Defects in complex oxide thin films for electronics and energy applications: challenges and opportunities

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Complex transition-metal oxides (TMOs) are critical materials for cutting-edge electronics and energy-related technologies, on the basis of their intriguing properties including ferroelectricity, magnetism, superconductivity, (photo- and electro-) catalytic activity, ionic conductivity, etc. These properties are fundamentally determined by the partially occupied TM d orbitals and the corresponding local coordination environments, which are sensitive to defects (or impurities), compositions, grain boundaries, surface and interfaces, etc. Recently, motivated by the advance in thin film epitaxy techniques, the complex oxide research community has shown great interest in controlling defects for enhanced or even unprecedented functional properties. In this review, we provide an overview on recent progress in tuning the functional properties of TMO thin films via defect engineering. We begin with a brief introduction to the defect chemistry of TMOs, including types of defects and their effects on local atomic structure, electron configurations and electronic structure, etc. We then review recent research efforts in engineering defects in TMOs for novel functionalities, such as ferroelectricity, magnetism, multi-ferroelectricity and dielectricity, two-dimensional electron/hole gas, metal–insulator transitions, resistive switching, ionic conductivity, photo-electrocatalysis, etc. We also provide insights into understanding the defect-structure–property relationship from the perspective of electronic structure. Finally, challenges and perspectives on control of defects for design of novel devices are discussed.

1. Background for complex transition-metal oxides

Complex transition-metal oxides (TMOs) have attracted intensive research interests in both materials science and condensed matter physics over the past decades, largely due to their broad range of properties from insulating to semiconducting or...
metallic, exhibiting many fascinating phenomena including (anti-)ferromagnetism (FM), (anti-)ferroelectricity, multi-ferroelectricity, ionic conduction, colossal magnetoresistance (CMR) and high temperature superconductivity, etc. These exotic properties arise from a complex hierarchy of competing interactions among spin, charge, orbital and lattice degrees of freedom, which are fundamentally underpinned by the electronic states of the partially occupied TM d orbitals. Driven by recent advances in fabrication of high-quality epitaxial thin films with an atomic-scale control via pulsed laser deposition (PLD) and molecular-beam epitaxy (MBE), TMOs are receiving fast-growing interests and hold great potential to outperform conventional semiconductors. However, the epitaxial thin films required for most applications are imperfect with far from optimum performance. Hence, many promised applications spanning beyond-Si information and communications technology (ICT) devices to a vast range of energy-related devices and sensors currently remain just promises. Furthermore, TMOs are also promising candidates as (photo-)electrocatalysts for the production of “green fuels” (principally H₂, syngas and even liquid hydrocarbons) by splitting H₂O and reducing CO₂ and as (anti-)ferroelectricity (FE), multi-ferroelectricity, dielectricity, optical and transport properties, electronic and energy devices. 

2. Defect chemistry in complex transition-metal oxides

2.1 Types of defects

Since this review focuses mainly on TMOs with a perovskite structure, we will use perovskite oxides as examples to illustrate the types of defects present in TMOs. Perovskite TMOs have a...
The chemical formula of ABO$_3$, as sketched in Fig. 1, A-sites are usually alkaline rare-earth cations, while B-site cations are usually TM cations with partially filled d orbitals octahedrally coordinated by six oxygen anions.

Point defects represent a deviation from the long-range periodicity of crystal lattice. The key types of point defects include vacancies (e.g., oxygen vacancies, V$_O$ and cation vacancies, V$_C$), interstitials and anti-site defects (Fig. 1a). A remarkable example can be found in the perovskite SrTiO$_3$, where the introduction of V$_O$ can turn the insulating SrTiO$_3$ into a metallic state, and even a dome-shaped superconducting phase dependent on carrier density concentrations. $^5$-$^7$ Further, the formation of Ti$^{3+}$ (3d$^1$) induced by V$_O$ can lead to a ferromagnetic interaction in diamagnetic SrTiO$_3$. $^8$ Through the formation of Sr vacancies, room-temperature ferroelectricity can be created in paraelectric SrTiO$_3$. $^9$ Moreover, by swapping the cation positions between Sr$^{2+}$ and Ti$^{4+}$ to form anti-site cationic defects of SrTi or TiSr, paraelectric SrTiO$_3$ become ferroelectric at room temperature and highly conductive channels can also be formed and controlled by the ferroelectric polarization. $^{10}$

Owing to the discontinuity of lattice and chemical environment, the interface provides a more favorable environment for defects with lower formation energy. These interface-related defects contain misfit dislocations (Fig. 1b), grain boundaries (Fig. 1c), polar discontinuity (Fig. 1d), and domain walls (Fig. 1e). Crystalline TMOs usually contain dislocations, grain boundaries, and domain walls, which reportedly exhibit a very different nature from the rest of the bulk matrix. The presence of these defects can significantly influence properties such as ionic and electrical conductivities, magnetism, and ferroelectricity. For instance, dislocations have been reported to creating ferromagnetic regions in anti-ferromagnetic NiO, $^{11}$ while grain boundaries of ferromagnetic La$_{2/3}$Ca$_{1/3}$MnO$_3$ can lead to paramagnetic properties. $^{12}$ In SrTiO$_3$, the dislocations and grain boundaries are generally considered to be charged largely due to nonstoichiometry, which may account for the unique electrical and ionic transport properties. $^{13,14}$ Also, electronic conductivity has been observed at ferroelectric domain walls in the insulating multiferroic BiFeO$_3$. $^{15}$

Oxygen octahedra (BO$_6$, Fig. 1g) plays a central role in the physical properties of many ABO$_3$ compounds. Their rotations lead to the reduction of the B–O–B bond angle, with profound consequences for magnetic and transport properties of various perovskite TMOs. In the rare-earth (R) nickelate RNiO$_3$ series of compounds, the reduction of the Ni–O–Ni bond angle is accompanied by a spectacular first-order metal-to-insulator transition, $^{16}$ whereas the magnetic superexchange interaction in manganites depends sensitively on the Mn–O–Mn bond angle and bond length. $^{17}$ Besides, reversible changes in the structural and electronic properties of TMOs can be achieved with electric fields by moving ions (e.g., H$^+$ and Li$^+$, Fig. 1f) into or out of TMOs. $^{18-21}$

2.2 Electronic structure consequences of defects

Due to the strong interactions between structural and electronic structures, coherently strained TMOs films and heterostructures...
have emerged as one of the most effective platforms to engineer novel functionalities. The nature of BO$_6$ rotations and structural deviations from ideal cubic symmetry alter key structural features like B–O bond lengths strongly influences TMOs electronic structure through properties such as d orbital occupancy and metal–oxygen orbital overlap. Tuning B–O bond lengths of TMOs by strain can break the degeneracy of eg orbitals by enhancing the electron occupancy in either in-plane $d_{x^2-y^2}$ orbital under tensile strain or the out-of-plane $d_{z^2}$ orbital under compressive strain (Fig. 2a).

Defects, impurities and interface break the regular periodicity of the crystal lattice, and more importantly introduce extra energy levels into the band gap, therefore leading to the change of electronic structure and physical properties of TMOs. The band structure of TMOs generally contains an empty TM $n$-$d$ derived conduction band (CB) and valence band (VB) with O 2$p$ hybridized with filled TM $n$-$d$ orbitals (Fig. 2b). The energy separation of the empty TM $n$-$d$ and filled TM $n$-$d$ orbitals is induced by the crystal field splitting and/or the intra-atomic electron–electron repulsion energies ($U_n$). The formation of defects in TMOs will introduce extra electronic states in the bands, leading to a range of novel physical properties.$^{22-25}$ The most critical factors of the defects include: (i) the energy positions of extra defect states relative to CB/VB; (ii) the local environment of the defects (coordination numbers and bonding length/angle); (iii) the number of occupied carriers, as schematic illustrated in Fig. 2c–h.

When extra electrons are introduced into the CB or extra holes into the VB, TMOs will become more conductive and sometimes a metallic state can be induced, as shown in Fig. 2c and d. More commonly seen cases would be defect levels with electrons located just below the CB, or the empty level located just above the VB, acting as shallow donors and shallow acceptors (Fig. 2e and f). Under these circumstances, defect levels could provide free electrons or holes by thermal excitation and increase the conductivity. Moreover, the Fermi level will also be changed. When the empty defect levels are located just below the bottom of CB, or levels with electrons are just above the top of VB, the defects will no longer introduce new carriers into the bands or alter the Fermi level, and in turn act as traps for electrons in CB or holes in VB, as shown in Fig. 2g–h. Sometimes the defect levels are far from the band edges, so that the free carriers cannot be generated under normal thermal excitations, these defects are known as deep states.

