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Chapter 1

Strain Effect in Epitaxial Oxide Heterostructures

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Abstract

In recent decades, extensive studies have been conducted on controlling and engineering novel functionalities in transition metal oxide (TMO) heterostructures by epitaxial strain. In this chapter, we discuss popular transition metal oxide thin films in the context of various research fields that are extensively studied in condensed matter physics. These materials include La$_{1.85}$Sr$_{0.15}$CuO$_4$ (a high temperature superconductor), SrRuO$_3$ (a highly conductive ferromagnetic metal), La$_{1.91}$Sr$_{0.09}$MnO$_3$ (a colossal magnetoresistive ferromagnetic metal), BiFeO$_3$ (a multiferroic oxide), LaAlO$_3$-SrTiO$_3$ (a conductive oxide interface), and LaNiO$_3$ (a strongly correlated metal). We focus on the appearance of novel functional properties from imposing epitaxial strain (compressive or tensile strain caused by the use of various lattice-mismatched substrates) on these films that cannot be observed in their bulk form. Subsequently, the intrinsic mechanisms for these novel phenomena are discussed based on experimental observations and theoretical modelling. We conclude that by using epitaxial strain, not only can thin film functionalities be tuned but many novel correlated phenomena can also be created. We believe that our collective efforts on the strain engineering of various transition metal oxide thin films will provide an insightful description of this emerging subject from a fundamental physics and nanoscale device applications point of view.

Keywords: oxides, substrates, thin films, strain effect, transport properties

1. Introduction

Matter can primarily be classified into three states: (1) gaseous, (2) liquid, and (3) solid (or condensed). In gaseous phases, the interactions among particles (atoms, molecules and ions) are very weak, and therefore they move freely. In liquid phases, the interactions between particles are comparatively strong. In solids, particles are closely packed or condensed, making the interactions between them the strongest compared to the other two states of matter.
Condensed matters (solids) are mostly crystalline; i.e., they have a periodic arrangement of atoms, ions or molecules. Depending on the periodicity of the atoms, they form different crystal structures. In nature, there are seven types of lattice structures: cubic (e.g., SrTiO$_3$), triclinic (e.g., FeSiO$_3$), monoclinic (e.g., BiMnO$_3$), orthorhombic (e.g., GdFeO$_3$), tetragonal (e.g., BaTiO$_3$), rhombohedral (e.g., BiFeO$_3$), and hexagonal (e.g., YMnO$_3$). Moreover, completely disordered systems displaying non-periodicity of atoms are called non-crystalline amorphous solids (e.g., glass). In reality, both types of systems show complex physics and chemistry with an immense number of functionalities [1].

Irrespective of their structural symmetry, three types of crystalline solids can be found either naturally or artificially, i.e., made in the laboratory. These include polycrystals, single crystals, and thin films. Polycrystalline materials are composed of many crystallites of various sizes that are oriented randomly (Figure 1a). Due to the random orientation of crystallites, they have many crystallite grains (~1 μm in size) with grain boundaries, twin boundaries and high porosity. As a result, polycrystals are occasionally considered dirty materials, and they show unusual behaviors at low temperature due to disorder. Polycrystals can be nearly several centimeters in size. Typically, the “solid-state reaction” method is used to synthesize polycrystalline materials [2].

Single crystals, in contrast, contain uniform orientations of their crystal lattices up to their edges, even at the macroscopic level; hence, there are no grain boundaries (Figure 1b). Therefore, it becomes easy to determine the various directions of a crystal and measure its properties along a particular direction. As a result, single crystals are regarded to be the cleanest and are very popular among the material science community as they reflect the exact properties of a material. Single crystals are nearly a few mm in size. For the most part, the floating-zone method, Czochralski method and Bridgman-Stockbarger method are used to grow high-quality single crystals [3]. A detailed analysis of these methods is beyond the scope of this chapter.

Thin films consist of very few layers of a solid material. They are typically deposited on structurally compatible metal oxide substrate surfaces (Figure 1c) by various thin-film deposition techniques [5]. Details about various thin-film deposition techniques are discussed later in

![Figure 1. Schematics of a (a) polycrystal, (b) single crystal, and (c) thin film. Polycrystals have many grains, whereas the crystal orientation in single crystals is uniform. Moreover, thin films are grown on structurally compatible metal oxide substrates. Polycrystalline figure was taken from Ref. [4].]
this chapter. Thin films are those with thicknesses ranging from a few angstroms to several nanometers (~4 Å to 1000 nm). Most thin films are made of oxides, particularly transition metal oxides (TMOs).

TMO thin films are one of the most investigated research topics in condensed matter physics as they show a variety of phenomena, e.g., metal insulator transitions (MIT), high-temperature superconductivity (HTSC), colossal magnetoresistance (CMR), and multiferroicity (coexistence of magnetism and ferroelectricity), as well as those exhibited by high-mobility two-dimensional electron gases (2DEGs), topological insulators (TI), and quantum spin-liquids (QSL) [6–20]. In TMOs, the d-orbital electrons of transition metal elements play a crucial role in determining the physical properties of a compound through the interplay between spin, lattice, charge, and orbital degrees of freedom (Figure 2a) [21–24]. Among the various types of TMOs, perovskites are a class of materials that shows almost all the properties mentioned above. They have been a deeply researched topic among physicists owing to their simple crystal structure (Figure 2b) [25, 26].

Perovskites, named after the Russian Mineralogist Count Lev Aleksevich von Perovski, have a general unit cell crystal structure of the ABO$_3$ type, where the A-site is an alkaline earth or rare earth metal and the B-site is a transition metal element (e.g., Fe, Co, Ni, Mn, Ti, Ru, and Ir). The structure can easily accommodate a wide range of valence states in both A- and B-sites (e.g. A$^{+1}$B$^{+5}$O$_3$, A$^{+2}$B$^{+4}$O$_3$, and A$^{+3}$B$^{+3}$O$_3$); so the variety of perovskite oxides is unlimited; for example, manganites, ruthenates, nickelates, titanates, and iridates [25]. CaTiO$_3$ was the first perovskite discovered by Gustav Rose in 1839 from samples found in the Ural Mountains in Russia. The B-site cation of ABO$_3$ perovskites is surrounded by six O anions, forming a corner-shared BO$_6$ octahedron (Figure 2c). This octahedral cage is the most important part of the crystal structure of these materials because the hopping of electrons from one d-orbital of the transition metal element to another d-orbital depends on the shape, size and position of this octahedron; thus, it affects the physics and chemistry of the material and the appearance of variety of phenomena [21–24].

![Figure 2.](http://dx.doi.org/10.5772/intechopen.70125)
In bulk polycrystals and single crystals, the shape, size and position of the BO$_6$ octahedra can be manipulated externally by inducing chemical pressure (replacing A-site or B-site cations with other transition metal elements), or by partial oxygen pressure (changing the pressure from the atmospheric one) [6]. Ceramic materials fail structurally under modest strain (typically < 0.1% under strain) as these materials are brittle and thus will crack under this magnitude of strain, limiting the ability of routes involving chemical substitutions to control these materials. Cations with different sizes lead to the distortion of the crystal lattice, which is usually quantified as the Goldsmith tolerance factor [27] $t_f$, given by

$$t_f = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$

where $r_A$, $r_B$, and $r_O$ represent the ionic radii of ions A, B and O, respectively. The stability and distortion of a crystal structure is indicated by the value of $t_f$. For a perfect cubic structure, $t_f$ is 1. Structure still remains cubic for 0.89 ≤ $t_f$ ≤ 1.0 [26]. For more lower value of $t_f$ it forms other types of crystal structures, resulting in structural transitions to orthorhombic, or rhombohedral states that have lower symmetry than the cubic state.

