High Carrier Mobility, Electrical Conductivity and Optical Transmittance in Epitaxial SrVO₃ Thin Films

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The urgent need of more performant transparent conducting electrodes is stimulating an intensive research on oxide thin films based on early transition metals (e.g. V, Nb, Mo, etc.), where it is expected that the partially occupied (i.e. nd^1 , nd^2 ...) conduction band gives rise to metallic conductivity. Growing thin films of these oxides typically requires an extremely low oxygen pressure. However, in growth methods involving hyperthermal kinetics (such as pulsed laser deposition), this may have severe detrimental effects on the electrical and optical properties of the film. Here, it is shown that the use of a non-reactive gas during a pulsed laser deposition process allows to obtain epitaxial SrVO₃ films with significantly low room temperature resistivity ($\rho \approx 31 \mu\Omega \text{ cm}$), large carrier mobility ($\mu \approx 8.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and residual resistivity ratio ($\text{RRR} \approx 11.5$), while improving optical transparency in the visible range. It is argued that the success of this growth strategy relies on the modulation of energetics of plasma species and a concomitant reduction of defects in the films. These findings may find applications in other oxide-based thin film technologies (i.e. ferroelectric tunnel memories, etc.) where growth-induced point effects may compromise functionalities.

1. Introduction

Transparent conducting oxides (TCOs) are of crucial interest in many technology areas, from architectural and photovoltaic applications to flat panel displays, to name a few.^[1] TCOs

combine seemingly mutually exclusive high electrical conductivity and plasma frequency in the infrared, to guarantee optical transparency in the visible range. Typical TCOs are based on wide-band gap oxides, thus being inherently transparent, doped with a suitable amount of carrier donors to promote metallic behaviour.^[2] To guarantee a large electron mobility, oxides with conduction or valence bands stemming from orbitals of s- and p-parentage, are the materials of choice. So far, the well-known ITO (insulating In_2O_3 doped with electron-donor Sn) is the most used TCO for flat panel displays and other high-tech applications.^[3] The effective mass (m_{eff}) of n-type carriers in conduction band of s-orbital parentage is relatively small. Consequently, the plasma frequency $\omega_p \approx \sqrt{n/m_{\text{eff}}}$ remains at high energies unless the carrier concentration (n) is kept relatively low, thus compromising a required high electrical conductivity (σ) by leading to a substantial resistivity (ρ). Typical values for ITO are: $\rho = 100\text{-}200 \mu\Omega \text{ cm}$, $\mu = 20\text{-}200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $\omega_p = 3.8 \times 10^8 \text{ MHz}$ (1.6 eV) for $n < 3 \times 10^{21} \text{ cm}^{-3}$.^[3] On the other hand, the use and availability of InO_2 impose severe concerns and alternative materials are required. To keep with the limitations described above while increasing the TCO films' conductivity, as required for advanced applications,^[1] the natural strategy has been to increase the carrier mobility by exploiting the spatially extended s-orbital-derived conduction bands of post-transition-metal cations. This approach led to the breakthrough discovery of the highly conductive amorphous $\text{InGaO}_3(\text{ZnO})_5$ (IGZO).^[4]

In a radically different approach, recent years have seen the rebirth of transition metal oxides as TCOs. Indeed, early transition-metal-based oxides should be intrinsically metallic by the presence of partially filled nd orbitals. For instance, SrVO_3 (SVO) single crystals are known to be metallic^[5] and early reports also indicated that the metallic character was preserved in thin films.^[6,7] Progress on SVO thin film growth have been achieved by using pulsed laser deposition (PLD),^[8-16] hybrid-MBE^[17-20] and pulsed e-beam deposition (PED).^[21,22] The metallic character of SVO, associated to an intrinsic large carrier density of about 10^{22} cm^{-3} ,

combined with strongly correlated behaviour of electrons in the 3d-band, which give rise to a large effective mass, should allow to reduce the plasma frequency from the ultraviolet (as in common metals) down to the visible or near infrared regions. This approach was exploited by Zhang *et al.*^[20] to demonstrate that SVO thin films displaying high conductivity with a plasma energy $\hbar\omega_p \approx 1.33$ eV, i.e. below the infrared, can be grown by hybrid-MBE.

However, the epitaxial growth of SVO is intricate as stabilization of V^{4+} is challenging (V^{3+} and V^{5+} are competing valence states, leading to the formation of spurious insulating phases).

