO}) \approx 3.86 \text{ Å}$, while the in-plane parameters coincide with those of the corresponding substrates. Consistently with the results of the SVO//STO above, SVO films on NGO and LSAT films are epitaxially strained. Therefore, within the experimental resolution, for SVO//NGO and SVO//LSAT $c/a \approx 1$.

In Figure 3b, we plot the $c$-axis parameters of all films. We also include the predicted cell parameter of epitaxially strained SVO films on the different substrates, calculated using the Poisson equation and assuming volume conservation.\[12\] It is clear that the $c$-axis values of the films, including $c(SVO/\text{LAO})$, are larger than that expected if a pure elastic compressive or tensile strain were acting on the SVO film. As mentioned above, a unit cell expansion is commonly observed in SVO films and attributed nonstoichiometric defects related to the extremely low PO$_2$ used during growth.\[11,12,16,17\] Recently, it has been reported that using a nonreactive gas in the PLD growth process, this effect can be mitigated\[29\] probably as a result of changing the Sr/V ratio or the oxidation state of species in the plume.\[13\]

The symmetric X-ray diffraction $\theta$–2$\theta$ scans do not reveal the presence of spurious phases in none of films grown at low pressure (PO$_2 = 4 \times 10^{-7}$ mbar). However, as the corresponding reflections may not be visible in symmetric scans, we collected 2D maps of the reciprocal space along $2\theta$ and $\chi$ angles. In Figure 3c (top panel) we show the $2\theta$–$\chi$ frame for SVO//STO samples. The intense (001) and (002) substrate reflections are well visible. The superimposed (001) and (002) SVO reflections are not distinguishable from those of the substrate, which is in agreement with the $\theta$–2$\theta$ scans (Figure 3a) and the lower resolution of the 2D detector. Importantly, no other reflections that could suggest the presence of spurious phases are visible in these films. We then conclude that films grown at the lowest pressure (PO$_2 = 4 \times 10^{-7}$ mbar) are single phase, as summarized in Figure 2. However, this is not the case for films grown at higher PO$_2$. In Figure 3c (bottom panel) we show a $2\theta$–$\chi$ frame of the SVO//STO sample grown at PO$_2 = 2 \times 10^{-5}$ mbar. In this map, additional spots that correspond to the (205) Sr$_3$V$_2$O$_8$ reflections are visible. Consistently, the AFM images of this SVO//STO sample (Figure S1, Supporting Information) show outgrowths which are associated to the Sr$_3$V$_2$O$_8$ phase identified in the 2D maps.\[13\] Similar results are observed in films grown at high PO$_2$ on LSAT substrates.

### 2.3. Electrical Transport Properties

We turn now to the electrical transport properties of the films with the focus on its dependence on structural mismatch and
the PO2 used during growth. In Figure 4a we show the room-
temperature resistivity $\rho(300\,K)$ of the SVO films grown on
different substrates at PO2 = $4 \times 10^{-7}$ mbar (squares) and PO2 = $2 \times 10^{-3}$ mbar (circle symbols). The resistivity is
minimal for the films grown on best-matched substrates (LSAT and NGO) and, for a given mismatch, the resistivity decreases
when reducing PO2. Accordingly, $\rho(300\,K)$ reaches its smallest value (at PO2 = $4 \times 10^{-7}$ mbar) for SVO//NGO films, where $f(SVO/\text{NGO}) = +0.52\%$. The resistivity value $\rho(300\,K, \text{NGO})$
= 85 $\mu\Omega\,\text{cm}$ is comparable to the state-of-the-art resistivity values of films of similar thickness grown, under similar conditions, by PLD ($\approx 35-90\,\mu\Omega\,\text{cm}^{11,13,15,29}$) and only 3 times larger than that of films grown by hybrid-MBE ($\approx 30-40\,\mu\Omega\,\text{cm}^{9,12}$).