However, as a result of chemical substitutions, disorder is introduced into the materials, which in most cases suppresses and even destroys the properties of a material. These difficulties can be overcome in a unique way in thin films by a disorder-free clean route approach. This can be achieved by growing thin films on substrates that are structurally compatible but have different cubic (pseudo-cubic) lattice constants. This is termed “strain engineering” in epitaxial thin films [28]. Once a strain effect is induced in a film, due to the change of energy scales of various degrees of freedoms (lattice, charge, spin, and orbital), it shows novel properties that cannot be found in parent bulk compound. This means that novel quantum-correlated phenomena can be obtained by the strain engineering of oxide heterostructures, which broadens the field and our understanding of condensed matter physics. In the next section, we will discuss how to grow such atomically controlled high-quality thin films and induce the strain effect in TMO heterostructure.

2. Thin film growth methods and substrates

In recent decades, significant advances have been made in synthesizing epitaxial thin films in the laboratory using various deposition techniques [5]. These methods are: (1) pulsed laser deposition (PLD), (2) molecular beam epitaxy (MBE), (3) off-axis radio frequency magnetron sputtering (RFMS), (4) metal-organic chemical vapor deposition (MOCVD), and (5) chemical solution deposition (CSD). By using these techniques, atomically controlled epitaxial thin films (epi means “above” and taxy means “in an ordered manner” in Greek), heterostructures and artificial superlattices can be grown. Among these techniques, PLD and MBE are the most popular ones adopted by the thin film community.

2.1. Pulsed laser deposition (PLD)

In 1986, the successful growth of HTSC YBa$_2$Cu$_3$O$_{7-δ}$ (YBCO, $T_c$ ~90 K) thin films by the PLD technique by Dijkkamp et al., generated great interest among the material science community,
as it provided an alternative method for making thin-film materials in the laboratory [29]. The PLD technique is probably the most commonly used method for growing oxide thin films [5, 30–32]. Films are grown inside a high-vacuum chamber. A homemade or commercially available polycrystalline target is ablated by an energy source (typically a KrF laser with a wavelength of 248 nm or a frequency-doubled Nd:YAG laser with a wavelength of 532 nm). When the target is ablated, it produces a highly energetic plasma plume from the target. This highly energetic plume contains ions and molecules that are then deposited onto the substrate surface, which is attached on a substrate holder and placed opposite the target along the same out-of-plane axis. The substrate temperature, which is controlled by a heater, is determined from outside the chamber using a pyrometer. The target-to-substrate distance is kept at ~40–50 mm as the dynamics and kinetics of the plume species are limited to a maximum critical distance from the target because of collisions. A schematic diagram of a PLD chamber is shown (Figure 3a) [33]. Gaseous atoms condense on a template created by the substrate to form a single crystal. During this process, one needs to fulfill the growing conditions, e.g., optimize the base pressure, gas (O$_2$, O$_3$, or Ar) pressure, substrate temperature, laser density, spot size, and substrate surface flatness. Since the whole process is a thermally non-equilibrium one, by tuning all these parameters and ultimately optimizing them, one can grow the highest quality atomically controlled epitaxial oxide thin films (Figure 3b) [15]. The in-situ growth process can be monitored in real time by using the reflection high-energy electron diffraction (RHEED) method.

The advantages of the PLD technique are: (1) in-situ stoichiometric transfer of composition from target to substrate; (2) compatible materials can be grown under oxygen pressures ranging from ultra-high vacuum (UHV) to atmospheric pressure; (3) materials ranging from ultra-thin homoepitaxial thin films to artificial superlattices can be grown with nanometer precision; (4) depending on the availability of the target material, a wide variety of films can be grown; and (5) materials are grown in a compact and inexpensive chamber. Furthermore, the disadvantages are: (1) sub-optimized growth conditions can lead to the non-stoichiometric films; and (2) due to the highly energetic plumes, macroparticles called “droplets” can be deposited on a substrate surfaces within a micrometer range [30]. Therefore, to grow the highest quality epitaxial thin films, one should be aware of these facts. There are many groups around the world who have been pioneers in growing artificial epitaxial single-crystalline thin films of the highest quality.

![Figure 3. (a) Schematic diagram of a PLD chamber used for growing epitaxial oxide thin films. (b) Schematic of a layer-by-layer view of two different materials grown on a substrate. Reprinted with permission from Refs. [15, 33]. Copyright 2013 Materials Research Society; Copyright 2012 IOP Publishing Ltd.](image-url)
2.2. Molecular beam epitaxy (MBE)

Molecular beam epitaxy (MBE) is also a method used to grow high-quality epitaxial thin films [5, 34]. It was invented in 1960s at Bell Labs by Arthur and Alfred Y. Cho [35]. The overall schematic of MBE is very similar to that of PLD thin film deposition. The only difference is the target material. Instead of a ceramic target, one uses “guns” called effusion cells (Figure 4a) [28, 36]. At the same time, one generates molecules from each cell using a highly intense laser beam (termed “atomic spray painting” by D. G. Schlom, a famous MBE thin film scientist) (Figure 4b) [28]. The spray duration is individually controlled for each beam by shutters. Once all the deposition conditions are satisfied, the ejected molecules travel to the substrate surface, condenses and form a single-crystalline thin film compatible with the substrate crystalline structure. One of the main advantages of MBE thin film growth is its extreme cleanliness; i.e., no dirt particles (highly energetic species) or unwanted gas molecules can interfere with or contaminate the single-crystal thin film growth.

2.3. Substrate selection for epitaxial thin films

Substrates seem to be the basis of all thin film growth. Choosing a suitable metal oxide substrate is an important factor for growing high-quality epitaxial thin films as the structure and properties of a thin film depends on the underlying substrate and the interfacial interaction...
between the substrate and film [38]. When choosing a metal oxide substrate for growing epitaxial films, one should consider the following factors:

1. Lattice matching between the substrate and film, which is important for the growth of most natural state films (structural compatibility).

2. No chemical reaction between the elements of the substrate and film (chemically compatibility).

3. Thermal-expansion matching between the substrate and film, as films are generally grown at high temperatures (good thermal-expansion match).

4. Surface quality of the substrate (e.g., free of cracks, unwanted particles, defects, and impure phases).

In most cases, the lattice constant and structure of a thin film should be compatible with those of the substrate to grow epitaxial films in their most natural state (Figure 5a). For most ABO$_3$ perovskites, their lattice constants range from 3.80 to 4.00 Å [39]. Fortunately, there are many perovskite single-crystal metal oxide substrates available commercially with lattice constants

![Diagram of structural relationship between the substrate and film](http://dx.doi.org/10.5772/intechopen.70125)

**Figure 5.** (a) Structural relationship between the substrate and film. For the most natural growth state of a film, a film’s lattice constant ($a_f$) should be similar to the substrate’s lattice constant ($a_s$), and the two should have structural compatibility. (b) List of cubic (pseudo-cubic) substrates and thin films within the lattice constant range from 3.70 to 4.00 Å. With a judicious choice of substrate, various atomically controlled high-quality thin films can be grown. Reprinted and adapted with permission from Ref. [41]. Copyright 2014 Materials Research Society.
ranging from 3.70 to 4.20 Å [28, 33, 40–42]. Among various available perovskite substrates, insulating SrTiO$_3$ is the most popular one. It has a cubic structure with a lattice constant of ~3.905 Å. There are also a broad range of substrates available with similar structures to that of SrTiO$_3$ while possessing different lattice constants and crystal orientations. These commercially available substrates include REScO$_3$ (RE = rare earths), La$_{0.18}$Sr$_{0.82}$Al$_{0.59}$Ta$_{0.41}$O$_3$ (LSAT), NdGaO$_3$, SrLaAlO$_4$, LaAlO$_3$, SrLaAlO$_4$, and YAlO$_3$ (Figure 5b). Thus, after careful consideration of all the important factors listed above and a film’s lattice constant, it is easy to choose a substrate suitable for the epitaxial growth of thin films.