For that reason, extremely low oxygen pressures ($PO_2 \approx 10^{-7}$ mbar) are required.^[9] It is instructive to notice that, whereas the room-temperature resistivity values of optimal films are reported to be in the 30-120 $\mu\Omega$ cm range independently of the growth technique used, the residual resistivity ratio RRR ($RRR = \rho(300\text{ K})/\rho(5\text{ K})$) is typically of about 2 for films grown by PLD and PED^[6,7,9-12,21,22] but it is dramatically larger ($RRR \approx 120-222$) for hybrid-MBE grown films.^[17,19,20] This observation implies that the growth process has a large effect on the carrier mobility (and hence the electrical conductivity), probably related to the presence of growth-induced defects in the film. Indeed, in PLD technique, the use of ultralow pressure ($\approx 10^{-7}$ mbar) during growth has important consequences on the spatial expansion and kinetic energy of the ablated species^[23,24] as well as on the self-sputtering and backscattering.^[25] Probably the most obvious is that energetic species can impinge upon the substrate and the growing film, with subsequent creation of various defects including non-stoichiometry. Therefore, at first sight, the possible use of PLD (or any other hyperthermal technique) for deposition of materials requiring extremely low oxygen pressures may appear to be challenging.

Here, aiming at understanding and controlling growth-induced defects in SVO films and monitoring their impact on their electronic properties, namely electrical resistivity, carrier density and mobility, and optical transmittance, we report on the properties of SVO films

grown by PLD under non-reactive Ar atmosphere. The reason behind is that a non-reactive gas could contribute to plasma thermalization and consequently, reduce the kinetic energy of the species in the plume and their flux at the film surface, as demonstrated in the growth of high-temperature superconductor films.^[23] It will be shown that using this strategy, the extension of the plume of laser-ablated species can be controlled (**Figure 1a**) and films grown under optimal Ar pressure display a remarkable reduction of their room-temperature resistivity down to $\approx 30 \mu\Omega \text{ cm}$, thus competing with the record values of hybrid-MBE films, and the residual resistivity ratio rises by about a factor 5 compared to reported SVO films grown by conventional PLD and PED, as summarized in Figure 1b. Importantly, the transparency of the films in the visible range is enhanced by the new growth process developed here and rivals that of the hybrid-MBE grown films.^[20] These findings indicate that TCO films such as SVO, and probably other materials requiring ultra-low oxygen pressure deposition conditions, can be grown with optimal properties by PLD or other more scalable techniques, as required for large scale applications. From a different perspective and beyond the scope of TCOs, SVO films have been explored in search of quantum confinement effects; indeed, orbital selective quantization and anomalous mass enhancement effects have been reported^[26,27] in PLD-grown films, and SVO is considered to be the *drosophila* model for strongly correlated physics.^[28] Moreover, as emphasized by Backes et al.,^[28] the role of defects is pivotal for a microscopic description of the spectroscopic features. The improved properties of SVO films reported here may stimulate revisiting some scenarios.

2. Results

2.1. Structural Characterization

In **Figure 2a** and **2b** we show a zoom of the θ -2 θ XRD scans around the (002) reflection of SVO//LSAT and SVO//NGO films grown at different P(Ar). We first note the presence of the (002) SVO reflections, whose position gradually shift with P(Ar). Only (00 l) reflections are

visible in broader angular scans (Supporting Information Figure S1), indicating a (00 l) textured growth. We note that the (002) SVO reflections of films grown on LSAT and NGO at $P(\text{Ar}) = 0$ mbar, that is at the base pressure of the chamber, can hardly be discernible from those of the substrate due to the close structural matching and a notorious SVO line-broadening associated to a limited size of the coherently-diffracting volume of SVO, as confirmed by AFM images (Supporting Information Figure S2). The asymmetric broadening around the substrate reflection, visible in Figure 2a and 2b, reflects the overlapping of a broad (002) SVO peak with the one of the substrate. The small intensity peak occurring at the left of the main substrate peak, is a spurious signal from the substrates (Supporting Information Figure S3). Accordingly, the corresponding c-axis parameters would be $c(\text{SVO//LSAT}) \approx 3.92$ Å and $c(\text{SVO//NGO}) \approx 3.90$ Å. It is clear that these c-axis values are larger than that of bulk SVO (dotted line in Figure 2c) and also larger than those expected if a genuine substrate-induced epitaxial tensile stress f ($\approx +0.6\%$) due to the structural mismatch ($f(\text{LSAT}) = +0.65\%$; $f(\text{NGO}) = +0.52\%$) was acting on the film. The expected strain-induced c-axis values calculated from the Poisson equation, that is assuming volume conservation,^[17,29] are shown in Figure 2c (dashed lines). Therefore, the observed expansion of c-axis is not due to the epitaxial (tensile) stress imposed by the substrate but it is likely related to growth-induced non-stoichiometry, as commonly found in SVO films.^[10,11,17,19,30]

