Wide-range strain tunability provided by epitaxial LaAl$_{1-x}$Sc$_x$O$_3$ template films

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Abstract. The dielectric diamagnetic LaAl$_{1-x}$Sc$_x$O$_3$ (LASO) ($x = 0$–1) is proposed for adjusting of the biaxial in-plane lattice parameter of oxide substrates in the wide range from 3.79 to 4.05 Å (6.5%). This range includes the pseudocubic lattice parameters of most of the currently investigated complex oxides. The in-plane lattice parameter of strain-relaxed LASO films depends linearly on the composition, and these films grow with a smooth surface. On several different LASO-buffered substrates, ferromagnetic La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) films have been grown in predetermined strain states. A series of 30 nm thick LSMO films on LASO-buffered LaSrAlO$_4$(001) demonstrates that continuously controlled coherent strains in a wide range, in this case from $-1$ to $+0.6\%$, can be obtained for the functional oxide films grown on LASO.

Biaxial strain has been shown to have a strong influence on the ferroelectric, ferromagnetic and superconducting properties of epitaxial oxide thin films [1]–[6]. Therefore, being able to control the exact amount of epitaxial strain induced by the substrate on a film is vitally important for its electronic function, e.g. in a spintronic device. A tunable template or so-called buffer layer, i.e. an epitaxial film having an in-plane lattice parameter that is predetermined by adjusting the chemical composition [7], helps us to overcome the problem arising from the fact that monocristalline substrates are available for certain distinct lattice parameters only [8].
Buffer layers are employed when minimization of strain is desirable in order to achieve bulk-like properties of the functional oxide film. Beyond this, recent work deliberately utilized biaxial strain to create or enhance specific physical properties such as ferroelectricity [1, 2]. An additional advantage of a buffer layer system over the use of different substrates is that other properties such as symmetry, surface morphology and chemistry can be kept essentially identical. A challenge, on the other hand, lies in achieving unstrained growth of the buffer on the substrate, whereas coherent growth of the functional film on top is desirable. Folkman et al [9] proposed the growth of RScO$_3$ buffers (R denotes a rare earth metal) where the lattice parameter is tuned from 3.94 to 4.05 Å by changing the R ion. Terai et al [7] reported on a Ba$_x$Sr$_{1-x}$TiO$_3$ (BST) buffer system where altering the Sr content is used to tune the lattice parameter continuously from 3.905 to 4.02 Å. A BaTiO$_3$ underlayer annealed at high temperature serves to trap dislocations and thus ensures an essentially dislocation-free BST buffer layer, whereas common single buffer layers naturally contain defects that are required for stress relaxation. The drawbacks of these and other known buffer systems are that (i) the lattice parameter does not cover a sufficiently wide range including the smaller oxides and/or (ii) they are mostly ferroelectric or paramagnetic themselves. The latter fact makes them less suitable for some investigations on ferroic oxides such as strain-induced ferroic order.

A specific motivation for the development of a tunable buffer system arises from the requirements for reversible biaxial strain modulation in epitaxial films using piezoelectric substrates, which provides direct access to the measurement of strain-dependent properties [4, 10, 11]. Ferroelectric Pb(Mg$_{1/3}$Nb$_{2/3}$)$_{0.72}$Ti$_{0.28}$O$_3$ (PMN-PT) substrates reach a uniform biaxial in-plane strain of $\leq 0.3\%$ and have been employed for dynamic strain control in several thin film materials [11–14]. Tunable buffer layers can significantly broaden the applicability of the method, since the as-grown strain of the functional film can be chosen as the starting point of the reversible strain experiment. Further, tunable buffers are useful for commercially available perovskite-type substrates, because most of them have smaller lattice parameters than the ferroelectric materials. This commonly leads to compressive strains unless appropriate buffer layers are used [8].