3. Strain in perovskite thin films

3.1. Strain engineering of perovskite thin films

Strain engineering is a unique way to create the novel functionalities in epitaxial oxide thin films [40–43]. From substrate-thin film relation point of view, when the lattice constant of a film ($a_f$) is dissimilar to the lattice constant ($a_s$) of a substrate, compression or elongation occurs within the film’s crystal structure and thus elastic strain is induced in the film [41]. For cases of dissimilar lattice constants ($a_f \neq a_s$), the structure of the thin film tries to take the structure of the substrate, causing structural changes (mainly the change in BO$_6$ octahedron rotation, tilting, and distortion, and/or the change in B–O bond length) to occur from the original atomic position. This is defined as the typical strain effect in thin films. Quantitatively, the amount of strain ($\varepsilon$) induced in a film is defined as

$$\varepsilon = \left(\frac{a_s - a_f}{a_f}\right)$$

where $a_s$ is the substrate lattice constant and $a_f$ is the film lattice constant.

Generally, compressive strain (Figure 6a) is induced in a film when $a_f > a_s$, whereas tensile strain (Figure 6b) is induced in a film when $a_f < a_s$. Under these epitaxial strain scenarios, the properties of functional oxide thin films can be drastically altered. Currently, the strain ($\varepsilon$) of ~2–3% is quite common in epitaxial oxide thin films, with highest strain to date of ~6.5% being imposed on multiferroic BiFeO$_3$ films grown on a highly lattice-mismatched (110) YAlO$_3$ substrate [43]. Thus, elastic strain is a viable route to observe materials with exceptional properties that cannot be observed in their bulk form by any other means [44, 45]. Although it looks simple, the intrinsic mechanism of the appearance of novel functionalities induced by the strain effect is quite complex to understand. In the next section, we briefly discuss about the intrinsic mechanism of the strain effect in perovskite thin films.

3.2. Mechanism of the strain effect in perovskite thin films

In post-Moore era, electronic devices with multifunctionality may offer a new alternative to replace the current silicon-based technology because the additional value the devices would
generate from multifunctionality may create an economically viable path superseding the miniaturization limit of silicon electronic devices. In this perspective, oxide electronics based on multifunctional properties of transition metal oxides looks promising [46, 47]. Even more exciting is the fact that advanced thin film growth techniques with atomic controllability provide further opportunities to design and synthesize artificial complex transition metal oxide heterostructures and superlattices to bring forth emergent physical properties, normally not seen in bulk states. However, despite the rapid progress and tremendous success in obtaining novel functionalities by the strain engineering of epitaxial oxide heterostructures, there is no general rule or theory available till date for predicting a material’s electronic, magnetic, or other functional properties. This is perhaps due to a lack of knowledge about fully resolved atomic structures, especially the position of non-trivial oxygen atoms, as no experimental tool has yet been developed for the direct observation of oxygen atoms. In view of the lack of an experimental tool of this kind for transition metal oxides, electronic structure calculations could play a role instead. J. M. Rondinelli and N. A. Spaldin’s recent article is particularly insightful in this regard, and we follow them briefly in this section [48].

The detailed structural distortion obtained by the movement of oxygen atoms due to strain is highly significant and it has a strong influence on the electronic properties of TMOs. In fact, just a small modification in an atomic structure would change the relevant energy scales (lattice, charge, spin, and orbital) and it is hard to predict functionalities as material properties are strongly dependent on the competition between these energy scales. To illustrate the effects of structural distortions in thin films, let us start with the ideal ABO$_3$ perovskite structure which is a simple cubic one with space group $Pmar{3}m$. The most important part of this structure is its corner-shared BO$_6$ (B = transition metal) octahedron, which results in an O–B–O–B chain with a 180° B–O–B bond angle (Figure 7a). There are very few systems that adopt this cubic structure (e.g., SrTiO$_3$); however, in practice, most perovskites show structural distortions that lower their symmetry from that of a highly symmetric cubic structure.
Rotations or tilts of BO$_6$ octahedra around the high-symmetry axes are the most common distortions in perovskite structures [49–51]. These are conveniently described by the Glazer notation [52, 53] and written as $a^b c^c$, where $a$, $b$, and $c$ are the axes around which rotation occurs and the superscripts indicate whether the octahedral rotation is in phase (+) or out of phase (−). Thus, $a$, $b$, and $c$ are not identical with the lattice constants; instead, they indicate that the nearest neighbor transition metal distances along that direction are equivalent. As perovskites are three-dimensional systems, a rotation or tilt in one direction restricts the rotation or tilt in other directions. Depending on the rotation or tilt of the BO$_6$ octahedra, the cubic structure can deform, leading to the symmetry lowering of other crystal structures (Figure 7b) [48–51].

Figure 7. (a) The ideal ABO$_3$ perovskite crystal structure showing tilt in all three directions. (b) Distortion of BO$_6$ octahedra along various directions, lowering the symmetry of the cubic structure and forming other crystal structure. The +ve sign indicates in-phase rotation ($c^c$), and the −ve sign indicates out-of-phase rotation ($c^c$). Reprinted with permission from Ref. [48]. Copyright 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
This structural distortion is imposed on a thin film by the appropriate choice of lattice-mismatched substrates. It is widely believed that the strain imposed by film-substrate lattice mismatch generally changes the in-plane lattice parameter, but exactly what occurs still remains unclear and moreover is difficult to determine experimentally. Two possibilities remain: (1) changes in the in-plane lattice parameter are offset by changes in the in-plane metal-oxygen B─O bond lengths (Figure 8a and b), or (2) while keeping the B─O distance fixed, the lattice mismatch is offset by a change in magnitude of the tilt patterns through the rigid rotation of the BO$_6$ octahedron (Figure 8c and d). This is highly significant as, for example, the magnitude and symmetry of a crystal field are affected by changes in the B─O bond length, whereas the strength and sign of a superexchange interaction are affected by changes in the B─O─B bond angle [48].

Quantitatively, changes in the B─O bond length and B─O─B bond angles of octahedra affect the bandwidth (W) of ABO$_3$ perovskites as follows:

$$W \propto \frac{\cos \psi}{d^{3.5}}$$  \hspace{1cm} (3)

where $\psi = (\pi - \phi)/2$ is the buckling deviation of the B─O─B bond angle $\phi$ from $\pi$ and $d$ is the B─O bond length (Figure 8e) [54]. Due to rigidity, it is hard to change the B─O bond-length. Thus, as a result of imposed strain, octahedral rotation and tilt angle changes, the electron hopping changes within the $d$-orbitals and thus changes a material’s functionalities. Changes in the bandwidth also affect the effective correlation as in general changes in these energy scales cause the appearance of novel functionalities in oxide heterostructures under strain.

Figure 8. (a) Contraction and (b) elongation of B─O bond lengths, $d$, in a coherently strained perovskite film. Contraction is due to compressive strain, whereas elongation is due to tensile strain. Alternatively, change in the in-plane lattice parameters are due to the rotation of octahedra (c) perpendicular to the plane of the substrate or (d) about an axis parallel to the plane of the substrate. (e) Rotation ($\theta$) and tilt ($\phi$) angle used to describe the substrate-induced changes of octahedra. Reprinted with permission from Ref. [48]. Copyright 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
Along with these changes in bond length, bond-angle and crystal symmetry that determine changes in the in-plane lattice parameters, another possibility for substrate-induced changes in lattice parameter remains: the defect stoichiometry or defect concentration of the material. Defect concentration, especially the oxygen concentration, is particularly important as films are generally grown under the high oxygen pressure or high vacuum. To accommodate the strain energy, it is easy to form oxygen vacancies. It is known that the higher the concentration of oxygen vacancies, the larger the lattice constants \[55\]. Since strain is induced by various lattice-mismatched substrates, it is difficult to establish whether changes in defect concentration are an intrinsic thermodynamic response due to strain or if they arise due to an extrinsic effect during the growth process.