As mentioned above, the use of a nonreactive gas during PLD growth allows to reduce films nonstoichiometry and to lower their resistivity $\rho(300\,K)$ down to $\approx 31\,\mu\Omega\,\text{cm}$; more importantly here, the overall trend of $\rho(300\,K)$ with the lattice mismatch is preserved. The same trend of $\rho(300\,K)$ with the lattice mismatch is also observed in the series of films grown at PO2 = $2 \times 10^{-3}$ mbar (circles). Therefore, data in Figure 4a indicates an important role of the film–substrate mismatch on the resistivity of SVO films.

The carrier concentration ($n$) and mobility ($\mu$) values, extracted from resistivity and Hall effect measurements, of films grown at the lowest PO2 ($4 \times 10^{-7}$ mbar) on different substrates, are shown in Figure 4b (diamonds and squares, respectively). We first note that the carrier concentration is almost constant ($n = 2.1 \times 10^{22} \text{ cm}^{-3}$) for films on LSAT, NGO, and LAO. This value is close to, but slightly larger than the value expected for stoichiometric SVO with V4+ (3d1) ($\approx 1.76 \times 10^{22} \text{ cm}^{-3}$). A perceptible larger 16% carrier concentration is observed for films grown on STO. We note that if the STO substrate would have opened a conducting parallel channel in the SVO//STO sample grown at the lowest pressure, then the measured carrier density would have been smaller but not larger. Therefore, a plausible reason is that the tensile strain imposed by the STO substrate favors a higher concentration of oxygen vacancies, that can provide additional carriers while reducing mobility. The carrier mobility reaches its largest value ($\approx 3.3 \text{ cm}^{2}\text{V}^{-1}\text{s}^{-1}$) for SVO grown on the best matching NGO substrate, being marginally smaller in films on LSAT and LAO. A more pronounced reduction ($\approx 1.2 \text{ cm}^{2}\text{V}^{-1}\text{s}^{-1}$) is observed in SVO//STO, consistent with an increased strain-related nonstoichiometry, as indicated above. As shown by Mirjolo et al. the use of a nonreactive gas during the PLD growth allows to increase the mobility up to above 8 cm$^{2}$V$^{-1}$s$^{-1}$, approaching the record values obtained in hybrid-MBE films ($\approx 10^{11} \text{cm}^{2}\text{V}^{-1}\text{s}^{-1}$).

The temperature dependence of the resistivity $\rho(T)$ and the residual resistivity ratio (RRR = $\rho(300\,K)/\rho(5\,K)$) of SVO films are also significantly different depending on the substrate used, as shown in Figure 4c,d, respectively. It can be appreciated that the SVO//NGO film displays the largest RRR (RRR $\approx 2.1$) (Figure 4d) and RRR gradually decreases in films on substrates having larger lattice mismatch. For instance, RRR $\approx 1.4$ for SVO//STO. Accordingly, the maximal RRR (minimal residual resistivity) is also obtained in films grown on well-matched

Figure 4. a) Room-temperature resistivity $\rho(300\,K)$ of films deposited on different substrates at PO2 = $4 \times 10^{-7}$ mbar (squares) and PO2 = $2 \times 10^{-3}$ mbar (circles). b) Carrier density (diamonds) and carrier mobility (squares) of the films grown at the lowest pressure (PO2 = $4 \times 10^{-7}$ mbar). c) Temperature dependence of the normalized resistivity $\rho(T)/\rho(300\,K)$ of the same films grown at the lowest pressure (PO2 = $4 \times 10^{-7}$ mbar); the corresponding structural mismatch is indicated. d) Residual resistivity ratio ($\text{RRR} = \rho(300\,K)/\rho(5\,K)$).
substrates (Figure 4d). We note in passing that the largest RRR values reported for SVO films grown by PLD under standard PO2 atmosphere were of only $\approx 1.7$.\[15,17\]

Overall, all data in Figure 4 strongly suggest that resistivity, carrier density, and mobility of SVO films grown under optimized conditions are primarily determined by the structural mismatch with substrates, maybe exacerbated by mismatch-controlled nonstoichiometry.