The creation of defects in ionic oxides such as MgO is difficult, due to the high formation energies.$^{26,27}$ However, many TMOs can tolerate high concentrations of defects under equilibrium conditions. These defects are often associated with deviation from ideal stoichiometry of the parent oxides, due to the relative ease of reducing or oxidizing of the metal ions.$^{23,28,29}$ Shallow levels are often induced with the break of perfect stoichiometry and determine the conducting behaviors of the resulted TMOs. The nonstoichiometry of TMOs could be
divided into metal excess and oxygen excess. The metal excess of oxide $M_2O_3$ could be achieved by the introduction of $V_O$ with a formula of $M_{a-b}O_b$, or through the introduction of metal cation interstitials with a formula of $M_{a+b}O_b$. In both cases, the nonstoichiometry results in the involvement of additional electrons and the related electronic properties depend on the extent of the electrons’ binding strength to cationic species. Once sufficient energies are provided to the metal excess oxides, electrons become itinerant and the oxides become n-type conductive. For example, SrTiO$_3$ could form Ti interstitials or $V_O$ to become a n-type semiconductor, or even a metallic state as mentioned in above section.\textsuperscript{30–32} Similarly, p-type conductivity could be achieved by extra holes introduced in oxygen-excess phases. These phases can be created by the introduction of metal cation vacancies with a formula of $M_{a-d}O_b$ or through the introduction of $V_O$ with a formula of $M_{a+b}O_b$.\textsuperscript{33–36} The p-type conductivity of undoped NiO is mainly achieved by Ni vacancies.\textsuperscript{33,34}

The above-mentioned compositional variation of the defective TMOs have a significant influence on the electronic properties, yet the realistic manipulation of these defects is largely confined into limited ranges. In an attempt to modulate the electronic properties in a wider range, alloyed doping is applied to control the conductivity of TMOs.\textsuperscript{37,38} Donor impurities are used to enhance n-type conductivities with doping cations in a higher valence than the TMO parent ions. The donor cations tend to introduce balancing defects due to the break of stoichiometry and charge balance, in the form of cation vacancies, anion interstitials and electrons. In the example of Nb doped SrTiO$_3$ or BaTiO$_3$, the substitution of Nb$^{5+}$ to Ti$^{4+}$ would introduce balancing electrons into the structure and thus enhance the n-type conductivity.\textsuperscript{36,39} The acceptor doping is achieved with cations with lower valence than the parent ions.\textsuperscript{40–43} In the example of Sr doped LaMnO$_3$, the substitution of Sr$^{2+}$ to La$^{3+}$ would introduce hole states of mostly Mn 3d characters via promoting Mn$^{3+}$ (3d$^4$) into Mn$^{4+}$ (3d$^3$) in order to keep the charge neutrality.\textsuperscript{40,41}

3. Manipulation of functional properties

3.1 Ferroelectricity

Ferroelectrics possess a polarization that is spontaneous, stable and electrically switchable.\textsuperscript{44} Due to the strong coupling between their electrical, mechanical, and optical responses, ferroelectric materials, especially metal oxides, have been widely investigated for a diverse range of applications such as non-volatile memory devices, sensors, capacitors, non-linear optical components, piezoelectric actuators, energy harvesting and storage, micro-electromechanical systems, and high-power electronic transducers.\textsuperscript{45–48} Ferroelectricity can be manipulated by the control of defects such as $V_O$, $V_C$, defect dipoles, misfit dislocations, grain boundaries and domain walls. $V_O$ are often seen as detrimental to a ferroelectric material, adversely affecting its leakage current and fatigue properties. In the case of (LaFeO$_3$)$_2$/(SrFeO$_3$) superlattice made up of two nonpolar oxides, however, the introduction of $V_O$ triggers the polar displacement of the Fe ions (Fig. 3a).\textsuperscript{39} Bulk SrMnO$_3$ has a paraelectric and G-type anti-ferromagnetic ordering below 233–260 K.\textsuperscript{39} When SrMnO$_3$ film is grown on a (LaAlO$_3$)$_{0.75}$(SrAlTaO$_3$)$_{0.25}$ (LSAT) substrate, epitaxial tensile strain ($\sim$1.7%) is accommodated by the creation of $V_O$, leading to formation of a polar state in this Mn d$^9$ system.\textsuperscript{51} Cation off-stoichiometric defects are also effective in creating and controlling the ferroelectricity. For example, SrTiO$_3$ is an incipient ferroelectric oxide where the ferroelectric order is quenched by quantum fluctuations. The polar nanoregions (PNRs) of nanometer-characteristic size can be naturally formed by the intrinsic Sr vacancies the growth of SrTiO$_3$ film.\textsuperscript{52} Lee et al. reported that the electrically induced alignment of these PNRs can create room-temperature ferroelectricity in strain-free SrTiO$_3$ films (Fig. 3b).\textsuperscript{9} Further, $V_C$ and $V_O$ can be formed together during synthesis of TMO films. These charged point defect complexes can be defined as defect dipoles due to the strong coupling of electrical and elastic dipolar of such defects to the lattice and polarization. For BiFeO$_3$ thin films, energetically preferred alignment of defect dipoles ($V_{bi}$ and $V_O$) parallel to the polarization direction has been demonstrated and used to control the local polarization switching and to achieve the macroscopic double-polarization switching and tri-state memory effects in BiFeO$_3$ films.\textsuperscript{53} A similar approach has been applied to ferroelectric BaTiO$_3$ and relaxor ferroelectric 0.68Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$-0.32PbTiO$_3$ (PMN-PT) films. Damodaran et al. observed an enhancement of ferroelectric Curie temperature in BaTiO$_3$ films through defect dipoles induced additional anisotropic lattice deformation.\textsuperscript{54} Defect dipoles-mediated reversible domain switching can be further used to improve the piezoresponse and realize a large reversible nonlinear electro-strains in BaTiO$_3$ single crystals.\textsuperscript{55} Formation and ordering of the defect dipoles can stabilize the direction of polarization against thermal fluctuations, and in turn, weaken the relaxor behavior in PMN-PT films.\textsuperscript{56} Due to the formation of $V_C$ and/or $V_O$, antisite cationic defects could emerge. For instance, swapping the cation positions between Sr$^{2+}$ and Ti$^{4+}$ to form anti-site defects of Sr$_{Ti}$ or Ti$_{Sr}$, the paraelectric SrTiO$_3$ becomes ferroelectric at room temperature.\textsuperscript{57} A similar observation was also reported in anti-ferroelectric PbZrO$_3$, where a nonpolar phase (anti-ferroelectric ordering) is only slightly energetically favorable compared to a polar phase (ferroelectric ordering). The ferroelectric ground state can be stabilized in PbZrO$_3$ films by Pb$^{2+}$ occupying B-site Zr$^{4+}$ positions.\textsuperscript{58}

The switching between polarized domains in ferroelectric oxides is mediated by nanoscale defects, such as misfit dislocations and grain boundaries.\textsuperscript{14,59–63} Using in situ transmission electron microscopy, Gao et al. found that misfit dislocations can exert a weak pinning force on domain wall motion in PbZr$_{0.52}$Ti$_{0.48}$O$_3$ films.\textsuperscript{60} Misfit dislocations can also induce polarization instability in PbZr$_{0.52}$Ti$_{0.48}$O$_3$ film under compressive strain (Fig. 3c).\textsuperscript{59} The flexoelectric effect induced polarization in SrTiO$_3$ has been predicted around misfit dislocations at room temperature.\textsuperscript{61} Gao et al. directly observed that stable localized electric dipoles exist near the dislocation
cores in a 10° small tilt grain boundary in SrTiO3 and further measured the flexoelectric polarization of ~28 μC cm−2 at the dislocation core.14

When the orientation of electric polarization in ferroelectrics is switched by an applied electric field, this often leads to the appearance of domains of differently oriented regions, separated by domain walls, coexisting in the thin films.64 Such domain walls become more technologically important as the dimensions of individual elements in electronic devices continue to shrink. Recently, a myriad of novel properties and functionalities have been discovered at domain walls in ferroelectric oxide films, such as BiFeO3. One of these intriguing properties is the enhanced conductivity (1 or 2 orders of magnitude higher) at the domain walls in ferroelectric oxide films, such as BiFeO3. One of these intriguing properties is the enhanced conductivity (1 or 2 orders of magnitude higher) at the domain wall compared to the surrounding domains (Fig. 3d).15 The origin of domain wall conductivities is still under debate. The lattice distortion and the consequent band gap lowering of domain walls, and the modification of Schottky barrier heights at the heterojunctions in the regions local to domain walls are the generally accepted mechanisms.15,65–67 In addition, domain walls can accumulate charged defects, such as Fe4+ cations and Bi vacancies in BiFeO3, leading to p-type domain-wall conductivity. An anomalous photovoltaic effect was found at domain walls in BiFeO3 film.67,68 Furthermore, the observed photovoltaic effect can produce voltages that are significantly higher than the bandgap, and electric-field control of domain wall structure allows the photocurrent to be reversed in direction or turn off.67,68

3.2 Magnetism

Magnetic TMOs provide an intellectually rich arena for fundamental scientific discovery and for the invention of faster, smaller, more energy-efficient technologies. V0, V0, grain boundaries, misfit dislocations and BO6 octahedral distortions have been reported as effective methods for changing magnetism. Perovskite manganites of Ln1−xA, MnO3 (Ln = La, Pr, Bi; A = Ba, Sr, Ca) have attracted intensive interest because of the fascinating
interplay between spin, charge, orbital and lattice degrees of freedom. The effect of grain boundaries on perovskite manganites has been studied intensively due to its strongly correlation with magnetoresistive (MR) effect. Gross et al. found that few nm wide grain boundaries of ferromagnetic La$_{2/3}$Ca$_{1/3}$MnO$_3$ film becomes paramagnetic (Fig. 4a), which strongly modifies the transport properties. Besides, experimental and theoretical calculations have shown that V$_O$ can change the hybridized Mn–O–Mn bond and increase the concentration of Mn$^{3+}$ ions, which affect the double exchange interaction and then modify the magnetic properties. The transformation from anti-ferromagnetism to ferromagnetism was observed in YMnO$_3$ film by the introduction of V$_O$. Li et al. reported that oxygen stoichiometry controls the ferromagnetic insulating state in LaMnO$_3$ film, but while bulk LaMnO$_3$ shows anti-ferromagnetism, NiO is one of most common natural anti-ferromagnetic oxides the study of which dates back to the dawn of the anti-ferromagnetism. To accommodate the ~7% lattice mismatch between NiO and SrTiO$_3$, high-density dislocations are formed in NiO film grown on a SrTiO$_3$ substrate (Fig. 4b). O K-edge electron energy-loss spectra (EELS) show the pre-peak around 528 eV is observed only in the spectrum taken at the dislocation core and is attributed to the formation of Ni deficiency. In turn, ferromagnetic ordering of individual dislocations has been discovered in anti-ferromagnetic NiO films.