4. Material properties tuned by epitaxial strain

4.1. A high temperature superconductor: \( \text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4 \)

In 1986, the discovery of HTSC in the cuprate oxide family by Bednorz and Müller generated considerable interest within the material science community, both in fundamental and applied research, due to the possibility obtaining oxides that are room-temperature superconductors \[56\]. \( \text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4 \) (LSCO) is one example of these oxides. \( \text{La}_2\text{CuO}_4 \) is an antiferromagnetic insulator, but upon doping divalent \( \text{Sr}^{2+} \) ions in the trivalent \( \text{La}^{3+} \) site, magnetism is suppressed, and the compound makes a transition from an insulating to a superconducting state \[57\]. LSCO has a \( \text{K}_2\text{NiF}_4 \)-type tetragonal structure with bulk lattice constants of \( a = 3.777 \) Å and \( c = 13.226 \) Å and space group \( P4_2/mnc \) (Figure 9a) \[58\]. It has quasi-two-dimensional copper-oxygen (Cu–O) planes, and superconductivity occurs within these planes \[59\]. In the bulk, around the optimal doping region, its maximum superconducting transition temperature is \( T_c \approx 25 \) K (Figure 9b and c) \[60\]. Its carrier doping remains within the Cu–O planes and the formation of electron pairs due to coupling between electrons and phonons seem to play a major role in achieving superconductivity \[61\]. Its critical temperature is controlled by either the density of electron pairs or the strength of electron pairing interactions \[62\].

In principle, external perturbation is applied to a material to enhance its functional properties, suggesting that substrate-induced strain might be a way to enhance the superconducting \( T_c \) of cuprates (Figure 10a) \[63–70\]. Indeed, Sato et al., and Locquet et al., grew \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) (LSCO; \( x = 0.1, 0.15 \)) thin films on two different substrates, such as \( \langle 0 \ 0 \ 1 \rangle \text{SrTiO}_3 \) and \( \langle 0 \ 0 \ 1 \rangle \text{SrLaAlO}_4 \) \[63, 64\]. Surprisingly, Locquet et al., observed that when films are grown on highly strained \( \langle 0 \ 0 \ 1 \rangle \text{SrLaAlO}_4 \) substrates \( (a_c = 3.75 \) Å), which produces \( \sim 0.5\% \) compressive strain onto these films, this amount of strain is enough to modify the superconducting \( T_c \), making \( T_c \) almost double to its value found in the bulk, i.e., \( T_c \approx 49.1 \) K (Figure 10b) \[64\]. Independently, Sato, also reported the same study (Figure 10c) \[69\]. This is thought to be associated with strain-induced lattice deformation, which modifies the energy scales, leading to the formation and condensation of superconducting pairs. It was also observed that the residual resistivity value \( (\rho (0 \) K)) decreases as \( T_c \) increases \[69\]. More specifically, increasing \( T_c \) has a clear correlation with low residual resistivity. As stated by Sato, an increase in Cu–O bond length enhances the electrostatic potential at the Cu site relative to that at the oxygen site in the Cu–O plane.
Figure 9. (a) Schematic representation of the K$_2$NiF$_4$-type tetragonal crystal structure of La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) with lattice constants of $a = 3.777$ Å and $c = 13.226$ Å. (b) Resistivity of bulk single LSCO, showing the appearance of superconducting $T_c$ upon divalent Sr hole doping. (c) Sr hole doping dependence temperature vs. the material properties phase diagram of LSCO, showing that the system makes a transition from an antiferromagnetic insulator to a superconducting phase with the increase in Sr doping. Crystal structure was drawn using VESTA software. Reprinted with permission [57, 60]. Copyright 1992 American Physical Society; Copyright 2013 Macmillan Publishers Limited.
Therefore, hole carriers are distributed more preferentially in itinerant states originating from the O 2p orbitals. As a result, antiferromagnetic spin fluctuation in the Cu—O plane is suppressed due to the reduction of the superexchange interaction between two adjacent Cu spins. Reduced spin fluctuation is the possible origin for reduction in $\rho(0 \text{ K})$ and increase in $T_C$ \cite{69}.

For compressively strained films grown on (0 0 1) SrTiO$_3$ substrate, which induced ~3% tensile strain on films, the $T_C$ was found to be ~10 K \cite{64}. Later, Božović et al., showed that with higher quality films (with much more oxygen intake as the films were annealed under an ozone atmosphere), $T_C$ could reach up to ~40 K for tensile-strained films grown on (0 0 1).
SrTiO$_3$ substrates and ~51.5 K for compressive-strained films grown on (0 0 1) LaSrAlO$_4$ substrates [68]. Recently, Lee et al., also showed that oxygen vacancies and thickness-dependent strain relaxation indeed play a crucial role in increasing the superconducting $T_c$ as lattice structures are highly sensitive to oxygen stoichiometry (Figure 10d) [70].

4.2. A highly conductive ferromagnetic metal: SrRuO$_3$

SrRuO$_3$ is one of the most promising oxide material among those used by thin-film researchers [71]. It is an itinerant ferromagnetic bad metal [72, 73]. Structurally, it has a GdFeO$_3$-type orthorhombic distorted perovskite structure at $T = 300$ K with lattice parameters of $a = 5.5670$ Å, $b = 5.5304$ Å, and $c = 7.8446$ Å and space group $Pbnm$ (Figure 11a) [74]. This structure is converted into a pseudo-cubic (pc) lattice with a constant of $a_{pc} \sim 3.93$ Å ($a_{pc} = \sqrt{a^2 + b^2} = d_{110}$ and $c_{pc} = c/2 = d_{002}$). Bulk SrRuO$_3$ shows structural phase transitions from orthorhombic to tetragonal at $T = 547$°C and then to cubic symmetry at $T = 677$°C, respectively [75]. This is associated with the occurrence of RuO$_6$ octahedral rotation, leading to a lowered structural symmetry from the ideal cubic perovskites.

In high-quality bulk single crystals, the $\rho$ is ~200 μΩ cm with a mean free path of electrons of ~10 Å at $T = 300$ K (Figure 11b) [73]. SrRuO$_3$ shows a ferromagnetic transition at the Curie temperature $T_c \sim 165$ K (Figure 11c) with a magnetic moment of ~1.6 μ$_B$ per Ru atom [76]. Although extensively studied, but the origin of its ferromagnetism, Stoner-type itinerant ferromagnetism vs. localized moment picture, is still under fierce debate because of contradicting experimental results and theoretical calculations [77, 78]. Due to its highly conductive nature and structural compatibility with other perovskite thin films, it is particularly interesting for its usefulness as a bottom electrode for BiFeO$_3$, BaTiO$_3$, or Pb(Zr,Ti)O$_3$ ferroelectric thin films used in electronic applications [79].