Of the highest interest is the observation in Figure 2a and 2b that when increasing the Ar pressure, the Laue fringes of the SVO films become clearly apparent indicating that their crystalline quality has largely improved. On the other hand, it can be appreciated that the (002) SVO reflection shifts towards larger angles, that is: smaller c-axis, when increasing $P(\text{Ar})$. This can be better appreciated in Figure 2c where the out-of-plane lattice parameters, determined from the θ -2 θ XRD scans, for SVO//LSAT (squares) and SVO//NGO (circles), are plotted against the Ar pressure. It is clear that the c-axis shrinks, from the larger value obtained when $P(\text{Ar}) = 0$ mbar, towards a value smaller than the bulk one and closely

approaching the c-axis value calculated on the basis of Poisson law and assuming a fully strained film. This suggests that SVO is stoichiometric when grown under a substantial Ar pressure and its crystal lattice is fully tensely strained. Therefore, by using an inert Ar buffering atmosphere during growth, the stoichiometry and the crystalline quality of the films are both improved. This observation dramatically illustrates the role of the energy of the impinging species on the film's quality. It is worth noticing that the atomic force microscopy images of samples grown using the $P(\text{Ar}) = 0.03$ mbar are remarkably flatter ($\text{rms} \approx 0.22$ nm), with well visible terraces and steps (on LSAT), than surfaces of films grown at the base pressure ($P(\text{Ar}) = 0$) where $\text{rms} \approx 0.45\text{-}0.50$ nm (Supporting Information Figure S4). At higher $P(\text{Ar})$, the surface becomes rougher and some crystallites are apparent. In agreement with earlier reports^[9] and our X-ray 2D reciprocal space maps (Supporting Information Figure S5), these crystallites correspond to the spurious $\text{Sr}_3\text{V}_2\text{O}_8$ phase. It is worth to stress that whereas it is known that the $\text{Sr}_3\text{V}_2\text{O}_8$ phase is formed under relatively rich oxygen atmosphere,^[9] here its presence becomes more prominent at nominally the same oxygen pressure (residual vacuum) but under higher $P(\text{Ar})$. A possible explanation could be that when increasing Ar pressure, scattering of plasma species increases, being more prominent for the lighter elements,^[24] and thus a V deficient flux of adatoms should be expected at the film surface, eventually leading to the formation of a sub-stoichiometric ($\text{V}/\text{Sr} < 1$) oxide, such as $\text{Sr}_3\text{V}_2\text{O}_8$. The $[\text{Sr}/\text{V}]$ concentration ratio in the SVO film and its dependence on $P(\text{Ar})$ has been explored by using Energy Dispersive X-ray spectroscopy (EDX) and X-ray Photoemission spectroscopy (XPS) (Supporting Information Figure S6). It is found that $[\text{Sr}/\text{V}]$ increases from $P(\text{Ar}) = 0$ to $P(\text{Ar}) = 0.3$ mbar, which we attribute to the gradual increase of the parasitic $\text{Sr}_3\text{V}_2\text{O}_8$ phase in the films, that blurs any possible change of stoichiometry of the SrVO_3 matrix.

Naturally, when increasing the Ar pressure in the chamber, the plasma becomes broader and the growth rate decreases. As shown in Figure 2d, the growth rate lowers down from ≈ 0.37 Å/pulse to ≈ 0.15 Å/pulse and thus the film thickness, at a given constant number of pulses, is

reduced from about ≈ 75 nm to ≈ 30 nm when increasing $P(\text{Ar})$. In passing, we note that if resputtering would have been suppressed by the high $P(\text{Ar})$ pressure, the growth rate in Figure 2d would show the opposite trend. Therefore, the non-observation of this feature implies that, in the explored pressure range, resputtering does not affect significantly the growth rate. In Figure 2d, the thickness values depicted are deduced either from the X-ray reflectivity data (XRR) (empty circles) or Laue fringes (filled circles) with good agreement (more details are given in Supporting Information Figure S7).