It is known that defects in solids, affecting carrier mobility, can be screened by carriers and therefore, the mobility is affected by the carrier density in an unconventional manner.\[33\]

To explore this effect, we focus on SVO//LSAT and SVO//STO films as illustrative examples of well and poor matched substrates, respectively, and analyze the relationship between carrier density and mobility of SVO films. In Figure 5 we plot $\mu$ versus $n$ for SVO//LSAT (squares) and SVO//STO (circles) films grown at the same temperature ($750 \degree C$) and varying PO2. Data in Figure 5 reveal important trends. First, at any PO2 the carrier mobility is larger for films grown on LSAT than on STO. Next, it is observed that for films on both substrates, an enhancement of mobility goes in parallel with an increase of carrier concentration ($\mu = n^b$, $b > 0$). The relevance of this observation is better appreciated by noticing that in conventional doped semiconductors, the opposite behavior is typically observed. Indeed, it is commonly found that $\mu$ decreases with increasing doping due to the enhanced scattering of carriers with dopant atoms. The reverse trend observed here bears some resemblance with properties of some strained semiconductors, such as Ba$_3$SnO$_5$, where a similar $\mu = n^b$ with $b > 0$ have been reported.\[6,30\] It has been argued that this unusual increase of mobility when increasing the carrier density is due to the enhanced screening of extended defects, such as dislocations, by the carriers (Figure 1c).\[13\] The confined and directional character of the relevant 3d orbitals forming the conduction band of SVO advances a strong sensitivity of carrier mobility to extended structural defects. Therefore, it may not be a surprise that the carrier-induced screening can efficiently increase mobility.

### 2.4. Microstructure

The observations above suggest that extended defects associated to structural mismatch play a major role on charge scattering and trapping. To get insight on this, the microstructure of the films grown at PO2 = $4 \times 10^{-7}$ mbar and $T = 750 \degree C$ were studied by transmission electron microscopy (TEM). Specimens from the SVO films grown on LAO, NGO, and STO were prepared in cross section geometry by focused ion beam (FIB) lift-out technique. Figure 6a–c (main panels) shows bright field images of SVO//LAO, SVO//NGO, and SVO//STO, respectively. It can be appreciated that all films present a sharp interface (see horizontal solid lines) with the substrate, homogeneous thickness of $\approx 70$ nm and a free surface with a roughness at the nanometer level. From these bright field images acquired in zone axis conditions, it can be seen that the films present an incoherent contrast, with obvious dissimilarities among them. In order to assess the density and nature of the crystal defects that may be responsible for the observed contrast, the crystals were oriented in two-beam conditions by tilting the specimen in the TEM. In opposition to zone axis condition, in which the crystal is oriented so that the Ewald sphere is tangent to a plane of nodes of the reciprocal lattice of the crystal, in two-beam conditions the crystal is oriented in such a way that only a family of reflections is in Bragg condition (the second beam being the direct beam). By acquiring bright field images in this condition, defects in the direction given by the intersection of the Ewald sphere with the reciprocal lattice of the crystal are strongly highlighted.

![Figure 5. Carrier mobility versus carrier density for SVO//LSAT (squares) and SVO//STO (circles) films deposited at various PO2.](image)