Eom et al. were the first to synthesize high quality metallic epitaxial SrRuO$_3$ thin films on various substrates [80]. The ferromagnetic transition temperature for these thin films were found be lower than the bulk value, $T_c \sim 150$ K, which is probably caused by the dimensionality and

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**Figure 11.** (a) Schematic view of the crystal structure SrRuO$_3$ showing both the orthorhombic and pseudo-cubic unit cell. Lattice parameters are $a = 5.5670$ Å, $b = 5.5304$ Å, and $c = 7.8446$ Å, with the pseudo-cubic ($a_{pc}$) one being ~3.93 Å. (b–c) Resistivity ($\rho$) and magnetization of SrRuO$_3$. The material was found be metal over the whole temperature range with $\rho \sim 200$ μΩ cm at $T = 300$ K. Magnetization measurement shows ferromagnetic ordering at $T_c = 165$ K. Reprinted with permission from Refs. [72–74]. Copyright 1996 IOP Publishing Ltd.; Copyright 1996, American Physical Society; Copyright 1999, American Institute of Physics.
strain effects [81]. Along with its electrode applications, due to its high metallicity upon ferromagnetic ordering, strain engineering of SrRuO$_3$ has become a popular research topic among thin-film scientists. Later, it has been found that the structural, metallic, and magnetic properties of SrRuO$_3$ thin films are highly sensitive to the substrate-induced strain (Figure 12a) [81–92].

The structural phase transition temperature ($T_S$) of SrRuO$_3$ is strongly affected by epitaxial strain. After imposing tensile strain on SrRuO$_3$ by growing films on (110) DyScO$_3$ substrates, an orthorhombic (stable in bulk phase) to tetragonal phase (stable at high temperature) transition could be observed at $T = 300$ K [84]. Strain imposed by substrates, induces additional rotation of RuO$_6$ octahedra, thus reducing the $T_S$ [84, 86].

Transport wise, $\rho$ at $T = 300$ K increases with the induced tensile strain (films grown on (110) GdScO$_3$ and (110) DyScO$_3$ substrates). The Ru–O–Ru bond angle is reduced when exerting tensile strain, which increases the effective correlation and thus reduces the bandwidth ($W$) (Figure 12b) [84]. Consequently, in the case of tensile-strained films, $\rho$ has a higher value at $T = 300$ K compared to that of the most natural state of a film. On the other hand, it has also been found that for compressive-strained films (films grown on (001) SrTiO$_3$, (001) LSAT, and (001) LaAlO$_3$ substrates), $\rho$ decreases, which is consistent with the increase in the Ru–O–Ru bond angle, decrease in effective correlation, and increase in bandwidth ($W$) (Figure 12c) [85]. The slight increase in the $\rho$ of films grown on (001) LaAlO$_3$ substrates is associated with either the rough surface quality of the films caused by the twin structure of (001) LaAlO$_3$ or the films being fully relaxed on this substrate (Figure 12d) [85].

![Figure 12](image-url)

Figure 12. (a) Schematic illustration of the strain effect in epitaxial orthorhombic SrRuO$_3$ thin films. Films on DyScO$_3$ are subject to tensile strain, whereas films on SrTiO$_3$, LSAT, and LaAlO$_3$ undergo compressive strain. (b) Schematic representation of RuO$_6$ octahedral rotation from the bulk, due to both compressive and tensile strain. (c–d) Effect of tensile strain and compressive strain on the resistivity of SrRuO$_3$. For the tensile strain case, overall resistivity increases, while for the compressive-strained case, resistivity decreases from its bulk value. (e) Effect of tensile strain. For the compressive strain case, overall resistivity decreases, while for the compressive-strained case, resistivity decreases from its bulk value. (f) Increase in saturation magnetization following the induction of compressive strain. The magnetic moment becomes ~2 $\mu_B$ per Ru atom, which is close to the theoretical value. Reprinted with permission from Refs. [84–86]. Copyright 2008 AIP Publishing LLC; Copyright 2010 AIP Publishing LLC; Copyright 2010 Wiley-VCH Gmbh & Co. KGaA.
Strain has definite effect on the magnetic properties of SrRuO$_3$. Inducing compressive strain on SrRuO$_3$ by using various lattice-mismatched substrates, e.g., (0 0 1) SrTiO$_3$, (0 0 1) LSAT, and (0 0 1) LaAlO$_3$ and its effect on magnetic properties has been investigated. The ferromagnetic $T_C$ has a strong substrate dependence as it was found be $T_C \approx 124$ K for films grown on (0 0 1) SrTiO$_3$ [85]. It has been found that the saturated magnetic moment ($M_s$) increases from its bulk value and maximum of $\sim 2 \mu_B$ per Ru atom for films grown on (0 0 1) LSAT substrates (Figure 12e). For more compressive-strained films (those on (0 0 1) LaAlO$_3$), the $M_s$ increases, possibly due to the deterioration in film quality caused by the twin structure of (0 0 1) LaAlO$_3$ substrates. The increase in $M_s$ in compressive strained case is associated with the better alignment of moments in a low Ru$^{4+}$ spin state. This higher value of magnetic moment was also expected based on the theoretical calculations [77].

Compressive and tensile strain-dependent physical properties have also been examined for the tetragonal phase of SrRuO$_3$. (1 1 0) NaGaO$_3$ substrates were used for imposing compressive strain, whereas (1 1 0) GdScO$_3$ substrates were used to induce tensile strain [90]. It has been found that tensile-strained films show low ferromagnetic ordering at $T_C \approx 100$ K, whereas compressively strained films show an almost bulk-like ferromagnetic transition at $T_C \approx 155$ K (Figure 13). Similar to the orthorhombic phase, compressive strain causes a lower residual resistivity ratio. The observations described above are associated with the deformation rather than the tilting of RuO$_6$ octahedra and thus the change in effective correlation [90–93].

### 4.3. A colossal magnetoresistive ferromagnetic metal: La$_{0.67}$Sr$_{0.33}$MnO$_3$

La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO) is an extremely important class of material in condensed matter physics [7, 94]. At $T = 300$ K, LSMO forms a rhombohedral crystal structure ($a = 3.869$ Å) with space group $R\bar{3}c$ (Figure 14a) [94]. Undoped LaMnO$_3$ is an antiferromagnetic insulator below $T_N = 139.5$ K [95]. Upon hole doping with divalent Sr$^{2+}$ in place of La$^{3+}$, it becomes a ferromagnetic metal (Figure 14b) [96]. Doped LSMO is a mixed valence compound with Mn$^{3+}$ ($3d^4$) and Mn$^{4+}$ ($3d^3$). The change in its magnetism was well explained by the double-exchange hopping mechanism [96]. It is a highly conductive oxide that is useful as a bottom electrode for thin film device applications. It shows ferromagnetic ordering above room temperature with $T_C \approx 360$ K (Figure 14c) [97], having a magnetic moment of $\sim 3.6 \mu_B$ per Mn ion [98]. Its $\rho$ changes greatly with the application of a magnetic field and shows colossal magnetoresistance (CMR; $\Delta \rho/\rho > 10^6\%$) (Figure 14d) [97], which is important in commercial applications, including magnetic field sensors, “read” heads of magnetic hard-disk drives and non-volatile magnetic random access memory (MRAM). Its half metallic behavior—i.e., spins are fully polarized within one band structure whereas others are empty—is highly important for spintronic applications [98]. It also shows compositional- and temperature-dependent MITs (Figure 14e) [99].