2.2. Transport Properties

The room-temperature resistivity $\rho(300\text{ K})$ of all SVO films as a function of $P(\text{Ar})$ is depicted in **Figure 3**. It is obvious that by increasing $P(\text{Ar})$ a substantial reduction of $\rho(300\text{ K})$, of about 60%, can be achieved in SVO films on both substrates. Further increase of $P(\text{Ar})$ above 0.1 mbar, produces a subsequent increase of $\rho(300\text{ K})$. The lowest $\rho(300\text{ K})$ values: $31\ \mu\Omega\text{ cm}$ (SVO//NGO) and $38\ \mu\Omega\text{ cm}$ (SVO//LSAT), are similar than those obtained in hybrid-MBE grown SVO films ($28\ \mu\Omega\text{ cm}$ ^[20]) and are smaller than most of PLD grown SVO films of similar thickness ($38\ \mu\Omega\text{ cm}$,^[9] $47\ \mu\Omega\text{ cm}$,^[11] $120\ \mu\Omega\text{ cm}$ ^[10]). The temperature-dependence of the resistivity down to 5 K was measured and used to determine the residual resistivity ratio (RRR) ($\text{RRR} = \rho(300\text{ K})/\rho(5\text{ K})$). In **Figure 4a** we show $\rho(T)/\rho(300\text{ K})$ of SVO//LSAT and SVO//NGO films grown at $P(\text{Ar}) = 0.2$ mbar. For reference, we also include the corresponding data for films grown at the base pressure $P(\text{Ar}) = 0$ mbar. It is clear in Figure 4a that using a suitable $P(\text{Ar})$, the $\rho(T)/\rho(300\text{ K})$ data show a larger slope and correspondingly, not only the room-temperature resistivity is reduced by using $P(\text{Ar})$ but the residual resistivity decreases as well. This can be better appreciated in Figure 4b where we plot the RRR for all films. The RRR systematically rises when increasing $P(\text{Ar})$, from about 2 in films grown at $P(\text{Ar}) = 0$ mbar, up to $\text{RRR} \approx 11.5$ in films grown on LSAT at $P(\text{Ar}) = 0.2$ mbar. Further increase of

P(Ar) reduces again the RRR. According to data in Figure 2d, films grown at different pressures have thicknesses varying between ≈ 70 -30 nm. As in this thickness range, the film resistivity does not depend significantly on the thickness (Supporting Information Figure S8), and thus their comparison should not be affected by size effects.

The obtained largest RRR values (≈ 11.5 and ≈ 7.5 , for SVO//LSAT and SVO//NGO, respectively) are definitely much larger, by roughly a factor 5, than earlier reports of SVO films grown by PLD (RRR ≈ 1.7 -2.4)^[9-11] or by pulsed e-beam deposition (RRR ≈ 1.6),^[21,22] as summarized in Figure 1b.

The carrier density (up triangles) and mobility (down triangles) of SVO//LSAT (upper panel) and SVO//NGO films (lower panel) are plotted in **Figure 5a**. One first notices that SVO films grown on LSAT and NGO at P(Ar) = 0 have a carrier density $n = 2.14 \times 10^{22} \text{ cm}^{-3}$ and $2.2 \times 10^{22} \text{ cm}^{-3}$, respectively. These value are very close to, although slightly larger, the value expected for stoichiometric SVO with V^{4+} ($3d^1$) ($\approx 1.76 \times 10^{22} \text{ cm}^{-3}$). We note that the XPS data of our SVO films grown at P(Ar) = 0 mbar are coincident with those reported for MBE in-situ grown *optimally oxidized* SVO films^[31] (Supporting information Figure S9). However formal assignment of the valence state of V to $3d^1$ configuration or others (i.e. $3d^0$, $3d^2$) is challenged by final state effects.^[31] The carrier mobility is $\mu \approx 2.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for SVO//LSAT and for $3.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for SVO//NGO. Data in Figure 5a show that there is a very remarkable increase of carrier mobility and density when increasing P(Ar) up to ≈ 0.1 -0.2 mbar and a subsequent decrease with further increase of P(Ar). Indeed, the carrier mobility is increased by roughly a factor two, achieving $\mu \approx 8.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for $n = 2.4 \times 10^{22} \text{ cm}^{-3}$ (SVO//NGO) when introducing the non-reactive Ar gas during growth. We notice that mobility in early PLD grown films was of $\approx 0.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ^[11] and ≈ 8 -9 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in hybrid-MBE films.^[17,20] Data in Figure 5a and 5b, clearly reveal than an increase of carrier concentration goes in parallel with an enhanced mobility ($\mu \propto n^b$, $b \approx 1$). The relevance of this observation is better

appreciated by noticing that in doped semiconductors the opposite behaviour is typically observed. Commonly, μ decreases with increasing doping due to the enhanced scattering with dopant atoms. The reverse trend observed here bears some resemblance with properties of some strained semiconductors, such as (Ba,Sr)SnO₃ or even n-GaN^[32] where a similar $\mu \propto n^b$ relation with $b \approx 1/2$ has been reported.^[33–35] It has been argued that this unconventional increase of mobility when increasing carrier density is due to the enhanced screening of defects, such as dislocations or impurities, by the carriers (n). In a similar scenario, scattering by ionized impurities in degenerate semiconductors leads to $\mu \propto n / Z_i^2 N_i$ where (Z_i , N_i) are the charge and concentration of ionized impurities.^[3] Therefore, as mentioned above, by using P(Ar) the plume-induced non-stoichiometry is reduced and consequently, a concomitant enhancement of mobility is expected, as observed.