![Figure 6. Cross-section of bright field TEM images of the SVO films grown on a) LAO, b) NGO, and c) STO substrates. Insets: bright field TEM images obtained by tilting the crystals to obtain two-beam conditions, highlighting the presence of defects in particular directions.](image)
The bright field images acquired in two beam conditions described above, are shown in the insets of Figure 6a–c. Different two beam conditions were set for all the SVO films: one corresponding to the family of planes stacked in the growth direction and the other in the perpendicular direction. In Figure 6a (inset) we show an image collected for the SVO film grown on the LAO substrate, which we remind here is subjected to a compressive stress. The image reveals a microstructure of defects consisting on planar defects oriented parallel to the substrate (compressive stress, LAO) (Figure 6a (inset)). In contrast, planar defects oriented perpendicular to the substrate can be observed in SVO grown on substrates imposing a tensile stress (STO) (Figure 6c (inset)). The presence of oriented planar defects in thin films grown on mismatched substrates, has been reported in other perovskite thin films, such as La0.5Sr0.5CoO3−x [34–36] or LaNiO 3−x [37] to name a few, and it is believed to be a signature of defects ordering (oxygen vacancies) to release epitaxial stress. More precisely, high resolution electron microscopy images of La0.5Sr0.5CoO3−x films grown on LAO and STO substrates, imposing -as in the present case- compressive and tensile stress respectively, clearly revealed a similar arrangement of planar defects. [36] In the present case, it cannot be excluded that planar defects could be related to the presence of Sr3V2O8, as identified in some XRD data. However, the observation that in SVO film grown on NGO substrate (Figure 6b (inset)), with a very small lattice mismatch, a much smaller density of defects was observed in both crystal orientations seems to favor the former scenario. The presence of these extended planar defects should impact the electronic transport. Indeed, for SVO//STO where the array of defects is perpendicular to the interface, the carrier mobility should be much obstructed than in SVO//LAO where these defects lay parallel to the interface. This is indeed, the trend observed in Figure 4b.

2.5. Optical Properties

Spectroscopic ellipsometry (SE) measurements were performed on SVO//(STO, LSAT, NGO, and LAO) films grown at PO2 = 4 × 10−7 mbar and at PO2 = 2 × 10−5 mbar. The real and imaginary parts of the dielectric constants (ε = ε1 + i ε2) and optical coefficients (n = n + i κ) were extracted from the SE data (see experimental section). Figure 7a,b shows the spectral dependence of ε1 and ε2 of some illustrative films. The shape of both components of the complex permittivity ε are in good agreement with earlier reports. [9] From ε1(ωp*) the screened plasma frequency ωp* can be determined by using the condition ε1(ωp*) = 0. Two salient features emerge from data
in Figure 7a. First, $\alpha_{\text{opt}}$ increases when reducing PO$_2$ during growth and second, for a given growth PO$_2$, $\alpha_{\text{opt}}$ is reduced in SVO/STO compared to SVO/LSAT. These trends can be better visualized in Figure 7c where we plot $E_{\text{opt}}$ versus $f$ values of these films. As seen, all $\alpha_{\text{opt}}$ values are around 1.2–1.3 eV, which is agreement with earlier reports for SVO/LSAT. To get a further insight on the implications of these observations, we recall that:

$$
\left( E_{\text{opt}} \right) = \frac{h^2 e^2}{\varepsilon_{\infty} m^*} \times n
$$

where $\varepsilon_{\infty}$ is the high frequency relative permittivity of the medium, $n$ is the free carrier density, $m^*$ is the free carrier effective mass, and $h$, $e$, and $\varepsilon_0$ stand for the reduced Planck constant, the electron charge and the free space permittivity, respectively. In Figure 7d we plot $E_{\text{opt}}$ versus $n$ (where $n$ is the carrier density determined from Hall effect, see Figure 4). This plot allows to conclude that the plasma energy increases when reducing PO$_2$ because the carrier density increases. Moreover, the smaller slope of the $E_{\text{opt}}$ plot observed in SVO//STO anticipates a larger effective mass of carriers in comparison to SVO//LSAT. Using $\varepsilon_{\infty} = 4$, as determined in bulk SVO, the effective mass $m^*$ can be computed from data in Figure 7d. For SVO//LSAT, we obtain $m^*(\text{LSAT}) = 4$ irrespectively on the PO$_2$. For SVO//STO we obtain a significant larger mass $m^*(\text{STO}) = 5$, which represents a 25% enhancement. It is worth to recall that in Sr$_{1-x}$Ca$_x$VO$_3$ bulk materials, $m^*$ was found to increase from 3.3 to about 4 when increasing $x$ due to internal chemical pressure.