A layered vacancy ordered brownmillerite (BM) structure can be topotactically transformed from a perovskite structure framework, in which one-sixth of the oxygen anions have been removed. The special feature of this structure-type provides a new pathway for modifying electronic structure (the hybridization between O 2p and TM d orbitals) and then tuning physical properties (magnetic, transport and optical properties) in TMO films. Using real-time X-ray diffraction, Cao et al. found the V$_O$-induced topotactic transition from perovskite (ferromagnetic metal) to BM (anti-ferromagnetic insulator) and vice versa in La$_{0.7}$Sr$_{0.3}$MnO$_3$ films (Fig. 4c). During the topotactic phase conversion, an intermediate phase (La$_{0.7}$Sr$_{0.3}$MnO$_{2.65}$) was also discovered. A similar topotactic phase transformation has also been observed in SrCoO$_{x}$, SrFeO$_{x}$, LaCoO$_{x}$, and SrCrO$_{x}$ films. For example, SrCoO$_{x}$ can experience a phase transition from the perovskite SrCoO$_3$ (P-SCO) to brownmillerite...
SrCoO$_{2+\delta}$ (BM-SCO) with an increase of V$_{O}$ concentration.\textsuperscript{76} Magnetic properties are simultaneously altered with an increase of V$_{O}$ concentration due to the change of Co valency, from ferromagnetic P-SCO to antiferromagnetic BM-SCO.\textsuperscript{82}

Epitaxial strain, caused by lattice mismatch between the film and substrate, can enhance or suppress the diverse properties of TMO films. To accommodate the lattice mismatch, long-range defect ordering, e.g. V$_{O}$, can be formed.\textsuperscript{83,84} Coupling between strain and V$_{O}$ has been widely studied in LaCoO$_3$ films, where long-range ferromagnetic ordering is observed, while bulk LaCoO$_3$ shows no magnetism at low temperature.\textsuperscript{85–88} Dark stripes in Z-contrast STEM images have been observed in ferromagnetic LaCoO$_3$ films grown on SrTiO$_3$ substrates (Fig. 4d).\textsuperscript{87} Biskup et al. attributed these stripes to V$_{O}$ ordering, where the dark stripes are ferromagnetic insulating regions and significant oxygen deficiency results in the lattice relaxation. This conclusion is based on the fact that there is no significant stoichiometry change for La and Co elements, and there are remarkably reduced O peak intensities in the striped regions observed in atomically resolved electron energy-loss spectroscopy (EELS). However, Choi et al. also reported the dark stripes in Z-contrast STEM images of LaCoO$_3$ films grown on the SrTiO$_3$ substrates and proposed that dark stripes originate from the modulation of the atomic arrangement, caused by the ferroelastic nature of the system, instead of V$_{O}$ ordering. This conclusion is obtained from there being no significant change in the oxygen non-stoichiometry observed in X-ray absorption spectroscopy.\textsuperscript{86} Up to now, it is still not clear whether the ferromagnetism in LaCoO$_3$ film is caused by strain-induced V$_{O}$ ordering or by strain-induced lattice modulation. When Sr is doped to LaCoO$_3$, V$_{O}$ are created to neutralize the charge difference between La and Sr. Consequently, dark stripes were observed in La$_{0.85}$Sr$_{0.15}$CoO$_3$ films and certainly originated from the formation of V$_{O}$ ordering.\textsuperscript{83}

The fascinating properties of perovskite TMOs are essentially determined by the interlinked and corner-connected BO$_6$ octahedra, whose bond lengths and bond angles determine the hybridization between TM d and oxygen 2p orbitals, significantly altering the interplay between spin, charge, orbital and lattice degrees of freedom.\textsuperscript{89–91} Tuning of the BO$_6$ octahedra has been widely studied by strain engineering, which changes the c/a ratio for achieving the orbital reconstruction. Using X-ray linear dichroism, Pesquera et al. investigated the orbital reconstruction and the symmetry breaking effect in La$_{2/3}$Sr$_{1/3}$MnO$_3$ films and found that the e$_g$ electrons of thick La$_{2/3}$Sr$_{1/3}$MnO$_3$ films prefer the d$_{x^2-y^2}$ orbitals under compressive strain and the d$_{z^2}$ orbitals under tensile strain.\textsuperscript{92} In the case of (La$_{2/3}$Sr$_{1/3}$MnO$_3$)$_m$/[BaTiO$_3$]$_n$ superlattice films, through strain engineering and a carefully designed superlattice geometry, the interfacial Mn cations favor the d$_{x^2-y^2}$ orbitals with c/a > 1 while the d$_{z^2}$ orbitals are stabilized for the inner Mn cations, resulting in an enhancement of ferromagnetic Curie temperature.\textsuperscript{93} On the other hand, recent studies demonstrated that oxygen octahedral coupling (OOC) at the hetero-interfaces can delicately tailor the local BO$_6$ octahedral rotations at an atomic-scale.\textsuperscript{94–98,379} Zhai et al. studied the (LaMnO$_3$)$_m$/[SrTiO$_3$]$_n$ superlattices and found that the magnitude of ferromagnetic magnetization is strongly correlated with MnO$_6$ octahedral rotations.\textsuperscript{99} A modulation of the emergent interfacial ferromagnetism was realized in (CaRuO$_3$)$_m$/[CaMnO$_3$]$_n$ superlattices, comprised of an anti-ferromagnet and a paramagnet, through controlling the rotation patterns.\textsuperscript{100} The magnetic anisotropy of La$_{2/3}$Sr$_{1/3}$MnO$_3$ and SrRuO$_3$ films can also be controlled by engineering the MnO$_6$ and RuO$_6$ octahedral rotations,\textsuperscript{101,102} respectively. It should be noted that the epitaxial strain also changes the BO$_6$ octahedral rotations in TMO films.\textsuperscript{103}

To minimize the strain effect on the changes of BO$_6$ octahedral rotations and to understand the correlation between the BO$_6$ octahedral rotations, electronic structure and physical properties in TMO films, Li et al. studied (La$_{0.9}$Ba$_{0.1}$MnO$_3$)$_m$/[SrTiO$_3$]$_n$ (only ~0.26% lattice mismatch) superlattices and achieved a long range (up to 12 unit cells) suppression of the MnO$_6$ octahedral rotations, a preferential occupation of the out-of-plane Mn d$_{3z^2-r^2}$ orbital and a reduced Mn e$_g$ bandwidth in La$_{0.8}$Ba$_{0.2}$MnO$_3$. Consequently, a new ferromagnetic insulating state with enhanced Curie temperature of 235 K emerges in La$_{0.8}$Ba$_{0.2}$MnO$_3$ (Fig. 4e).\textsuperscript{109}

### 3.3 Multi-ferroelectricity and dielectricity

The ability of multiferroic materials to couple magnetic and ferroelectric orders continues to attract intensive interest because of their potential applications in spintronics and memory devices.\textsuperscript{104–108} Such materials are, however, rare as a consequence of the competing requirements for ferroelectricity and magnetism.\textsuperscript{109} Multi-ferroelectricity can be modified or created by domain walls, misfit dislocations, V$_{O}$ and atomic displacements. Until recently BiFeO$_3$ was the only materials with this functionality at room temperature.\textsuperscript{110,111} To relax the misfit strain associated with the lattice mismatch between the BiFeO$_3$ film and the substrate, the formation of crystallographic defects, such as domain walls and dislocations, might occur. Domain walls in multiferroics can manifest a net magnetic moment even if the domains themselves are anti-ferromagnetic or paramagnetic.\textsuperscript{112} He et al. reported a strong magnetoresistance in domain walls of BiFeO$_3$ films grown on DyScO$_3$ substrates.\textsuperscript{113} Edge dislocations in BiFeO$_3$ films have been observed by scanning transmission electron microscopy.\textsuperscript{114} Agrawal et al. found the presence of Bi and Fe atoms in dislocation cores which result in uncompensated Fe spins along the dislocations and give rise to a magnetic signal in BiFeO$_3$ film.\textsuperscript{115}