Due to its rich electronic and magnetic phase diagram (Figure 14e) [99], it is highly desirable to investigate the change in functionalities or appearance of novel states in LSMO by inducing the strain effect. Several groups have reported on the effect of strain on the electronic and magnetic properties of LSMO [100–111]. To observe the strain-dependent magnetic phase diagram, Tsui et al., grew epitaxial LSMO thin films on various substrates, such as (0 0 1) LaAlO$_3$, (1 1 0) NdGaO$_3$, (0 0 1) LSAT, and (0 0 1) SrTiO$_3$ [103]. By using four different substrates, the
strain ranged from compressive to tensile strain as follow; −2.0% compressive strain for films grown on (0 0 1) LaAlO$_3$, −0.25% compressive strain for films grown on (1 1 0) NdGaO$_3$, +0.25% tensile strain for films grown on (0 0 1) LSAT, and +0.85% tensile strain for films grown on (0 0 1) SrTiO$_3$. Compressively strained film on (0 0 1) LaAlO$_3$ substrates show in-plane compression and out-of-plane expansion in their lattice parameters. In contrast, tensile-strained films on (0 0 1) SrTiO$_3$ show the opposite effect. For films grown on the other two substrates with very low strain, they show very weak out-of-plane expansion in their lattice parameters. For compressively strained films on (0 0 1) LaAlO$_3$ substrates, there is a strong suppression of $T_c$ from its bulk value; i.e., $T_c$ is reduced from 360 to 300 K. There is an increase in in-plane magnetization compared to out-of-plane magnetization, which indicates the presence of easy-plane anisotropy. Films grown on (0 0 1) SrTiO$_3$ substrates show magnetic ordering below $T_c$ ~320 K. On the other hand, films grown on the almost lattice-matched substrates, i.e., films

![Figure 13. Compressive (on NdGaO$_3$) and tensile (on GdScO$_3$) strain-dependent resistivity of tetragonal phase SrRuO$_3$ thin films. A striking feature was obtained in magnetic ordering. For tensile-strained films (on GdScO$_3$), resistivity is higher than the bulk value and the magnetic ordering temperature is reduced with ferromagnetic $T_c$ ~124 K. For compressive-strained film (on NdGaO$_3$), resistivity and magnetic ordering are very close to the bulk values with ferromagnetic $T_c$ ~155 K. Reprinted with permission from Ref. [90]. Copyright 2013 AIP Publishing LLC.](image_url)
grown on (0 0 1) LSAT and (1 1 0) NdGaO₃ substrates, show magnetic ordering below \( T_C \sim 340 \) K. Field-dependent magnetization measurements confirm the presence of perpendicular magnetic anisotropy for films grown on (0 0 1) LaAlO₃ substrates, whereas films grown on (0 0 1) SrTiO₃ exhibit easy-plane magnetic anisotropy at low \( T \). For the films grown on (0 0 1) LSAT and (1 1 0) NdGaO₃ substrates, the presence of distorted easy-plane anisotropy was confirmed by magnetization measurements\(^{103}\).

Recently, Adamo et al., performed a comprehensive study on the strain effect on the electronic and magnetic properties of LSMO with biaxial strain ranging from −2.3 to +3.2% by using the following substrates: (1 0 0)\( \_\_ \)LaAlO₃, (0 0 1) LaSrGaO₄, (1 1 0) NdGaO₃, (0 0 1) LSAT, (0 0 1) SrTiO₃, (1 1 0) DyScO₃, (1 1 0) GdScO₃, (1 1 0) SmScO₃ and (1 1 0) NdScO₃ (Figure 15a–c)\(^{108}\). \( \rho \) show a strong strain dependency on the MIT temperature. For low strain values, low temperature \( \rho \) is closer to the single-crystal value. The MIT value for films grown on (1 1 0) NdGaO₃ is \( T_{MIT} > 390 \) K, whereas the MIT transition value for films grown on (0 0 1) SrTiO₃ is around \( T_{MIT} = 370 \pm 10 \) K. Films with high compressive strain show fully insulating behavior over the entire \( T \) range (Figure 15d). For films under higher tensile strain, at \( T = 300 \) K, \( \rho \) is nearly 1 \( \Omega \) cm. The magnetization behavior of these films is quite similar to that observed by Tsui et al.. The observed magnetic behavior and change in \( T_C \) exhibit a strong strain dependence (Figure 15e), which is in good agreement with the theoretical predictions of Millis et al.\(^{112}\).
4.4. A multiferroic oxide: BiFeO$_3$

Bismuth ferrite, BiFeO$_3$ (BFO), is probably the most promising compound in condensed matter physics [9]. It possesses a rhombohedral distorted perovskite structure ($a = b = c = 5.63$ Å, $\alpha = \beta = \gamma = 59.4^\circ$) with space group $R\bar{3}c$ at $T = 300$ K (Figure 16a) [113–115]. There is a coexistence of its magnetism and ferroelectricity, that’s why BiFeO$_3$ is called a multiferroic (Figure 16b and c) [115]. In principle, the coexistence of ferroelectricity and magnetism is a very rare phenomenon as ferroelectricity requires B-site ions with $d_0$ electronic configurations, whereas magnetism requires B-site ions with $d^n$ ($n > 0$) electronic configurations [116]. Therefore, multiferrocity is a very unique phenomenon in condensed matter physics. Bulk single-crystal BiFeO$_3$ shows G-type antiferromagnetic ordering below the Néel temperature at $T_N = 643$ K [117]. In BiFeO$_3$, Fe moments are coupled ferromagnetically with the pseudo-cubic [1 1 1]$_c$ planes, whereas they are antiferromagnetically coupled between neighboring planes. In the bulk, an additional long-range cycloidal magnetic modulation is superimposed on the antiferromagnetic ordering, which results in a rotation of the spin axis through the crystal [43]. It also exhibits ferroelectricity below $T_C = 1103$ K with a polarization ($P$) value of $\sim 3.5$ μC/cm$^2$ along (001)$_c$ and $\sim 6.1$ μC/cm$^2$ along [1 1 1]$_c$ [118]. Recently, the polarization value of highly pure single-crystal BiFeO$_3$ was found to be $\sim 100$ μC/cm$^2$ along the [1 1 1]$_c$ [119]. Due to its

Figure 15. (a) Epitaxial growth of compressive- and tensile-strained La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO) films. Films grown on LaAlO$_3$, LaSrGaO$_4$, NdGaO$_3$, and LSAT are subject to compressive strain, whereas films grown on SrTiO$_3$, DyScO$_3$, GdScO$_3$, SmScO$_3$, and NdScO$_3$ are subject to tensile strain. The appearance of thickness fringes in the X-ray diffraction patterns shows the high crystallinity of each film. (b) Change in lattice parameter and (c) evolution of biaxial strain with the judicial choice of substrates for LSMO thin films. (d and e) Resistivity and magnetization of compressive- and tensile-strained films. Highly tensile- or compressive-strained films show insulating behavior (due to the strain and intrinsic atomic disorder effect), whereas metallic behavior was obtained for films that were exposed to moderate tensile or compressive strain. Magnetization measurements show that the ferromagnetic ordering temperature decreases as the tensile strain increases. Reprinted with permission from Ref. [108]. Copyright 2009 AIP Publishing LLC.
multiferroic properties above $T = 300$ K, it is a very promising candidate for room-temperature magnetoelectric device applications [120].

Wang et al., were the first to synthesize high quality epitaxial BiFeO$_3$ heterostructures on (0 0 1) SrTiO$_3$ substrates by using the PLD method and observed multiferroic properties [115]. They observed that these films display a spontaneous $P ~ 60 \mu$C/cm$^2$ at $T = 300$ K, an order of magnitude higher than the bulk value. After this finding, it has been shown that the structural, polar, and magnetic behavior of BiFeO$_3$ thin films are highly sensitive to substrate-induced strain, i.e., the strain promoted by using different lattice-mismatched substrates [121–137].