The complex refractive index of the film and substrate extracted from the ellipsometry measurements were used to calculate the sample reflectivity $R_{\text{calc}}(\omega)$, assuming a simple model consisting of a substrate and a SVO film, and to compare it with experimental data. Fourier transform infrared reflectometry (FTIR) measurements have been used to determine $R_{\text{exp}}(\omega)$ at normal incidence. The experimental $R_{\text{calc}}(\omega)$ and $R_{\text{exp}}(\omega)$ data for some illustrative films are shown in Figure S5 in the Supporting Information. Data reveal that both $R(\omega)$ display a minimum at around 600 nm ($\approx 2$ eV). This observation is in agreement with results from Boileau et al. although we emphasize that the minimum of $R(\omega)$ cannot be taken as a measure of $\alpha_{\text{opt}}$, due to the substrate contribution to the reflectivity measurements. It is of the highest interest to notice that all samples, irrespectively of their DC conductivity, display a remarkably small $\varepsilon_{\text{rel}}(\omega)$ in the visible range (Figure 7b), which is a signature of small absorption. It thus follows that, within the explored growth conditions range, although electrical conductivity and plasma frequency can be modulated, the optical absorption remains almost unperturbed.

### 2.6. X-Ray Absorption and Orbital Occupancy

In section 3.5 we have shown that the effective mass of carriers in SVO films on STO is larger than that of SVO films on LAO, LSAT, and NGO substrates. As films on different substrates appear to be under different strain state, a natural question arises: Which is the role of strain on orbital occupancy and ultimately on bandwidth broadening? Indeed, it is well known that substrate-induced stress on epitaxial films of oxides breaks the orbital degeneracy and promotes a selective electron occupancy in well-defined orbitals, that affects transport properties. The X-ray absorption (XAS) at metal L$_2,3$ edges in epitaxial metal oxide films, is sensitive to the relative orientation of the polarization direction of the incoming X-ray beam with respect to the film surface. This gives rise to an X-ray linear dichroism (XLD), defined as $\Delta$ = $I(E_{\text{ab}}) - I(E_{\text{c}})$, different from zero if final states with different symmetry are not equally available; $I(E_{\text{ab}})$ and $I(E_{\text{c}})$ are the intensities of the absorption of light with the electric field (polarization) parallel to the film plane ($E_{\text{ab}}$) or perpendicular to it ($E_{\text{c}}$). For an epitaxial (001) SVO film, as in the present case, $E_{\text{ab}}$ is probing electronic states with (xy) symmetry and $E_{\text{c}}$ is probing electronic states with (xz, yz) symmetry. In the particular case of V-3d, if the electron occupancy at the (xy) and (xz, yz) orbitals is not identical, a nonzero XLD should be apparent. XLD will be different depending if the lower lying state is (xy) or (xz, yz), that is depending on the sign of the energy difference $\Delta E_{\text{ab}} = E_{\text{ab}} - E_{\text{c}}$, where $E_{\text{ab}}$ and $E_{\text{ab}}$ are the corresponding energies. Notice that $\Delta E_{\text{ab}} > 0$ has to be found in presence of an in-plane expansion of the equatorial bonds in VO$_6$ and $\Delta E_{\text{ab}} < 0$ corresponds to an out-of-plane expansion of O–V–O bonds in VO$_6$.