In V$_{O}$-ordered brownmillerite SrFeO$_{2.5}$ (anti-ferromagnetic insulator), by controlling the 1D FeO$_4$ tetrahedral chain network, Kang et al. reported the realization of a room-temperature ferroelectric ferromagnetic in SrFeO$_{2.5}$ film.\textsuperscript{116} Li et al. demonstrated that V$_{O}$ create Ti$^{5+}$ 3d$^1$ defect states, mediating the ferromagnetic coupling between the localized Eu 4f$^7$ spins, and an increase in the off-center displacement of Ti ions, enhancing the ferroelectric Curie temperature in Eu$_{0.8}$Ba$_{0.2}$TiO$_{3-\delta}$ film.\textsuperscript{117,118} Similar achievements of ferroelectricity and ferromagnetism was also observed in YMnO$_3$ films by the manipulation of V$_{O}$.\textsuperscript{73}
Engineering specific atomic displacements or geometric design has been applied to design a single-phase multiferroic. Hexagonal LuFeO₃ is a geometric ferroelectric with the greatest known planar rumpling.¹¹⁹ In the (LuFeO₃)ₙ/(LuFe₂O₄)₁ superlattices, Mundy et al. introduced the individual monolayers of FeO during the growth to construct formula-unit-thick layers of ferromagnetic LuFe₂O₄ within the LuFeO₃ matrix and further demonstrated that the severe rumpling imposed by the neighbouring LuFeO₃ enhances the magnetic transition temperature of LuFe₂O₄ to 281 K and also drives LuFeO₂ into a ferroelectric state (Fig. 5a).¹²⁶ Moreover, electric-field control of magnetism has been realized at 200 K. Through the engineering of octahedral tilts, room-temperature ferroelectric ferromagnetic and magnetoelectric coupling have been realized in (Ca₂Sr₁₋ₓ)₁₋ₓTb₁.₅Fe₀.₅O₇.¹²¹ Choi et al. and Chen et al. reported room-temperature multiferroic films based on two partially miscible phases of BiFeO₃ and BiMnO₂.¹²²,¹²³

Dielectric materials exhibiting temperature- and frequency-stable permittivity as well as dielectric tunability and sufficiently low dielectric loss, continues to arouse considerable interest motivated by their myriad device miniaturization and high-energy-density storage application.¹²⁴,¹²⁵ Dielectricity can be tuned by VₓOₓ, VₓCₓ misfit dislocations and dipolar defects. Lee et al. demonstrated that the presence of (SrO)ₓ crystallographic shear planes in SrₓTiO₃₋ₓOₓ₊₁ film provides a means of locally accommodating non-stoichiometry (Sr vacancies), which significantly reduces the dielectric loss and achieves the dielectric tunability (20% at 50 kV cm⁻¹) across the entire microwave range (Fig. 5b).¹²⁶ Vertically aligned nanocomposites (VANs) with ordered vertical heterointerfaces provide an effective platform to tune the dielectric properties. Lee et al. studied the dielectric tunability in BaₓSr₁₋ₓTiO₃₋ₓSmOₓ VAN films and reported the achievement of a low dielectric loss (tan δ < 0.1) and high and stable dielectric tunability (75% at 200 kV cm⁻¹) at room temperature.¹²⁷ A very low dielectric loss (tan δ ~ 0.01) and relative large dielectric tunability (49% at 400 kV cm⁻¹) was further reported in SrTiO₃:SmOₓ VAN film.¹²₈ Yang et al. explored BiFeO₃:SmO₂ VAN films and found that dielectric loss and leakage current were reduced compared to plain BiFeO₃ films (Fig. 5c).¹²₉,¹³₀ The increased vertical interfacial area and reduced VₓOₓ in the BiFeO₃ phase are responsible for these improved properties. Enhanced ferroelectric Curie temperatures and reduced leakage current were also reported in BaTiO₃:Sm₂O₃ VAN films.¹³₁,¹³² Li et al. found that the misfit dislocations are formed at the vertical interface due to a large vertical lattice strain. The movement of VₓOₓ is confined at the vertical interface and hampered by the misfit dislocations, which contributed to a relaxation behavior in BaTiO₃:Sm₂O₃ VAN film.¹³³ Dipolar defects are created by the change of VₓOₓ concentration and further interact with the off-centered Ti ions, which results in dielectric relaxation in Eu₀.₅Ba₀.₅TiO₃₋ₓδ films.¹³⁴

![Fig. 5](image-url)
3.4 2DEG and 2DHG

The emergence of conducting interface can be promoted by polar discontinuities. Ohtomo et al. reported the discovery of a two-dimensional electron gas (2DEG) at the LaAlO$_3$/SrTiO$_3$ heterostructures based on this idea.$^{135}$ Both compounds are band insulators ($E_{\text{gap}} = 5.6$ eV for bulk LaAlO$_3$ and $E_{\text{gap}} = 3.2$ eV for bulk SrTiO$_3$). However, when a LaAlO$_3$ layer is deposited layer-by-layer on top of a (001) TiO$_2$-terminated SrTiO$_3$ substrate, the interface switches to a metallic state when the LaAlO$_3$ layer thickness exceeds 3 unit cells.$^{136}$ These experimental observations have generated a lot of interest in the SrTiO$_3$-based interfaces,$^{137,138}$ due to their potential applications in novel electronic devices and rich physics arising from the complex electronic correlations.$^{139-141}$ Although significant attempts have been paid to understand the LaAlO$_3$/SrTiO$_3$ interface, the origin of interfacial conductivity is still under debate. From the very beginning, the conductivity observed at the LaAlO$_3$/SrTiO$_3$ interface was attributed to the polar discontinuity.$^{135}$ This polar catastrophe scenario emerges from a simple valence counting consideration. As shown in Fig. 6a, the TiO$_2$ and SrO planes are neutral, however, the LaO and AlO$_2$ layers are polar and carry a positive and negative charge of $+1$ e and $-1$ e per unit cell, respectively. The diverging electric potential can be compensated by electron transfer from LaAlO$_3$ to the interfacial SrTiO$_3$ layer with the formation of the n-type interface. The polar catastrophe picture explains many of the features of the electron gas at the LaAlO$_3$/SrTiO$_3$ interface, in particular the existence of a critical thickness for the onset of metallic behavior. However, some unresolved inconsistencies between theories and experiments still exist. For example, the predicted sheet carrier densities and their variation with LaAlO$_3$ thickness have not been observed in experiments yet.$^{136,142}$

Besides the polar discontinuity, the defects (e.g., $V_O$) and cation intermixing are also invoked to understand interfacial conductivity.$^{143,144}$ It was found that charge transport depends sensitively on the growth conditions, especially on the oxygen pressure $P_{O_2}$ indicating that $V_O$ could be an alternative doping mechanism.$^{135,145-147}$ Temperature-dependent sheet resistance $R_{\text{sheet}}$ depends dramatically on the growth pressure (Fig. 6b). For $P_{O_2} \sim 10^{-6}$ mbar, the observation of a larger carrier density originates from the doping of $V_O$ to the SrTiO$_3$ substrate. For

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**Fig. 6** (a) Sketch of two mechanisms, polar discontinuity and oxygen vacancies, for inducing mobile electrons at the LaAlO$_3$/SrTiO$_3$ interface. Reproduced with permission.$^{3,378}$ Copyright 2018 Wiley-VCH and Copyright 2013 American Physical Society. (b) Temperature-dependent sheet resistance $R_{\text{xx}}$ for the interface between LaAlO$_3$ and SrTiO$_3$. Reproduced with permission.$^{135}$ Copyright 2004 Springer Nature. (c) AlO$_2$/LaO/TiO$_2$ interface showing the fractions of elemental Ti and La from the Ti-L and La-M edges, as well as the Ti$^{3+}$ fraction determined from a least-squares fit to the Ti-L edge from Ti$^{3+}$ and Ti$^{4+}$ reference spectra. There is excess Ti$^{3+}$ on the substrate side of the interface. Reproduced with permission.$^{149}$ Copyright 2006 Springer Nature. (d) Left: Schematics that depict the electronic reconstruction across the oxide heterostructure. Right: Hall resistance $R_{\text{H}}$ versus magnetic field $\mu B$ for the top and bottom interfaces at 4 K. The top interface clearly shows a positive slope, which indicates p-type conductivity, whereas the bottom interface shows a negative slope, which indicates n-type conductivity. Reproduced with permission.$^{150}$ Copyright 2018 Springer Nature.
between $10^{-4}$ and $10^{-2}$ mbar, the observation of conductivity is believed to be confined to the interface. When the $P_{O_2}$ is above $10^{-2}$ mbar, the reported results are more diversified, such as insulating, superconducting and magnetoresistance effects.\textsuperscript{147,148} Atomic-resolution electron energy loss spectroscopy (EELS) revealed that the interface is not chemically sharp, with some La/Sr and Ti/Al intermixing included (Fig. 6c).\textsuperscript{149} Such chemical doping could also be the source of the carriers at the interface, with the interface layer behaving as a La$_{1-x}$Sr$_x$TiO$_3$ film, which are responsible for the interfacial conductivity. Recently, Lee \textit{et al.} reported the observation of a two-dimensional hole gas (2DHG) in (001) SrTiO$_3$/LaAlO$_3$/SrTiO$_3$ heterostructures (Fig. 6d).\textsuperscript{150} The SrTiO$_3$ substrate is terminated at TiO$_2$. Depth-resolved cathodoluminescence spectroscopy (DR-CLS) was used to support that the formation of 2DHG is not attributed to the VO$_2$.