2.3. Optical Transmittance

In **Figure 6a** we show the optical transmittance of the bare LSAT substrate together with that of SVO films, about 50 nm thick, grown using either the base pressure ($P(\text{Ar}) = 0$) (red line) or an argon pressure $P(\text{Ar}) = 0.1$ mbar (blue line). It is interesting to note that the films grown under Ar have a slightly larger transparency than those grown at the base pressure. This observation is consistent, as argued above, with a reduction of light-absorbing point defects in the films grown under Ar. Moreover, it can be appreciated that the transparency of Ar-grown films is similar to that reported for films of similar thickness (63 %) (indicated in Figure 6a by a dashed line) grown by hybrid-MBE.^[20] The improved optical transmittance of the films is well visible in the picture shown in Figure 6b. Finally, the plasma energy of the SVO/LSAT film grown at $P(\text{Ar}) = 0$ mbar, can be roughly estimated from the zero-crossing of the real part of the permittivity, occurring at ≈ 1.2 eV (Supporting Information Figure S10). This value is very close to the screened plasma frequency (≈ 1.33 eV) reported for hybrid-MBE grown thin

films^[20] (Supporting Information Figure S10). To obtain the unscreened plasma frequency, necessary to compute the correlation-enhanced effective mass, a complete analysis of the optical conductivity is required, which is beyond the scope of this manuscript. For hybrid-MBE SVO thin films,^[20] having a similar screened plasma frequency and similar conductivity values, the unscreened plasma energy $\hbar\omega_p$ was evaluated to be ≈ 2.1 eV; a similar value should be expected here. Using $n \approx 2 \times 10^{22} \text{ cm}^{-3}$ this would indicate a correlation-renormalized effective mass of about $m_{\text{eff}} \approx 3$, consistent with the 3d nature of the orbitals forming the conduction band of SVO.

3. Conclusion

Overall, the data shown above indicate that the resistivity of SVO films on lattice matched substrates (LSAT and NGO) is critically determined by harsh growth conditions, namely the extremely low pressure required in the growth chamber, and the concomitant presence of energetic species impinging the film and the subsequent creation of point defects in the latter. We have shown that, to some extent, increasing the pressure of a non-reactive gas during growth, allows to obtain SVO films with optimized properties (higher room-temperature electrical conductivity and carrier mobility). We claim that, as deduced from the structural data information, the improvement of the electrical quality factors of the films goes in parallel with a reduced density of plume-induced non-stoichiometry-related defects in the films and a concomitant reduction of the unit cell volume. We argue that point defects, most likely non-stoichiometric defects, are the bottleneck to obtain optimally conducting films when growth requirements impose using low-oxygen process in the growth chamber. The use of a partial pressure of non-reactive gas appears as a simple way to optimize films properties. This unconventional approach to grow oxide thin films may pave the way towards the development and integration of transition metal TCOs in the latest technologies. Although here we have

chosen to use a non-reactive gas to modulate the laser plume, other alternative strategies, such as tuning the laser fluence could be investigated for the search of similar effects.

4. Experimental Section

Samples preparation: Films were grown on single crystalline perovskite substrates: (001) $(\text{LaAlO}_3)_{0.3}-(\text{Sr}_2\text{AlTaO}_6)_{0.7}$ (LSAT), and (001) NdGaO_3 (NGO). Here NGO is indexed with a pseudo-cubic unit cell. The lattice mismatch, defined as $f = [a_s - a(\text{SVO})]/a_s$, where $a(\text{SVO}) = 3.842 \text{ \AA}$ is the cell parameter of bulk SVO^[5,20] and a_s is the cell parameter of the substrate ($3.868 \text{ \AA}$ and $3.863 \text{ \AA}$ for LSAT and NGO, respectively) is $f(\text{LSAT}) = +0.65\%$ and $f(\text{NGO}) = +0.52\%$. Thus, an epitaxial growth would impose a tensile strain on the film in both cases. Films were grown by PLD using a KrF excimer laser at 5 Hz and a fluence around 2 J cm^{-2} . A fixed number of 2000 pulses was used. The $\text{Sr}_2\text{V}_2\text{O}_7$ target was prepared by solid state reaction of SrCO_3 and V_2O_5 mixed in stoichiometric amounts. Films were deposited at 750°C . The base pressure at the growth temperature is of about $P \approx 2 \times 10^{-6} \text{ mbar}$ (corresponding to a residual oxygen partial pressure of roughly $\text{PO}_2 \approx 4 \times 10^{-7} \text{ mbar}$). A series of films was grown under argon pressure $P(\text{Ar})$ ranging from $P(\text{Ar}) = 0 \text{ mbar}$ to 0.3 mbar . After growth, films were cooled to room temperature by switching off the substrate heater, while keeping the same pressure as used for the growth.