In Figure 8a we show the combined V-L$_{2,3}$ and O-K XAS spectra of the SVO films grown on STO, NGO and LAO substrates, selected because they display the maximal (STO tensile, LAO compressive) and minimal (NGO) mismatch. The V-L$_{3}$ and L$_2$ edges (at 519 and 524 eV) are signatures of the dipole transitions from 2P$_{1/2}$ to 3d and from 2P$_{3/2}$ to 3d orbitals. The double peak (appearing at 530 eV) of the O-K prepeak is a fingerprint for the V$^{++}$ valence state. The relative intensity of the L$_{2,3}$ as well as the splitting of the O-K prepeak are characteristic of V$^{++}$ in an octahedral coordination. A detailed inspection of the low energy side of the L$_3$ peak (see Figure 8b) reveals a fine structure where three peaks can be identified. As shown by cluster calculations of the appearance of these peaks is prominent in tetragonally distorted VO$_6$ octahedra. In Figure 8b it can be appreciated that these features are more prominent in SVO/STO than in SVO/(NGO and SVO/LAO), and according to the previous statement, we conclude that in SVO/STO, the VO$_6$ octahedra have a larger tetragonal distortion than in SVO/(NGO and SVO/LAO).

A more direct evidence is provided by the XLD data shown in the following. In Figure 8c we present the XLD = $I(E_{\text{ab}}) - I(E_{\text{c}})$ data of SVO//(STO, NGO, LAO) films. To appreciate the implications of the data in Figure 8c, we remind here that theoretical cluster calculations of XLD for $\Delta E_{\text{ab}} > 0$ and $\Delta E_{\text{ab}} < 0$ predicts XLD spectra that are virtually opposite one another, and thus comparison with experimental data should allow to discern between $\Delta E_{\text{ab}} > 0$ and $\Delta E_{\text{ab}} < 0$. The XLD data in Figure 8c show that for SVO films, the overall trend is similar to the above predicted $\Delta E_{\text{ab}} > 0$ case. Interestingly, as clearly shown by data in Figure 8c, the height of the most intense XLD peak, which is the most sensitive to the magnitude of $\Delta E_{\text{ab}}$, is somewhat larger in SVO/STO than in SVO/(NGO, LAO). It has also been predicted that the features appearing at the low-energy side of L$_3$ are more sensitive to tetragonal distortion for $\Delta E_{\text{ab}} > 0$ than for $\Delta E_{\text{ab}} < 0$. In Figure 8b it can be appreciated that these features...
are more visible in SVO//STO than in SVO//NGO and SVO//LAO, and according to the previous statement, we conclude that in SVO//STO, $\Delta t_{2g}$ is positive ($>0$) and larger than in SVO//NGO and SVO//LAO. Therefore, the VO$_6$ octahedra in SVO//STO are under a larger tensile in-plane stress than in SVO//NGO and SVO//LAO. Although in principle $\Delta t_{2g}$ could be deduced by comparing multiplet calculations with experimental spectra, we content ourselves here by using XLD to discern between tensile or compressive strain.

Overall, from both XAS and XLD data we conclude that: i) a tetragonal crystal field breaks the symmetry of the $t_{2g}$ manifold into ($xy$) and ($xz$, $yz$) states; ii) as $\Delta t_{2g} > 0$, the $t_{2g}(xy)$ states lay lower in energy than $t_{2g}(xz, yz)$ and thus they have a higher electron occupancy (see Figure 8d for the unstrained and strained VO$_6$ octahedra and the $t_{2g}$-manifolds).

### 3. Conclusion

We have shown that SrVO$_3$ films grown under different oxygen pressure and on substrates having different structural mismatch, thus imposing different (tensile or compressive) epitaxial stress, clearly show distinct transport properties. The carrier mobility is found to be the largest in SVO films grown on matching substrates and lowering when films are grown on substrates imposing a large tensile or compressive strain. Although the film conductivity, carrier density and mobility are found to depend on the growth conditions (mainly the oxygen pressure) as expected in presence of growth-induced point defects (Figures 1b and 4) the dependence on these parameters on substrate mismatch is fully preserved, thus suggesting that the substrate plays a major role. Interestingly, the reduction of mobility is asymmetric, being more pronounced in case of tensile stress (SVO//STO) but only marginally larger in case of compressive stress (SVO//LAO).