The fundamental questions on the origin of the carrier, the carrier density, the shape of the confining potential and the role of electronic correlations are too complicated and still can’t be answered at the LaAlO$_3$/SrTiO$_3$ interface and other similar systems. More comprehensive discussions can be found in other review papers.\textsuperscript{3,151–153}

### 3.5 Metal–insulator transitions

Understanding metal–insulator transitions in strongly correlated materials is one of the major challenges in condensed matter physics,\textsuperscript{154–158} with implications for both fundamental science and technology.\textsuperscript{159,160} Strain, VO$_2$ and BO$_6$ octahedral distortions have been applied for manipulating metal–insulator transition behaviour. An archetypal correlated material is VO$_2$, showing a pronounced metal–insulator behavior from low-temperature insulating monoclinic (M1) phase to high-temperature metallic rutile (R) phase near room temperature (341 K in bulk).\textsuperscript{161} Epitaxial strain and VO$_2$ defects have been widely used in order to control metal–insulator transition dynamics for achieving a shape phase transition in VO$_2$ epilayer films.\textsuperscript{162–166} Using electrolyte gating with an ionic liquid, Jeong \textit{et al.} reported that the suppression of the metal–insulator transition in VO$_2$ film is achieved by electric field-induced VO$_2$ formation for reducing the valence state of V$^{4+}$ to V$^{3+}$ (Fig. 7a).\textsuperscript{167} However, creation of VO$_2$ by ionic liquid gating is possibly linked with both hydrogen intercalation whence a trace of water remains in the ionic liquid and degradation of the entire film under high electric field.\textsuperscript{164,168} By growing the VO$_2$–$d$/VO$_2$ bilayer films on TiO$_2$ substrates, Lee \textit{et al.} found that an interface interaction between VO$_2$–$d$ and VO$_2$ can suppress the electronic correlations for controlling the metal–insulator transition.\textsuperscript{169} By annealing VO$_2$ films at an ultralow oxygen partial pressure ($P_{O_2} \sim 10^{-24}$ atm), the formation of VO$_2$ led to a change of the band structure (Fig. 7b) and an appearance of a metallic state down to 1.8 K.\textsuperscript{165} Moreover, the VO$_2$ film can revert back to its original state by a simple annealing process in oxygen.

As discussed above, during the transformation of a layered VO$_2$ ordered brownmillerite structure to a perovskite structure framework, the modification of electronic structure, such as the hybridization between O 2p and TM d orbitals, is responsible for the reversible change between the brownmillerite insulating state and the perovskite metallic state. This phenomenon has been widely observed in La$_{0.7}$Sr$_{0.3}$MnO$_{3-x}$, SrCoO$_{3-x}$, SrFeO$_{3-x}$, LaCoO$_3$, and SrCrO$_3$ films.\textsuperscript{76–81} Taking SrFeO$_3$ as an example, SrFeO$_{3.5}$ exhibits insulating (or semiconducting) behaviour in the BM structure while SrFeO$_3$ shows metallic behaviour in the perovskite structure. By using different growth atmospheres (oxygen partial pressure) or by modifying the interfacial strain by changing the growth substrates, V$_2$O$_5$ concentration could be successfully controlled and could therefore modulate the conductivity and metal–insulator transition.\textsuperscript{81,170}

The properties of perovskite rare-earth nickelates, RNiO$_3$ (R = La–Lu), have been attracting enormous attention owing to a rich temperature-composition phase diagram including a metal-to-insulator phase transition coinciding with a nickel charge ordering.\textsuperscript{16,171,172} The origin of the metal-to-insulator transition has been widely debated in the literatures.\textsuperscript{173–176} The unoccupied states at the bottom of the conduction band have substantial oxygen character, corresponding to an oxygen

![Fig. 7](https://example.com/fig7.png)

**Fig. 7** (a) Sheet resistance versus temperature for various gate voltages varying from 0 to 1.8 V for VO$_2$/TiO$_2$. Reproduced with permission.\textsuperscript{167} Copyright 2013 AAAS. (b) Schematic illustration of the band structure of pristine VO$_2$ in the insulating state (top) and metallic state (bottom left), while the band structure of oxygen-deficient VO$_{2-d}$ is shown in bottom right, where strong charge filling in the $\pi^*$ and $d_x$ orbitals occurs. Reproduced with permission.\textsuperscript{165} Copyright 2017 American Physical Society. (c) Temperature-dependent resistivity of (LaFeO$_3$)$_n$–(SmNiO$_3$)$_n$ superlattices and 30 uc SmNiO$_3$ film. Reproduced with permission.\textsuperscript{183} Copyright 2018 National Academy of Sciences.
ligand hole consistent with a negative charge transfer character for the system. In a non-disproportionated structure, the nickel sites have nominal valence 3+ and the oxygen ligand holes are distributed equally among all of the NiO$_6$ octahedra, resulting in a d$^L$L configuration, where L denotes an oxygen ligand hole. V$_O$ in the rare-earth nickelates can modify the electronic structure and act as electron donors. The added electron can be regarded as converting nickel from 3+ to 2+, or as converting the nickel site in the NiO$_6$ octahedron from d$^8$ to d$^6$. This results in a large on-site bandgap stemming from holes being distributed equally among all of the NiO$_6$ octahedra, nickel sites have nominal valence 3+ and the oxygen ligand hole. V$_O$ in the rare-earth nickelates can modify the electronic structure and act as electron donors. The added electron can be regarded as converting nickel from 3+ to 2+, or as converting the nickel site in the NiO$_6$ octahedron from d$^8$ to d$^6$. This results in a large on-site bandgap stemming from the electron–electron correlations and the crystal field splitting. As a result, metal–insulator transitions of LaNiO$_3$, NdNiO$_3$ and SmNiO$_3$ films can be controlled by the formation of V$_O$. Recently, Mercy et al. identified that the breathing mode responsible for the metal–insulator transition in the perovskite nickelates is triggered by NiO$_6$ octahedral rotations and tilts. Based on this idea, in the case of the (LaFeO$_3$)$_n$/(SmNiO$_3$)$_n$ superlattices, Liao et al. demonstrated that the metal–insulator transition in the SmNiO$_3$ layer can be adjusted by the modulation of NiO$_6$ octahedral tilt (Fig. 7c). 

### 3.6 Resistive switching

Resistive random-access memory (RRAM or ReRAM) is one of the most promising emerging devices for logic-in-memory operations, attracting great attention due to the possibility of high-density integration, plausible scalability, ultra-fast access time, low power consumption and ease of fabrication. ReRAMs can be divided into two categories: electrochemical metallization cells ReRAMs – also called conductive bridge random access memories – and valence change mechanism ReRAMs – also called redox random access memories ReRAMs. Resitive switching behaviour can be manipulated by controlling cations, V$_O$ and interfaces. In electrochemical metallization cells, a nanoscale conductive metallic path between a working electrode/anode (often electrochemically active, such as Ag or Cu) and a counter electrode/cathode (often inert, such as Pt, Au or TiN) is formed or broken by the generation, movement and reduction of mobile metal cations (i.e., Ag$^+$ or Cu$^{2+}$). Valence change mechanisms occur in a wide range of TMOs. In TMOs, anions such as oxygen ions (or, equivalently, V$_O$) are more mobile than the cations when they are thermally and/or electrically activated. Therefore, understanding how the resistance of TMOs is influenced by V$_O$ is very important. Generally, V$_O$ will affect the resistance and contribute toward the introduction of resistive switching phenomena in one of three ways: (1) V$_O$ tend to cluster and generally form filamentary shapes under an electric field (Fig. 8a). When such clusters are formed, the resistance of the local region becomes much lower than that of the surrounding oxide matrix, and the low-resistance state (LRS) and high-resistance state (HRS) will therefore be determined by the creation and rupture of the conducting filaments (CFs), respectively. (2) V$_O$ can control the Schottky barrier characteristics. In a typical capacitor sample geometry, an interface is formed between the metal electrode and the TMOs films. Depending on the difference of work functions between the metal electrode and the TMOs, a Schottky barrier can be formed. Under an external bias, the distribution and density of V$_O$ can vary, which affects the height and width of the Schottky barrier and leads to a change in the resistance of the sample. (3) V$_O$ can also form trap sites for electrons inside the Schottky barrier region. In this situation, the Schottky barrier can be modulated by the neutralization of the V$_O$ due to the trapping of electrons, inducing resistive switching phenomena.