As said, at $T = 300$ K, BiFeO$_3$ adopts rhombohedral symmetry (R-phase). With the availability of various substrates, compressive (−) or tensile (+) strain can be induced on the film, which changes its structural symmetry as octahedral tilt is highly sensitive to strain. Commercially available perovskite substrates such as (1 1 0) YAlO$_3$, (0 0 1) LaAlO$_3$, (0 0 1) LAST, (1 1 0) DyScO$_3$, (1 1 0) GdScO$_3$, (1 1 0) SmScO$_3$, (1 1 0) NdScO$_3$, and (1 1 0) PrScO$_3$ impose a strain on BiFeO$_3$ of ~6.5%, ~4.5%, ~2.6%, ~0.5%, ~0.1%, +0.2%, +0.9% and +1.2%, respectively, -ve sign being the compressive strain and +ve sign corresponds to tensile strain. For cases of low compressive or tensile strain, BiFeO$_3$ shows monoclinic (M) phases (Figure 17a–f) [120]. In general, for R-phase BiFeO$_3$, the ratio of lattice parameters $c/a$ is ~1. When grown on high lattice-mismatched (0 0 1) LaAlO$_3$ substrate, the ratio of lattice parameters $c/a$ shows a large increase to a value of ~1.23 [124, 128]. This high $c/a$ value can be regarded as being similar to a tetragonal ($T_d$)-phase or super $T_2$-phase of BiFeO$_3$. Upon imposing even higher compressive strain by using (1 1 0) YAlO$_3$ substrates, BiFeO$_3$ makes a transition to a fully $T_d$-phase (Figure 17g) [124, 134]. The transition from R-phase to $T_d$-phase was thought to be an isosymmetric monoclinic symmetry phase transition [128]. However, it was actually shown that octahedral tilt disappears, and the sudden jump in the $c/a$ ratio can be attributed to structural relaxation through an out-of-plane shift. In contrast, imposing moderate tensile strain by using high lattice-mismatched (1 1 0) NdScO$_3$ substrates results in BiFeO$_3$ in a novel orthorhombic (O) phase [132].
First-principle calculations also suggested that with a tensile strain of 2% or more, the ortho-
rhombic phase in BiFeO$_3$ can be stabilized. This is associated with the oxygen octahedral tilt
exhibiting short atomic bonds and zig-zag cation displacement patterns. Consequently, the
strain effect in BiFeO$_3$ induces very high structural flexibility, which changes the structure
from R-phase to M-, T$_G$-, and O-phases or even mixed (R + O) ones [43, 128, 131].

One of the key aspects of the strain-induced scenario is to increase the out-of-plane $P$ in
strained BiFeO$_3$ thin films. One of the goals is to induce strain and raise the $P$ above
100 $\mu$C/cm$^2$ at $T = 300$ K. However, in the rhombohedral phase, whatever the growth direction is, the projected $P$ along the [1 1 1]$_c$ increases by only up to ~20% compared to its initial value (Figure 18a) [133]. First-principle calculations suggested that suppressing octahedral
tilt favors an increase in \( P \), whereas the presence of tilts instead favors a change in the direction without changing the \( P \) [130]. Recent theoretical calculations suggest that if highly strained \( \text{BiFeO}_3 \) is grown with \( P4mm \) structure, then it would show a high \( P \) of \( \sim 150 \, \mu \text{C/cm}^2 \) along the \([0 0 1]\), and \( \sim 100 \, \mu \text{C/cm}^2 \) along the \([1 1 1]\), which has been found experimentally in the super tetragonal-phase [137, 138].

To address how G-type antiferromagnetism is affected by strain effects, Sando et al., studied the strain effect within the range of \(-2.6\%\) (compressive strain) to \(+1.0\) (tensile strain) for the \( R \)-phase of \( \text{BiFeO}_3 \) (Figure 18b) [135]. By using Mössbauer and Raman spectroscopies combined with Landau–Ginzburg theory and effective Hamiltonian calculations, they observed different magnetic structures for different amounts of strain. For low compressive strain, there exists a bulk-like cycloidal spin modulation with non-collinear order, whereas for moderate tensile strain, they observed a new cycloidal phase with a propagation wave vector...
along [110]. For the high compressive- or tensile-strained case, the magnetic state was found to be a pseudo-collinear antiferromagnetic one.

4.5. A conductive oxide interface: LaAlO$_3$-SrTiO$_3$

SrTiO$_3$ and LaAlO$_3$ are both band insulators with band gaps of ~3.25 eV and ~5.6 eV, respectively [139, 140]. Along [0 0 1], SrTiO$_3$ unit cells consist of charge-neutral layers of SrO and TiO$_2$, whereas LaAlO$_3$ consists of polar layers of LaO$^{1+}$ and AlO$_2$$^{-1}$ (Figure 19a and b) [14]. In 2004, Ohtomo and Hwang discovered that if band insulator LaAlO$_3$ (LAO) is grown on top of another band insulator, SrTiO$_3$ (STO), with atomic precision, the interface of LAO-STO can be highly conducting, which results in a two-dimensional electron gas (2DEG) at the interface [14]. Surprisingly, conductivity was observed for only one type of interface: LaO-TiO$_2$ (n-type), whereas insulating characteristics were observed for AlO$_2$-SrO (p-type) interfaces (Figure 19c) [141]. With this discovery, a tremendous interest has emerged among the thin-film community to deposit each and every thin film material with atomically controlled interfaces. Later, it was found that the LAO-STO interface not only is highly conductive but can also show coexistence of superconductivity and magnetism, the quantum Hall effect, and the Rashba effect [18, 142–145]. Based on various experimental observations, the origin of 2DEG, interfacial charge distribution vs. oxygen vacancy scenario is still under debate [146, 147].

Since the atomic configuration of a substrate’s topmost layer plays a key role in forming 2DEGs at interfaces between two non-conducting oxides, it would be highly desirable to study the formation of 2DEGs at oxide interfaces with the strain effects [148–155]. Bark et al., grew LAO-STO interfaces on various substrates, such as (1 1 0) NdGaO$_3$, (0 0 1) LSAT, (1 1 0) DyScO$_3$, and (1 1 0) GdScO$_3$ (Figure 20a) [148]. By using four different substrates, the strain ranged from compressive to tensile strain as follow; −1.21% compressive strain for films grown on (1 1 0) NdGaO$_3$, −0.96% compressive strain for films grown on (0 0 1) LSAT, +1.11% tensile strain for films grown on (1 1 0) DyScO$_3$, and +1.59% tensile strain for films grown on (1 1 0) GdScO$_3$. They have shown that imposing tensile strain on SrTiO$_3$ destroys the 2DEG, whereas exerting compressive strain leads to the 2DEG nature being retained but with a reduction of carrier concentration compared to that of unstrained LAO-STO interfaces (Figure 20b). Using theoretical calculations, they suggested that this behavior is associated with the built-in polarization in SrTiO$_3$ as it was observed that with induced strain, polarization can have build up in pure SrTiO$_3$ as well [44]. This polarization is directed away from the interface and creates a negative polarization opposing that of the polar LaAlO$_3$ layer. It has also been calculated that the distortion of interfacial Ti–O octahedra enhances with increases in in-plane compressive strain, which also modulates the carrier concentration [152]. Applied in-plane compressive strain also reduces the carrier concentration. On the other hand, under tensile strain, the interfacial charge carrier density increases, which is consistent with the theoretical calculations [155]. It has been found that when moving from the compressive-strained to the tensile-strained scenario at the LAO-STO interface, the Ti–O bond length becomes elongated, which confines the Ti $d_{xy}$ orbital electrons at the interface, thus increasing the sheet carrier concentration ($n_s$) at the interface. For the compressively strained scenario, the Ti–O bond length decreases and the Ti $d_{xy}$ orbital cannot hold all the electrons at the interface; hence, the remaining electrons are transferred to a deeper layer, reducing the carrier concentration at the interface.
To observe the correlation and strain effect induced by the topmost polar layer, Ariando et al., grew various combination of polar/non-polar ABO$_3$ perovskites, e.g., NaAlO$_3$/SrTiO$_3$, PrAlO$_3$/SrTiO$_3$, and NdGaO$_3$/SrTiO$_3$ (Figure 20c) [150]. They found that these interfaces are also conducting and form 2DEGs. They also claimed that the interfacial strain and electron correlation caused by the polar layers seem to control the carrier density and mobility at the interface (Figure 20d). The presence of large octahedral distortion due to strain also plays an important role in observing...
these novel phases. Instead of growing various rare earth-based polar ABO$_3$ perovskites, Jang et al., directly grew monolayers of rare-earth oxides (RO, R = La, Pr, Nd, Sm, and Y) to observe the correlation effect at interfaces (Figure 20e) [149]. Surprisingly, they found that some oxides (La, Pr, and Nd) forms 2DEGs at the interface, whereas an insulating interface is formed in the case of SmO and YO. Based on the observations and theoretical calculations, they claimed that this is due to the correlation effect at the interface. Independent theoretical calculation also suggest that in-plane strain can induce metal-insulator transitions at oxide interfaces [155].