Using first principle calculations Sclauzero et al. have predicted that epitaxial strain on SVO has basically two effects. First, a crystal field of tetragonal symmetry breaks the degeneracy of the $t_{2g}$ electronic triplet and, irrespectively of the sign of strain, the electronic correlations will be reinforced and approaching SVO to an insulator Mott regime. Second, stretching the M–O bonds should have a similar effect, whereas bond shortening should have the opposite effect, that is enhancing the hopping amplitude and thus promoting a more metallic character. Therefore, for tensile strain a more insulating character of SVO is expected whereas for a compressive strain, band narrowing and hopping-amplitude enhancement cancel out their contributions and only minor changes of carrier mobility are expected. Our XAS and XLD data provide clear evidence of the strain-induced breaking of symmetry and stabilization of the $xy$ orbitals in STO compared to other substrates (Figures 1a and 8). This is consistent with...
the c/a < 1 distortion of the unit cell of SVO/STO, inferred from X-ray diffraction data. Charge redistribution enhances xy orbital occupancy, narrows the electronic bandwidth, and enhances the effective mass of carriers in films on STO compared to other substrates. This is precisely the result obtained from ellipsometry measurements, where \( m^a(SVO/STO) \approx 1.25 \times m^a(SVO/LSAT) \) (Figure 7). However, this 25% enhancement of the effective mass of carriers in SVO/STO cannot account for the observed \( \approx 200\% \) larger resistance in SVO/STO compared to SVO/LSAT (or other substrates) (Figure 4a). Therefore, other effects should play a bigger role on DC transport properties.

The TEM images have provided evidence of the existence of arrays of planar defects in SVO films grown on mismatched substrates and their orientation is compatible with the observed modification of mobility, more (less) pronounced in SVO films on STO (LAO). This is the trend observed for the resistivity and carrier mobility of SVO films grown on different substrates (Figure 4a,b). Remarkably, it is found (Figure 5) that carrier mobility increases when increasing carrier concentration. This observation favors the view that electrical conductivity and mobility in these strained films, although affected by the heavier electron mass in tensile strained films, are primarily governed by microstructural effects, namely stress-induced planar defects (Figure 1c). Therefore, one could anticipate that avoiding strain relaxation, maybe by using thinner SVO films, the genuine effects of band reconstruction due to epitaxial strain will become more apparent on the DC electric transport properties. Otherwise, only optical conductivity (thus plasma frequency) is sensitive to these effects. From a practical point of view, it is remarkable that the optical transparency window remains in the visible range for all studied films irrespectively on the growth conditions and substrates, thus suggesting that the harsh conditions required to grow optimal SVO films may not be a limitation for future applications.

4. Experimental Section

Samples Preparation: SVO films were grown on cubic single crystalline perovskite substrates having different cell parameters: SrTiO\(_3\) (STO, 3.905 Å), (LaAlO\(_3\))\(_{0.3-}\)(Sr\(_2\)AlTaO\(_6\))\(_{0.7}\) (LSAT, 3.868 Å), NdGaO\(_3\) ( NGO, pseudocubic) 3.863 Å, and LaAlO\(_3\) (LAO, 3.791 Å). Bulk SVO was cubic with a(SVO) = 3.842 Å \([11,42]\). Therefore, the structural mismatch between SVO and the substrate, defined as \( f = [a_S - a(SVO)]/ a_S \), where \( a_S \) is the cell parameter of the substrate was \( f(STO) = 1.159\% \), \( f(LSAT) = -0.65\% \), \( f(NGO) = -0.52\% \), and \( f(LAO) = -1.37\% \). As-received (001)-oriented single crystals (cubic and pseudocubic settings) were used as substrates. Films were grown by pulsed laser deposition (PLD) (excimer laser, 248 nm wavelength) at a frequency of 5 Hz, a fluence of around 2 \( J \) cm\(^{-2}\), and the number of laser pulses was 2000. A \( Sr_2V_2O_7 \) target was prepared by solid state reaction of stoichiometric arrays of planar defects in SVO films grown on mismatched substrates, thus suggesting that the optical transparency window enhances the effective mass of carriers in films on STO compared to other substrates. This is precisely the result obtained from ellipsometry measurements, where \( m^a(SVO/STO) \approx 1.25 \times m^a(SVO/LSAT) \) (Figure 7). However, this 25% enhancement of the effective mass of carriers in SVO/STO cannot account for the observed \( \approx 200\% \) larger resistance in SVO/STO compared to SVO/LSAT (or other substrates) (Figure 4a). Therefore, other effects should play a bigger role on DC transport properties.