Resistive switching devices are normally in the form of metal-dielectric-metal two-terminal junctions. The interface between metal electrode and the TMOs films plays a critical role in the resistive switching. Using vertical heterointerfaces in vertically aligned nanocomposite (VAN) films for studying resistive switching has been reported. Different from lateral heterostructures, VANs exhibit a much higher density of vertical interfaces which can be used for improving resistive
switching. Lee et al. reported that due to the structural incompatibility of SrTiO$_3$ and Sm$_2$O$_3$, the possible formation of V$_O$ was found at vertical heterointerfaces.\textsuperscript{196} The Joule heating-accelerated drift of V$_O$ localized at vertical heterointerfaces reduces the wide fluctuation in switching parameters (Fig. 8b). In self-assembled Sm-doped CeO$_2$ and SrTiO$_3$ VAN films, large on–off ratios and high reproducibility were achieved by the separate tailoring of nanoscale ionic and electronic channels.\textsuperscript{197}

Although great progresses have been made in valence change mechanism ReRAMs, mastery of the conduction mechanism is still incomplete. To identify and understand failure mechanisms, characterization methods, such as voltage-sweep and voltage-pulse measurements, electrochemical cyclic voltammetry, and \textit{ex situ} and \textit{in situ} electron microscopy have been used. However, limited success is achieved in fully understanding the switching dynamics. Recently, a spectroscopic technique to optically characterize \textit{in situ} resistive switching effect was reported.\textsuperscript{198} Resistive switches arranged in a nanoparticle-on-mirror (NPM) geometry were developed, exploiting the high sensitivity to morphological changes occurring in the tightly confined plasmonic hotspot within the switching materials (Fig. 8c).\textsuperscript{199} This provides a non-destructive technique to understand the switching dynamics.

Recently published reviews provide more comprehensive discussions on classification of resistive switching phenomena/mechanisms, other microscopic origins of resistive switching in TMOs, resistive switching related technological issues (e.g., fluctuation, sneak-paths and multilevel switching) and neuromorphic computing based on resistive switching which has drawn extensive attention due to its promising capability in processing massive data in the Internet of Things and big-data workloads.\textsuperscript{199–203}

### 3.7 Ionic conductivity

One of the leading technologies for future power generation is the solid oxide fuel cell (SOFC).\textsuperscript{204–206} One important challenge in improving SOFC technology is to reduce the working temperature to 500–700 °C. Over several decades, developing new electrolyte materials with high ion conductivity has been the primary activity. The oxygen diffusivity ($D$) scales almost linearly with V$_O$ concentration when the value of V$_O$ is low. On the other hand, oxygen diffusion is a thermally activated process where $D$ can be described by the Boltzmann relationship as

$$D = D_0 \exp\left(\frac{-E_m}{k_B T}\right),$$

where $D_0$ is a constant and $E_m$ denotes migration enthalpies or energy barrier along this path. Compared to linear relationship between $D$ and V$_O$ concentration, $D$ changes exponentially with $E_m$ which makes it a critical parameter to reduce.\textsuperscript{206} The oxygen migration energy can be modified by misfit dislocations, V$_O$, elastic strain, BO$_6$ octahedral distortion, and so on.

Yttria-stabilized zirconia (YSZ) is the material mostly used in SOFCs because of its mechanical stability, chemical compatibility with electrodes, and high oxygen ionic conductivity. Engineering misfit dislocation and V$_O$ at heterogeneous interfaces have been used to improve the charge-carrier density and enhance the ionic conductivity. For example, Garcia-Barriocanal et al. reported an eight-orders-of-magnitude enhancement of YSZ conductivity in epitaxial multilayers consisting of two unit cell YSZ and thick SrTiO$_3$, which attributes colossal enhancement of ionic conductivity to either V$_O$ or O disorder in the interfacial plane.\textsuperscript{207} Density-functional calculations revealed that colossal ionic conductivity in YSZ/SrTiO$_3$ multilayers can be explained in terms of lattice-mismatch strain and O-sublattice incompatibility at the interface (Fig. 9a).\textsuperscript{208} However, these experimental results still have to be independently verified, as there are some debates as to whether the conductivity of YSZ/SrTiO$_3$ multilayers is purely ionic.\textsuperscript{209} Sillassen et al. reported that interfacial effects dominate the conductivity at the low temperature (<350 °C), showing more than three orders of magnitude enhancement in YSZ films compared to bulk YSZ.\textsuperscript{210} The observed enhancement in lateral ionic conductivity is caused by a combination of misfit dislocations and elastic strain at the interface (Fig. 9b and c). Similar evidences for misfit dislocations related to fast ion conduction in lateral heterostructures are reported in numerous experimental and theoretical studies.\textsuperscript{211–215}

Vertically aligned nanocomposite (VAN) films have been also developed to improve the ionic conductivity and design state-of-the-art ionic devices.\textsuperscript{216,217} Compared to the oxygen ion diffusion along lateral interface direction in the lateral heterostructures, VANs allow fast oxygen ion transport along the out-of-plane direction which is the favored charge flow direction of SOFCs. Enhanced ionic conductivity values by over 2 orders of magnitude, compared to plain YSZ films, was reported in YSZ/SrTiO$_3$ VAN films (Fig. 9d).\textsuperscript{218} The improved crystallinity of YSZ nanocolumns in VAN film was proposed to explain the enhanced ionic conductivity. Similar to YSZ/SrTiO$_3$ VAN films, the enhancement in vertical ionic conductivity has been also demonstrated in VAN systems of YSZ:GDC\textsuperscript{218} (Gd-doped CeO$_2$) and SrTiO$_3$:SDC (Sm-doped CeO$_2$).\textsuperscript{219}

Very recently, Gao et al. reported that, through the creation of La$_{0.9}$Sr$_{0.1}$Ga$_{0.95}$Mg$_{0.05}$O$_3$–δ/DyScO$_3$ superlattice films, both expanded unit-cell volume and large octahedral rotations can be realized in La$_{0.9}$Sr$_{0.1}$Ga$_{0.95}$Mg$_{0.05}$O$_3$–δ (LSGM), which shows an enhancement of ionic conductivity (Fig. 9e).\textsuperscript{220} This provides a new pathway for the rational design of ion-conducting perovskite electrolytes \textit{via} controlling BO$_6$ octahedral rotations.

### 3.8 Photo-electrochemical and electrocatalysts

Electrochemical water splitting to produce storable hydrogen (also referred to as “solar fuel”) driven by solar energy or by electricity from renewable energy (e.g., photovoltaics) is widely seen as a promising pathway towards a globally sustainable energy future. The key to enabling these approaches is the development of abundant, low-cost, stable semiconductor materials to harness solar energy and efficient electrocatalysts to accelerate the water oxidation reaction.\textsuperscript{221} Complex TMOs are appealing materials for these purposes, owing to their earth-abundance, good stability and tunable physicochemical properties \textit{via} doping and defect engineering (especially V$_O$, V$_C$ and lattice distortions).\textsuperscript{222–224}
To achieve effective implementation of solar driven photoelectrochemical water splitting (PEC), stringent requirements on the material properties should be satisfied, including an appropriate bandgap for sufficient light absorption, adequate band edge potentials to drive redox reactions, favorable carrier diffusion length to ensure the effective progress of the interface reaction. TMO semiconductors such as TiO$_2$, Fe$_2$O$_3$ and BiVO$_4$ have attracted intensive attention for the last decades. However, their PEC performance is still far from the standard of practical applications, because of limitations in materials properties. For example, TiO$_2$ has a much too large bandgap (3.0–3.2 eV) for visible light absorption. Fe$_2$O$_3$ has a low bandgap of ~2.1 eV, but is inherently limited by its low electrical conductivity, short diffusion length (2–4 nm) and lifetime (<10 ps) of photoexcited carriers. Doping, alloying and defect engineering are widely used as strategies to enhance the PEC activity with the purpose of: (i) decreasing the bandgap for efficient visible light absorption and (ii) optimizing the carrier transport. Doping can introduce extra energy levels within the bandgap (for example, Bi$^{3+}$ 6s$^2$ state hybrid with Ti$^{4+}$ d$^0$ orbital) to narrow the bandgap value. On the other hand, it has been shown that Fe$_2$O$_3$ can be p-type doped by divalent cations such as Mg$^{2+}$ and n-type doped with tetravalent cations such as Ti$^{4+}$, Sn$^{4+}$, etc. Doped Fe$_2$O$_3$ can remarkably enhance the PEC activity toward water oxidation compared with undoped counterparts. The same trend of enhanced PEC activity was also achieved in Mo$^{6+}$ or W$^{6+}$ doped BiVO$_4$.