4.6. A strongly correlated metal: LaNiO$_3$

The physics of strongly correlated materials, i.e., those having strong electronic correlations, is remarkably rich and complex and cannot be understood within the framework of conventional theories of metals and insulators [21, 22]. For example, in strongly correlated nickelate materials, spin, lattice charge, and orbital degrees of freedom result in competing interactions. Due to this, these materials show exotic phases [156–158]. Among strongly correlated materials,
nickelates, more specifically LaNiO$_3$ is a strongly correlated Mott metal [159, 160]. LaNiO$_3$ has a highly distorted rhombohedral structure with lattice parameters of $a = b = 5.4573$ Å, $c = 13.1462$ Å, and $\alpha = \beta = \gamma = 60.49^\circ$ and with space group $R\bar{3}c$ (Figure 21a) [161]. Its pseudo-cubic lattice constant is $a_{pc} = 3.84$ Å. It is highly metallic over the entire temperature range (Figure 21b) [162]. It is the only member in the perovskite nickelate family ($RE$NiO$_3$, $RE =$ rare earths) which shows no long-range magnetic ordering [156–158].

The functionalities of strongly correlated rare-earth nickelates are highly sensitive to external perturbation, e.g., chemical pressure and atmospheric pressure [156–158]. Thus, it would be very interesting to investigate the ability of strain-based perturbation (i.e., by using various lattice-mismatched substrates) to obtain novel functionalities in LaNiO$_3$. Several groups have reported the strain dependent transport properties in epitaxial LaNiO$_3$ thin films [163–172]. Moon et al., investigated in detail the transport properties of tensile- and compressive-strained LaNiO$_3$ systems. They grew 10-unit cell ultra-thin LaNiO$_3$ films on (1 1 0) YAlO$_3$, (0 0 1) SrLaAlO$_4$, (0 0 1) LaAlO$_3$, (0 0 1) SrLaGaO$_4$, (0 0 1) LSAT, (0 0 1) SrTiO$_3$, and (1 1 0) GdScO$_3$ substrates (Figure 22a) [167–169]. They investigated $\rho$ of tensile-strained films and observed that when the tensile strain increases, LaNiO$_3$ gradually evolves from the Mott to the Mott-Anderson regime; i.e., correlation and disorder play a crucial role at low temperature (Figure 22b) [163, 167].

The authors have also investigated the Hall effect ($1/R_H \propto T$; $R_H =$ Hall coefficient) in both the compressive- and tensile-strained cases (Figure 22c) [168]. They claimed that the evolution of the linear $T$ dependent transport coefficient is quite similar to that of hole-doped cuprate superconductors. By using density functional theoretical (DFT) calculations, they claimed that strain-induced changes in transport properties arise from changes in the low-energy electronic band structure that induces self-doping, i.e., a transfer of charge between the O p and Ni d states. Using detailed quantitative structural analysis and theoretical calculations May et al., found that strain systematically modifies both the Ni–O–Ni bond angles and Ni–O lengths in this functional perovskite oxide (Figure 22d) [164, 172], which has strong effect on its strain-dependent transport properties.

Figure 21. (a) Schematic representation of the distorted rhombohedral crystal structure of LaNiO$_3$, showing highly distorted NiO$_6$ octahedra with lattice parameters of $a = b = 5.4573$ Å and $c = 13.1462$ Å. The pseudo-cubic unit cell is $3.84$ Å. (b) Resistivity of bulk polycrystalline LaNiO$_3$, showing it is a paramagnetic metal without any indication of magnetic ordering over the entire temperature range. Reprinted with permission from Refs. [161, 162]. Copyright 2015 Elsevier B. V. Ltd.; Copyright 2014 American Physical Society.
Figure 22. (a) Schematic representation of compressive and tensile strain imposed on LaNiO$_3$ by various metal oxide substrates. (b) Low-temperature resistivity of strained LaNiO$_3$ films. With an increase in tensile strain, resistivity at room temperature increases, although the resistivity minima also decrease. (c) The temperature-dependent Hall coefficient (1/R$_H$) for strained LaNiO$_3$ films grown on various substrates. With an increase in compressive strain, 1/R$_H$ becomes almost linearly dependent on temperature (1/R$_H$ $\propto$ T), thus bearing a striking resemblance to the behavior of cuprate superconductors. (d) Tensile strain increases rotation of octahedra along the [1 0 0] and [0 1 0], and decreases it along the [0 0 1]. (e) Compressive strain reduces the rotation along the [1 0 0] and [0 1 0], and increases it along the [0 0 1]. Reprinted with permission from Refs [164, 167, 168]. Copyright 2010 American Physical Society; Copyright 2013 American Chemical Society; Copyright 2011 IOP Publishing Ltd and Deutsche Physikalische Gesellschaft.
5. Summary

In principle, material functionalities arise from the coupling between spin, lattice, charge, and orbital degrees of freedom. Lattice strain is thus found to be a unique way to engineering the functionalities of many TMOs, which modifies above energy scales. Here, we presented the effect of strain-dependent functionalities of various TMO-based thin films: (1) a high temperature superconductor, La_{1.85}Sr_{0.15}CuO_4, (2) a highly conductive oxide, SrRuO_3, (3) a colossal magnetoresistive metal, La_{0.67}Sr_{0.33}MnO_3, (4) a multiferroic oxide, BiFeO_3, (5) a conducting oxide interface, LaAlO_3-SrTiO_3, and (6) a strongly correlated metal, LaNiO_3. The aforementioned materials all show rich and complex structural, electronic, magnetic and polar phase diagrams that are dependent on epitaxial strain, which is mainly caused by modifications of their crystal structures and the effects of these modification on the coupling of their various degrees of freedoms (relevant energy scales). More specifically, tailoring the shape, size, and position of BO_6 octahedra by strain give rise to new functionalities in ABO_3 perovskite oxides. Strain-dependent MITs, increase in magnetic transition temperature and ferroelectric polarization can be observed in these materials. Obtaining novel properties by designing artificial oxide heterostructures and the subsequent new physics resulting from the strain effect have always been an interesting topic of research among the thin-film community as cheap and environment friendly oxide thin film-based electronic devices are highly in demand in industry. Although there has been vast progress in the strain-dependent tuning of material properties, there is still long way to go to fully understand the intrinsic mechanisms and theoretical developments behind these strain-dependent phenomena. Nevertheless, strain has provided an avenue to explore materials with novel functionalities. We believe that our experimental investigations along with insightful explanations will provide readers with an easier way to understand the strain effect in epitaxial oxide heterostructures and utilize it to explain the fundamental physics and to commercialize oxide-based electronic devices.

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