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Structural Characterization: XRD (Cu-K\(_{α1}\)) radiation measurements were done using either a PANanalytical X’Pert MRD (θ-2θ scans) or a Bruker AXS D8 Advance equipped with a GADDS 2D detector (2θ–θ frames). Film thickness was determined by X-ray reflectivity (XRR). Within the explored (T, PO\(_2\)) range of parameters, the thickness of all films was found to be within the 70–80 nm range. Topographic measurements were done by using an atomic force microscope (AFM) in tapping mode. Specimens for TEM observation were prepared in cross section geometry by FIB using the lift-out technique. TEM images were acquired using JEOL J2100 as well as JEOL J2010F microscopes, both operated at an accelerating voltage of 200 kV.

Transport Measurements: Electrical resistivity was determined by Van der Pauw method on unpatterned films, and Hall effect measurements were performed to determine carrier density and mobility. Measurements were performed in a PPMS Quantum Design system with magnetic fields up to 9 T.

Optical Characterization: Variable-angle spectroscopic ellipsometry (VASE) measurements were carried in reflection mode at ambient conditions using a SOPRALAB GESE5 ellipsometer. The ellipsometric spectra (Δ, Ψ) were recorded in the 230–990 nm spectral range at incident angles θi = 65°–75°. Optimized conditions were found to be θi = 65° for LAO, LSAT, and NGO and θi = 68° for STO. Data sets were analyzed with WinEllii software. The SE data of the substrates were fitted first. Then, using the structure air/film/bulk-substrate, dielectric and optical coefficients (\( ε = ε_1 + i ε_2 \) and \( η = n + i κ \)) of the films were obtained (assuming isotropic ε). Films thickness was previously determined by XRR and inserted in the structure. FTIR measurements were performed using a Hyperion 2000 (Bruker) microscope.

Synchrotron Experiments: XAS was measured at the V-L\(_{2,3}\) edges at 300 K using linearly (either horizontal or vertical) polarized light and probed the XLD as the difference between the two light polarizations. To get access to the difference in orbital occupancy of t\(_{2g}\)-(xy, yz, xz) states, XAS spectra have to be taken for \( E//ab \) and for \( E//c \) (later shortened as \( E_a \) and \( E_c \), respectively, where ab and c indicate in-plane and out-of-plane X-ray electric field E directions, respectively). Due to geometrical constraints, following common practice, the spectra were collected in grazing incidence with the X-rays incidence direction \( k = 60° \) with respect to the surface normal. The photocurrent was measured in the total electron yield (TEY) mode. Average XAS spectra were obtained by averaging the intensities of both linear polarizations (parallel to the surface normal \( I(E_a) \) and perpendicular to it \( I(E_c) \)) as \( I(ε) = (I(E_a) + I(E_c))/2 \). The XLD signal was plotted as \( I(E_a) - I(E_c) \). The XAS experiments were performed at BOREAS beamline\([43]\) of ALBA synchrotron.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.
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