Here, a dielectric diamagnetic buffer system with a wide tuning range consisting of the perovskite parent compounds LaAlO$_3$ (LAO) and LaScO$_3$ (LSO) is introduced. By composition control using B-site random mixing, the biaxial in-plane lattice parameter of strain-relaxed epitaxial LaAl$_{1-x}$Sc$_x$O$_3$ (LASO) films is linearly tunable in the range of $a_{\text{LAO}} = 3.79$ Å $< a < a_{\text{LSO}} = 4.05$ Å. Due to the dielectric and diamagnetic nature of the parent compounds [15], the LASO buffer can be readily employed for metallic, superconducting, ferroelectric or ferromagnetic functional layers. Its suitability for the strain-engineered growth of functional thin films is demonstrated for the example of La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) grown coherently on relaxed LASO layers, resulting in continuously controlled strains of $-1\% < \varepsilon = (a - a_0)/a_0 < 0.6\%$, with the pseudocubic bulk lattice parameter $a_0$ for LSMO. Further, LASO allowed us to grow compressively strained films on the much larger PMN-PT substrates.

Epitaxial LASO films were grown by on-axis pulsed laser deposition (PLD) on (001)-oriented substrates of TiO$_2$-terminated SrTiO$_3$ (STO), LaSrAlO$_4$ (SLAO), LAO and PMN-PT. The deposition was performed at an optimized oxygen pressure of $p$(O$_2$) = 20 millitorr and a substrate temperature of 650°C for PMN-PT to avoid lead interdiffusion and 700°C for the other substrates. The compositionally controlled growth of LASO films was performed by alternating ablation [16] from ceramic LaAlO$_3$ and LaScO$_3$ targets by a KrF excimer laser ($\lambda = 248$ nm) with a 25 Hz repetition rate and a fluence of $1.25$ J cm$^{-2}$. LSMO films on top
Figure 1. In-plane lattice parameter of 50 nm thick LASO films on SLAO(001) and STO(001) substrates as a function of the LASO composition. The solid line denotes the nominal pseudocubic bulk lattice parameter assuming a linear dependence. Inset: AFM topography image (15 x 15 µm²) of the x = 0.23 film on SLAO.

of LASO buffers were grown at $p(O_2) = 100$ millitorr and 10 Hz. Finally, the as-prepared films were cooled to room temperature in $p(O_2) = 100$ torr. In situ high-pressure reflection high-energy electron diffraction (RHEED) was utilized to monitor the film quality and growth modes. RHEED intensity oscillations were observed in the beginning of the LASO deposition, indicating layer-by-layer growth, and they were used for determining the growth rate (0.09 per pulse) in order to ensure a constant LASO film thickness of $d = 50$ nm. Due to the reduced surface quality, no RHEED oscillations could be seen for PMN-PT substrates; hence, the average growth rate from the other substrates was used to estimate the thickness of the films grown on PMN-PT. Structural characterization was performed by means of a Panalytical X’Pert MRD x-ray diffractometer with Cu Kα radiation. Θ–2Θ scans revealed that the LASO films have a pure perovskite phase and are (001) oriented. In-plane and out-of-plane lattice parameters were determined from single scans through the 00l and l0l reflections and/or reciprocal space maps (RSM) at the 103 reflections. The surface morphology of the deposited LASO thin films was investigated using tapping mode atomic force microscopy (AFM). Even in the case of fully relaxed films on the SLAO substrates, the surfaces are smooth with a root-mean-square roughness < 0.3 nm, and the terrace structure of the substrate is maintained in the film (figure 1, inset). This roughness of as-grown buffer layers is suitable for the coherent growth of the functional layer on top.