Samples characterization: Structural characterization, film thickness and cell parameter measurements were done by X-ray diffraction (XRD) using either a Bruker A25 D8 Discover (θ - 2θ scans) or a Bruker D8 Advance GADDS using a 2D Vantec-500 detector (2θ - χ scans). Film thickness was determined from X-ray reflectivity data and from the fitting of Laue fringes^[36] (when present). Topographic images were collected by atomic force microscopy (AFM) in dynamic mode. Electrical resistivity was determined by van der Pauw method, and Hall effect measurements were done on unpatterned films to determine carrier density and mobility. Measurements were performed in a PPMS Quantum Design system with magnetic

fields up to 9 T. A Cary 5 UV-Vis-NIR spectrophotometer was used for optical transmission coefficient measurement.

Supporting Information

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

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Figure 1. a) Pictures of the SVO plasma during PLD deposition in vacuum or under argon pressure of 0.1 mbar. To provide a suitable scale, the target-to-substrate distance is indicated. Sketches below each picture highlight the occurring phenomena. Green arrows length illustrates the kinetics of species reaching the substrate. In the case of the deposition in vacuum, red arrows represent re-sputtering process. b) State-of-the-art electrical resistivity values of SVO films at room-temperature (red solid circles) and at low temperature (5 K) (blue circles) grown by different techniques, as indicated. Data for SVO single crystals (bulk) are also included. Data reported in this work are shown by stars.

Figure 2. X-ray diffraction θ - 2θ scans, zoomed around the (002) SVO reflections of: a) SVO//LSAT, and b) SVO//NGO films grown at various $P(\text{Ar})$. The number on top of each scan indicates the corresponding $P(\text{Ar})$ in mbar. c) Out-of-plane cell parameters of SVO on LSAT (squares) and NGO (circles) films as function of $P(\text{Ar})$. The horizontal dotted line indicates the c-axis of SVO single crystal; the predicted c-axis lengths associated to the tensile epitaxial strain imposed by LSAT and NGO substrates, calculated assuming unit cell conservation, are shown by dashed lines: LSAT (blue, bottom) and NGO (red, top). d) SVO film thickness (left axis) and growth rate (right axis) dependence on $P(\text{Ar})$ of films deposited on LSAT (squares) and NGO (circles). Filled symbols correspond to thickness values extracted from Laue fringes while empty symbols stand for XRR determined thickness. Error bars are indicated when they are larger than the symbol size.

Figure 3. Room-temperature resistivity $\rho(300\text{ K})$ of SVO films grown on LSAT and NGO substrates under various $P(\text{Ar})$.

Figure 4. a) Temperature-dependence of the normalized resistivity $\rho(T)/\rho(300\text{ K})$ for SVO films on LSAT and NGO substrates, grown under $P(\text{Ar}) = 0.2$ mbar. Data for similar films grown at the base pressure $P(\text{Ar}) = 0$ mbar are also included. b) Residual resistivity ratio ($\text{RRR} = \rho(300\text{ K})/\rho(5\text{ K})$) as a function of argon pressure for films grown on LSAT and NGO substrates.

Figure 5. a) Carrier density (up triangles) and carrier mobility (down triangles) of SVO on LSAT (upper panel) and on NGO (lower panel) as a function of the deposition argon pressure $P(\text{Ar})$. b) Relationship between carrier mobility and carrier density for SVO films grown on LSAT and on NGO, grown under different $P(\text{Ar})$ (in mbar, indicated by the numbers next to the data points). Error bars, mainly affecting carrier density due to uncertainty in film thickness, are indicated.

Figure 6. a) Optical transmittance of SVO films on LSAT, about 50 nm thick, deposited either at $P(\text{Ar}) = 0$ mbar (red) or at $P(\text{Ar}) = 0.1$ mbar (blue). Transmission spectrum of the pristine LSAT substrate is also included (black). For reference, the maximal transmittance in the visible range of state-of-the-art SVO films grown on LSAT by hybrid-MBE^[20] is included (dashed line). b) Picture of the three samples displayed on the background ordered as in the legend of figure a).