Defect engineering is another approach to tuning the band structure and therefore PEC performance of TMOs, especially...
V$_{O}$, V$_{C}$, and lattice distortion. V$_{O}$ provide donor states to increase n-type conductivity, while V$_{C}$ provide acceptor states for p-type conductivity. Furthermore, the defects also provide favorable adsorption sites for chemical reactions to enhance the activity. Cui et al. prepared black TiO$_2$ nanotubes (B-TNTs) with abundant V$_{O}$ via the Al reduction method, which shows 5 times higher applied bias photon-to-current efficiency (ABPE) than that of TNTs and a larger visible light photosresponse region from 400 nm to 460 nm. The new donor level at about 0.7 eV below the conduction band minimum (CBM) corresponding to the formation of V$_{O}$. Yim and coworkers attribute the bandgap state in TiO$_2$ (110) to bridging V$_{O}$ by ultraviolet photoemission spectroscopy and scanning tunneling microscopy. But the contribution of interstitial Ti is also proposed in another work. Because of the increased carrier density and the lowered activation energy for charge transport, the separation and migration of photo-excited carriers can be effectively improved. However, excess V$_{O}$ may trap photoelectrons and act as recombination centers, and then decrease the photocurrent. The above effects also hold for BiVO$_4$. Furthermore, the presence of V$_{O}$ has the ability to work as active site for PEC water splitting and enhance the adsorption energies of H$_2$O$_{ads}$, OH$_{ads}$, and O$_{ads}$ (Fig. 10a). The strong interaction indicates that an increased overlap between Bi 6s, V 3d and O 2p orbitals, and then accelerates the hole transfer at electrode/electrolyte interface.

The oxygen reduction reaction (ORR) and OER are the essential processes for water splitting, fuel cell, and metal-air batteries. However, the ORR and OER process involve four electron transfer processes with sluggish reaction kinetics. Precious Pt and Ir based electrocatalysts are needed, limiting its large-scale utilization. Low-cost TMOs electrocatalysts such as Co$_3$O$_4$, NiO, LaNiO$_3$, La$_{1-x}$Sr$_x$CoO$_{2-y}$, etc., have been developed in the past few decades. The presence of defects significantly affects the band structure of catalysts and the local bond environment of defect sites, and hence manipulates the adsorption sites, energy, and configuration of the reactant or various intermediate species. Ling et al. synthesized CoO nanorods with oxygen-terminated {111} facets, where contain a large number of O-vacancies. It is worth mentioning that an additional state of hybridization of O 2p, Co 3d and Co 3s appears in the bandgap when introducing V$_{O}$, which results in the lowest adsorption energies of intermediates on active sites, as shown in Fig. 10b. During the reaction process, owing to $\Delta$$G_{\text{ORR}}$ $\approx$ $\Delta$$G_{\text{OER}}$ $\approx$ $\Delta$$G_{\text{O2}}$ $\approx$ 0, that the {111}-V$_{O}$/CoO surface can adsorb and desorb easily. Based on the single-crystalline ultrathin Co$_3$O$_4$ model, it was able to further discuss the effect of defects on electrocatalytic performance by introducing vacancies into specific crystal facets. The Co$_3$O$_4$ {111} surface with rich V$_{O}$ exposed second-layered Co sites and then these Co atoms become the active sites under the influence of neighboring O atoms. This structure exhibits a low overpotential.
of 220 mV and improved electrical conductivity. In addition, superfluous VO will affect the stability of electrodes, filling heteroatoms in favor of compensating the coordination numbers and increasing the binding between intermediates and surface of electrocatalysts.266

Defects can also cause charge compensation and also play as scattering centers to affect the transport properties like mobility and conductivity, and even create lattice distortions and form strain. Cheng et al. prepared a rutile β-MnO₂ with native VO, and the charge is compensated by the reduction of Mn⁴⁺ to Mn³⁺.267 It is remarkable that a new crystal structure appeared except a typical pyrolusite lattice, which can be explained by introduced VO. In this case, electrodes exhibit a more positive potential and a large current for ORR. The work of Zhao et al. emphasized that the Mn³⁺ active sites of ultrathin δ-MnO₂ nanosheets contribute to half-metallicity and strong H₂O adsorption.268 There are two valences, Co⁵⁺ and Co³⁺, in Co₃O₄. Some studies have demonstrated that Co⁵⁺ is the key active site of the OOR, and that relative ratio of Co²⁺/Co³⁺ can be tuned by controlling the concentration of VO.266,269 Besides, the methane catalytic combustion of Ca-doped LaFeO₃ perovskites show a directly correlation to the amount of Fe⁴⁺, which results from the formation of VO.²⁷⁰

In addition, grain boundaries, steps, and edges also belong to defects. It is generally true that these defects are thermodynamically unstable, and have high energy and low coordination number, which leads to improved electrocatalytic performance. The broken symmetry near grain boundaries increases the binding energy of intermediate species.²⁷¹,²⁷² However, in some cases of photocatalysis, it is easy to be trapped and recombined when charge carriers transfer through the grain boundaries and then inhibit catalytic activity.²⁷³,²⁷⁴

### 3.9 Ionic doping

Ionotronics is an emerging technology that aims to induce a large change of transport properties through the movement of ionic doping by an external stimuli. By moving ions, such as H⁺, Li⁺, Na⁺ and Mg²⁺, into or out of TMOs under an electric field, reversible changes in the structure, electronic structure and physical properties of TMOs can be achieved. Ionic doping across solid–liquid interfaces can be realized using ionic liquid, aqueous solutions or water. In ionic liquid gating, due to a very strong electric field ($\geq 10\, \text{MV cm}^{-1}$) formed at the interface, hydrogen ions can be intercalated into TMOs from the ionic liquid, or oxygen ions can be moved out from TMOs, depending on the polarity of the electric field. As shown in Fig. 11a, using ionic liquids, controlling the insertion and extraction of hydrogen and oxygen ions independently of each other can direct reversible phase transformations among three different materials phases: H$_2$SrCoO$_{2.5}$, brownmillerite SrCoO$_{2.5}$ and perovskite SrCoO$_{2}$²⁷⁵ Consequently, Lu et al. observed a dramatic modulation of electronic, magnetic and optical properties by changing the valence state of Co and Co 3d and O 2p orbital hybridization. Moreover, the electric-field control of three different magnetic ground states was also reported (Fig. 11b).²⁷⁶ Very recently, the tuning of thermal conductivity was further demonstrated by triggering the "tri-state" phase transitions in SrCoO$_{2.5}$ films (Fig. 11c).²⁷⁷ Similar reversible phase transformations mediated by hydrogen and oxygen ions was also observed in VO$_2$, ZnO$_x$, WO$_x$, SrRuO$_3$, La$_{1-x}$Sr$_x$MnO$_3$, La$_{0.5}$Sr$_{0.5}$MnO$_3$/SrIrO$_3$ superlattice films, etc. ²⁸⁶,²⁸⁷ Water was also used as a gating medium for achieving hydrogen doping.²⁸² The ionization of water to form H⁺ and OH⁻ occurs when a bias voltage over 1.23 V is applied between an electrode and TMOs in water. Thus, under a positive electric field, H⁺ can be intercalated into TMOs.
It has been reported that a water-infiltrated nanoporous glass or a humid air gap can be used for controlling the channel conductance in SrTiO$_3$ and VO$_2$ field effect transistors, respectively.$^{281,284}$ In addition, H$^+$ doping through solid-gas interface was studied in SmNiO$_3$ and VO$_2$ films.$^{20,276,285}$ Pt electrodes were used for achieving effective H$^+$ doping, which changes electron doping and suppresses the electronic transport via electron–electron correlations.$^{20}$

Ionic doping across solid-solid interfaces can be realized using solid state electrolytes. When a positive bias is applied across a proton-storing solid-state electrolyte, hydrogen ions can be injected into TMOs. The advantage of this doping method is that not only H$^+$ but also Li$^+$, Na$^+$, and Mg$^{2+}$ intercalation can take place in a controlled manner by gating through electrochemical cells. As shown in Fig. 11d, pristine room temperature SmNiO$_3$ is a semiconductor with a narrow bandgap.$^{20,286}$ After ionic doping, it becomes a strongly correlated insulator, with a bandgap on the order of 3 eV, where Ni$^{3+}$ is reduced to Ni$^{2+}$. Furthermore, electric-field-induced ion injection is non-volatile and reversible. After removal of an applied electric field, ionic dopants remain in TMOs, and the application of a reverse electric-field can be used to remove them. Therefore, these phenomena can be exploited for the use in non-volatile memory devices with cross-bar or related geometries.

The reversible manipulation of physical and chemical properties in TMOs using ionic doping can be used in a wide range of applications, such as electronics ($e.g.$ sensors,$^{287}$ nonvolatile memory,$^{288}$ smart windows, etc.$^{19,289}$), energy ($e.g.$ catalysis for water splitting, fuel cell, etc.$^{290–292}$), and emerging research directions ($e.g.$ biomimetic machine learning, synaptic transistor, etc.$^{179,293–296}$). More comprehensive discussions on these topics can be found in recent published reviews.$^{21,282,297}$

### 3.10 Wide bandgap oxide semiconductors

Wide bandgap oxide semiconductors are widely utilized in the field of flat-panel displays (FPDs), sensing devices and power electronics due to their fascinating opto-electrical properties, compositional diversities, structural stability and adjustable bandgap values.$^{41,298–304}$ Motivated by the great promises of oxide semiconductors and devices, great efforts have been made to modulate their performances from different angles including mobility, carrier type (electron or hole), crystallinity, transparency, etc. Defect engineering has been one of the core strategies in controlling oxide semiconductor properties.$^{302–304}$

Here we will take some representative oxide semiconductors (ZnO, In$_2$O$_3$, IGZO) as examples, to discuss how the control of defects, such as V$_{Do}$, V$_C$, and interstitials, could help to shape materials and devices.