The strain relaxation required for the LASO layer poses a challenge, which depends on several parameters. These include the lattice misfit, the crystalline and the surface quality of the substrate as well as the LASO thickness. Two series of 50 nm thick LASO films of varied composition were grown to study the strain relaxation: one on SLAO(001) ($a = 3.750 \text{ Å} < a_{\text{LASO}}$ for all LASO compositions, $c = 12.77 \text{ Å}$) and another on TiO$_2$-terminated STO(001) ($a = 3.905 \text{ Å}$) with lattice match near the middle of the LASO composition spread. On SLAO substrates, the measured values for $a_{\text{LASO}}$ track the calculated linear dependence on the composition (figure 1). Apart from some scattering due to the errors from the lattice parameter determination and small differences in sample preparation, the LASO buffer system
clearly allows linear compositional tuning of $a_{\text{LASO}}$. In contrast, LASO films on STO substrates show a strong tendency to accommodate epitaxial strain: they grow coherently or almost fully strained in a compositional range of about $x = 0.1$–0.5, resulting in in-plane strains of $\leq 2\%$ (figure 1). Thus, 50 nm thick LASO films do not serve as tunable buffer layers on TiO$_2$-terminated STO substrates for much of the entire composition range. Avoiding the strained growth of LASO can be achieved by reducing the substrate surface quality (e.g. by using mixed-terminated STO), by increasing the LASO thickness or possibly by altering the deposition conditions.

On piezoelectric PMN-PT an additional intermediate layer has been used, since LAO cannot be grown epitaxially on PMN-PT. STO was chosen for this purpose since it has been shown to grow epitaxially on PMN-PT with low roughness [14]. STO underlayers of $d \geq 10$ nm lead to a good crystalline quality of the subsequently grown LASO films. As the results shown below indicate, the use of an epitaxial STO layer (rather than a TiO$_2$-terminated STO crystal) in combination with a larger LASO thickness (120 nm) leads to a strain-relaxed LASO film.

The effective function of the LASO template layers has been demonstrated on 30 nm thick LSMO films, that have been deposited on LASO-buffered SLAO and PMN-PT substrates. The LASO composition was chosen to provide strain of opposite sign with respect to that expected from the substrate misfit. On bare SLAO substrates, LSMO ($a = 3.876$ Å) would be compressively strained or relaxed. As seen from the RSM through the 103 reflection (figure 2(a)), the LASO $x = 0.5$ buffer yields a LSMO film under a tensile strain of 0.7% ($a_{\text{LSMO}} = 3.920$ Å). Secondly, the bare PMN-PT substrate with $a = 4.02$ Å induces tensile strain in LSMO [10], whereas an LASO $x = 0.1$ buffer, with an STO underlayer as described above, allows us to prepare a compressive strain state of $-1.6\%$ ($a = 3.820$ Å). These examples show that the substrate strain can be effectively altered to a predetermined strain level by using the LASO buffer system.
The full range of strain tunability has been tested for the example of 30 nm thick LSMO films on SLAO substrates. Figure 3 shows the in-plane and out-of-plane lattice parameters, $a_{\text{LSMO}}$ and $c_{\text{LSMO}}$, as a function of the LASO composition. $a_{\text{LSMO}}$ has been continuously tuned through the range of $a_{\text{LSMO}} = 3.83$–3.92 Å. Coherent growth of LSMO on the relaxed buffer layers has been obtained for $a_{\text{LSMO}} = 3.84$–3.90 Å, as indicated by the blue line in figure 3, yielding tunable coherent strains of $-1\% < \varepsilon < 0.6\%$. Partial strain relaxation occurs outside this range, but a large residual strain is maintained.

To summarize, LASO has been proposed as a wide-range tunable buffer system for the strain-controlled growth of functional oxide films, which is suitable, in particular, for the investigation of strain-induced ferroic orders. The in-plane lattice parameter of strain-relaxed LASO films depends linearly on the composition, and these films can be grown with a smooth surface. The conditions for strain-relaxed growth have been addressed. The effective function of LASO has been demonstrated on ferromagnetic La$_{0.7}$Sr$_{0.3}$MnO$_3$ films grown in continuously controlled strain states predetermined by the LASO composition on several different substrates. The substrate misfit has been effectively masked by the LASO template; for example, compressively (tensily) strained LSMO films are obtained on larger (smaller) PMN-PT (SLAO) substrates. In a film series on SLAO substrates for exploring the full range of strain tunability, 30 nm thick LSMO films have been grown with a controlled coherent in-plane strain between $-1.0$ and $0.6\%$. Such film series with a continuously controlled biaxial strain show promise of being advantageous for both, systematic investigations of fundamental strain effects in complex oxides and the utilization of their strain-dependent ferroic properties.

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