Transparent conductors are pivotal to information society, and early transition metal oxides, such as SrVO_3 , seem to be called to play a big role. However, the growth of SrVO_3 thin films using pulsed laser deposition, or any other common hyperthermal growth technique, has remained elusive. The use of an inert gas during pulsed laser deposition allows to obtain SrVO_3 films with enhanced electrical properties and optical transparency, thus solving current bottlenecks.

Keyword: transparent conducting oxides

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High Carrier Mobility, Electrical Conductivity and Optical Transmittance in Epitaxial SrVO_3 Thin Films

Supporting Information

High Carrier Mobility, Electrical Conductivity and Optical Transmittance in Epitaxial SrVO_3 Thin Films

*Mathieu Mirjolet, Florencio Sánchez and Josep Fontcuberta**

Figure S1. X-ray diffraction θ - 2θ scans of: a) SVO/LSAT and, b) SVO/NGO films grown at various $P(\text{Ar})$. The number on top of each scan indicates the corresponding $P(\text{Ar})$, in mbar.

Figure S2. AFM topographic images ($1\ \mu\text{m} \times 1\ \mu\text{m}$) of SVO films on LSAT (left images) and on NGO (right images), grown at the lowest pressure corresponding to $P(\text{Ar}) = 0\ \text{mbar}$. Insets are $250\ \text{nm} \times 250\ \text{nm}$ zooms. It can be appreciated that films have a granular structure, with typical lateral sizes below $\approx 50\ \text{nm}$.

Figure S3. X-ray diffraction θ - 2θ scans of pristine (a) (001) LSAT and (b) (110) NGO substrates.

Figure S4. AFM topographic images, $5\mu\text{m} \times 5\mu\text{m}$ in size, of SVO films grown at various $P(\text{Ar})$ on LSAT (top images) and NGO (bottom images). Insets in some images are $1\mu\text{m} \times 1\mu\text{m}$ images emphasizing the outgrowths formed at film surface when growth is performed at higher $P(\text{Ar})$.

Figure S5. XRD 2θ - χ frames of SVO on LSAT films grown at: a) $P(\text{Ar}) = 0 \text{ mbar}$ and, b) $P(\text{Ar}) = 0.2 \text{ mbar}$. Whereas only the LSAT reflections are visible in the left image (due to the limited resolution of the 2D detector), spots corresponding to (205) reflections of $\text{Sr}_3\text{V}_2\text{O}_8$ are visible in the right image.

Figure S6. Dependence of the relative concentration of [Sr/V] as a function of the P(Ar) used during film growth, deduced from: a) EDX, and b) XPS analysis. Details are given in the text below.

Energy Dispersive X-ray spectroscopy (EDX) measurements have been done on SVO//NGO samples to extract an estimate of the film composition. Experiments have been performed with an electron energy of 15 keV and the Sr-L and V-K lines. We note that there is some overlapping of the V-K line with the Nd-L one (coming from the substrate) that may induce a systematic error in the calculated concentrations, and so we restrict to consider the [Sr/V] ratio trend rather than their absolute values. In Figure S6a above we include data taken on 5 different regions for each film. It can be appreciated that there is a dispersion of [Sr/V] of about 8%, which is rather common in EDX analysis. One could also tentatively infer a slight tendency to enrich the Sr contents of the samples by about 7-9% when P(Ar) increases. However, as a phase segregation of $\text{Sr}_3\text{V}_2\text{O}_8$ occurs, at least at the film surface, the observed increase of [Sr/V] could be simply a result of the increasingly presence of $\text{Sr}_3\text{V}_2\text{O}_8$ phase, when P(Ar) increases, rather than a change of the film composition itself.

We had also performed XPS measurements. Samples cannot be measured in-situ but transferred to the XPS chamber via ambient atmosphere exposure. On the other hand, it is obvious that samples grown at different conditions cannot be grown simultaneously. Therefore, when samples are XPS-measured they have been in contact with atmosphere during an avoidably different amount of time. Although Ar^+ sputtering can be done to clean the surface, it is known that this process may result on alterations of the material's structure, so we prefer here to focus on fresh non-sputtered samples. In Figure S6b we show the relative change of the [Sr/V] ratio of samples grown at three different P(Ar). Data have been evaluated from the integration of the XPS data taken in the appropriate spectral regions, after removing the baseline by using standard protocol and CasaXPS software. Data have been collected at normal incidence. Two different sets of lines have been used for quantization. We first used Sr-3d and V-2p lines to evaluate [Sr/V] using the atomic sensitivity factors provided the CasaXPS. Results are included in Figure S6b (down green triangles). At first sight the data would suggest a reduction of the Sr/V ratio of about 6% when increasing the P(Ar). However, the extremely surface sensitive character of XPS precludes to strongly support the conclusion above. Indeed, if instead of the V-2p line one uses the V-3s line, which although having a smaller intensity and thus a relatively larger error bar, has a binding energy smaller and thus a kinetic escape energy of electrons larger and correspondingly is less sensitive to surface effects, the [Sr/V] ratio displays the opposite trend as shown in Figure S6b (up red triangles). The [Sr/V] ratio evaluated using the Sr-3d and V-3s lines, in spite of the larger error bar associated

to the weak V-3s signal, suggest that it increases with P(Ar). This conclusion is in qualitative agreement with that derived from the EDX data (Figure S6a).

In summary, the EDX and XPS data could be interpreted as providing some hint towards some slight enrichment of [Sr/V] with P(Ar) in the SVO film. However, as X-ray diffraction and AFM clearly indicate the progressive formation of $\text{Sr}_3\text{V}_2\text{O}_8$ precipitates at the surface, the observed Sr enrichment does not necessarily reflect an actual Sr enrichment in the SVO structure, which could be fully stoichiometric. It thus follows that the impact of P(Ar) on the actual composition of the film cannot be derived neither from EDX nor from XPS data.

Figure S7. a) Examples of X-ray reflectivity scans of SVO films on LSAT grown under various P(Ar) (indicated by the numbers, in mbar, on the right of the spectra); b) Illustrative examples of fitting of Laue fringes observed in the XRD θ -2 θ scans to determine the film thickness and out-of-plane cell parameter. We determined a thickness of $t = 46.9$ nm and c -axis $c = 3.824$ Å for the film of SVO on LSAT grown under P(Ar) = 0.1 mbar and; c) $t = 30.6$ nm and $c = 3.823$ Å for a film grown under P(Ar) = 0.3 mbar. A description of the fitting method can be found in Pesquera et al.^[1]

Figure S8. Thickness dependence of the resistivity of SVO films grown on LSAT and NGO at different $P(\text{Ar})$ (as indicated by the labels (mbar)).

Figure S9. XPS V-2p spectra of SVO films grown at: a) $P(\text{Ar}) = 0$ mbar, and b) 0.3 mbar. In the panel c) we include the corresponding spectrum from an optimally oxidized film from Lin et al.^[2]

In SrVO_3 the valence state of V is expected to be 4+, implying a $3d^1$ occupation and a metallic character, as observed. The XPS data around the O-1s and V-2p peaks of films grown at different $P(\text{Ar})$ are shown in Figure S9 above, where we also include for convenience the XPS data of the optimally oxidized SVO film reported by Lin et al.^[2] From their multiple peak analysis,^[2] they conclude that the V-2p_{3/2} line can be decomposed into three components (as indicated in Figure S9c) having binding energies of 517.9, 516.2 and 514.5 eV which correspond to nominal d^0 (V^{5+}), d^1 (V^{4+}), and d^2 (V^{3+}) components, respectively. Their relative intensities vary with the oxidation state of the sample and the relative weight of final state effects. The XPS data of our $P(\text{Ar}) = 0$ mbar sample (Figure S9a) is very similar to that of the optimally oxidized sample from Lin et al. although the V-2p_{3/2} line in our case occurs at 517 eV, probably due to calibration differences. We strength that the films of Lin et al. were grown and measured in-situ. Therefore, the presence a similar d^0 component in our spectrum, accompanying the d^1 one, shall not be taken as a signature of over-oxidation but rather as a result of surface reconstruction and final state effects.

The XPS data of the film grown at $P(\text{Ar}) = 0.3$ mbar (Figure S9b) shows an enhanced d^0 contribution that reflects a higher oxidation state at the surface. This is fully compatible with the experimental observation (x-ray diffraction and AFM) of the formation of $\text{Sr}_3\text{V}_2\text{O}_8$ crystallites at the film surface.

Figure S10. Real part (ϵ_1) of the optical permittivity obtained by using spectroscopic ellipsometry measurements on a SVO film deposited on LSAT at $P(\text{Ar}) = 0$ mbar. The zero-crossing of ϵ_1 (obtained by b-spline interpolation of the experimental data) signals a screened energy plasma (defined as $E_{\text{op}} = hc / \lambda(\epsilon_1 = 0)$) of about 1.2 eV. Spectroscopic ellipsometry measurements were performed using an Imaging Ellipsometer Nanofilm EP4 from Accurion GmbH.

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