ZnO is probably the most remarkable oxide semiconductor. With a direct bandgap of 3.4 eV, large exciton energy (60 meV), low cost and easiness of growing large single crystals, ZnO seems like a very attractive candidate for optoelectronics.$^{305,306}$

Despite its intrinsic advantages, the lack of control over dopants and defects hindered its further application to practical devices, thus stimulated a boom over investigating the defect chemistry in ZnO.$^{302,307–310}$ The as-grown ZnO crystals normally exhibit n-type conductivity, which was initially attributed to the native defects such as Zn interstitials, Zn vacancies or V$_O$ (Fig. 12a).$^{302,305}$ However, V$_O$ has been proven to be deep donors.$^{311–313}$ and Zn vacancies form as compensating acceptors in n-type ZnO.$^{314,315}$ Zn interstitials are proved to be shallow donors,$^{315,316}$ yet they are unstable at room temperature due to their mobile nature.$^{317,318}$ Group-III donors (B, Al, Ga, and In) and H impurities account for most of the n-type conductivity in ZnO samples. To reach an applicable doping level of n $\sim 10^{20}$ cm$^{-3}$ as required by a transparent conductor, H is a shallow donor in ZnO and has been shown great improvement of carrier concentrations with the magnitude of 3 orders.$^{319–322}$ Despite multiple experimental and theoretical investigations having been devoted to the microscopic structure of H in defects$^{323–326}$ and its complex with Zn vacancies or other impurities,$^{327–329}$ its interaction with the ZnO crystal lattice or components and the mechanism of modulating carrier transportation are still not very clear.

In$_2$O$_3$ is firstly known as the parent material of widely used transparent conducting oxide indium-tin-oxide (ITO)$^{330–333}$ In the last decade, In$_2$O$_3$ itself has been rediscovered to be a wide-bandgap semiconductor with great potential and has received lots of attentions from the semiconductor physics community,$^{299}$ due to its fascinating structural,$^{334–337}$ mechanical,$^{338–340}$ and electronic properties.$^{341–344}$ The explorations of the influence of defects on conductivity of In$_2$O$_3$ has a long history. Bierwagen et al. summarized the results of Hall mobility and Hall electron concentration in unintentionally doped, In$_2$O$_3$ thin films and bulk samples and observed a qualitatively similar trend, that simultaneously increased in electron mobility and decreased electron concentration, consistent with O$_2$ annealing reduced donor concentration, as shown in Fig. 12b.$^{299}$ Discrepancies remain regarding the nature of native defects. DFT calculations within LDA/GGA by Lany et al.$^{311}$ and Limpijumnong et al.$^{345}$ reached the conclusion that V$_O$ are deep donors, while Agoston et al. calculated them to be shallow donors using the hybrid-functional method within DFT.$^{346,347}$ Calculations by Tang et al. suggested that even though V$_O$ creates deep donor levels,$^{348}$ In interstitials lead to shallow donors and their coupling with V$_O$ could give rise to even shallower donors. The native defects also have important influences on the doping modulation of In$_2$O$_3$. While dopant solubility is sufficient in In$_2$O$_3$, native defects normally act as compensating centers, i.e., donor-type defects V$_O$ and In interstitials tend to counteract p-type doping, while acceptor-type defects, i.e. In vacancies and O interstitials, counteract n-type doping.$^{313,349}$ The control over the In$_2$O$_3$ native defects concentrations could be realized by simply adjusting the growth conditions. For example, V$_O$ could be controlled by varying the growth atmosphere or by adding an additional O$_2$ annealing process.$^{350,351}$

Amorphous indium gallium zinc oxide ($\alpha$-IGZO) is one of the most successful commercialized oxide semiconductors in this century, widely used in thin-film transistors (TFTs) for high-resolution displays.$^{298,352–355}$ Defects have a significant
influence on a-IGZO materials and TFTs, i.e., while most defects are detrimental to device performance, some defects actually play a positive role in improving carrier density.\textsuperscript{304,356,357} VO, metal–metal bonds and H incorporation are the three main defect types present in channel region of a-IGZO TFTs.\textsuperscript{358} VO could participate in several different local coordination structures: (i) ‘Corner-share’ structure formed by VO coordinated with small numbers of cations, (ii) ‘Free space’ structure formed by VO adjacent to a large open space and (iii) ‘Edge/Face-sharing’ structure formed by VO surrounded by many cations, as shown in Fig. 12c.\textsuperscript{298} The ‘Corner-share’ and ‘Free space’ structures act as both deep and shallow traps, reducing the electron concentration.\textsuperscript{359} The deep traps mainly result in the increase of subthreshold swing and indirectly increase the device operating voltage, while shallow traps contribute to the hysteresis in device performance.\textsuperscript{360–362} The ‘Edge/Face-sharing’ structure act as shallow donors, which is the main source of carriers in a-IGZO and thus vital for device charge transport.\textsuperscript{298,352,363,364}

Several methods have been proposed to control VO in a-IGZO, including modulating the growth atmosphere (oxygen partial pressure)\textsuperscript{165–167} and post deposition annealing.\textsuperscript{368,369} The metal–metal bonds are associated to VO, formed by the binding of uncoordinated metal ions caused by deficient oxygen to eliminate the dangling bonds.\textsuperscript{355} Additional sub-gap states are induced near CBM by metal–metal bonds and could significantly increase the off-state leakage current $I_{\text{off}}$.\textsuperscript{356,370,371} Reduction of metal–metal bonds generally follows the path with the decrease of VO, yet they are harder to eliminate for the additional energy required to break the bonds.\textsuperscript{357} The incorporation of hydrogen could happen during annealing processes or by diffusion of other materials in TFT devices, i.e., gate dielectrics, passivation layers or buffer layers.\textsuperscript{372–374} The role of hydrogen in a-IGZO varies under different H concentrations. At lower concentrations lower than $\sim 2 \times 10^{21}$ cm$^{-3}$, hydrogen improves the device performance by passivating O-related defects either through bonding with weakly bound oxygen to form $-\text{OH}$ or replacing the VO, thus reducing hysteresis and increasing carrier density.\textsuperscript{375–377} At higher concentrations above $2 \times 10^{21}$ cm$^{-3}$, additional hydrogen in a-IGZO might create a conductive channel near the dielectric interface that negatively shifts the
4. Summary and perspective

Recent progress in the growth of high-quality TMOs epitaxial thin films, together with exploration of new systems and with the application of different stimuli to tune the structures and defects within them, has led to intriguing new physical phenomena. These phenomena are limited not only to the bulk of the films but also to the heterointerfaces between the different materials. There is huge potential range of new applications stemming from these, influencing every sector of industry from transport to energy to ICT to medicine. In this review, we highlight some of the many fascinating physical properties, ranging from insulating to semiconducting or metallic, exhibiting phenomena from ferroelectricity to transparency. We show how the underlying physics relies on the control of electronic structure, which is determined by the partially occupied TM d orbitals, the hybridization between TM d and oxygen 2p orbitals and the corresponding local atomic structures. We also highlight the importance of defects to electronic structure and chemical structure, and show the benefits of precise defect engineering for enhancing physical properties. However, we also show how that the strong influence of defects in TMOs is something of a double-edged sword: certain defects being engineerable and critical for realizing a desired functionality, while others are detrimental to expected properties and hard to control. In this latter regard, there are still many challenges to be solved, some key ones being summarized as following:

(1) Unlike misfit dislocations, grain boundaries and domain walls, point defects formed by cation/oxygen vacancies and ionic doping (e.g., H⁺ and Li⁺) are ‘invisible’ because of their dilute concentrations. There is a huge demand for new techniques to be available that can allow us to observe cation/oxygen vacancies and ions at low concentrations and with large spatial accuracy. Therefore, new ways to directly and simply characterise these point defects and to quantify their presence are of utmost importance for understanding defect-structure-property relations in memristors, in wide bandgap oxide semiconductors, at functional heterointerfaces, etc. With such techniques, a new world will be opened up for TMOs science and applications.

(2) Defects, strain and interfaces are usually entangled for tuning the functionalities in TMOs thin films. Hence, great care must be taken to separate these parameters from one another so as to enable their individual influence on the physical properties to be understood. On the other hand, similar to the implementation of semiconductors in devices, an important question is how to achieve precise control of defect (or impurity) concentrations and distributions in TMOs thin films. This will be important as there is an increasing drive towards miniaturization of electronic circuits and devices based on TMOs thin films. Furthermore, to achieve novel functionalities which utilise defects, an important question is how to dynamically characterise/control/tune the distribution of defects. To fulfill these purposes, many characterisation techniques (e.g., photoemission spectroscopy, transmission electron microscopy, scanning tunneling microscopy, scanning probe microscopy, X-ray techniques) usually working under vacuum conditions and/or room temperature, need to be customized to work in controlled environments and high temperatures, thereby enabling characterisation under in situ or even in operando conditions to monitor the dynamics of defects. Also, combining in situ and in operando techniques and first-principles calculations will allow for increasingly accurate characterisation of defects, strain and interfaces, and undoubtedly will improve the understanding of their individual roles in TMO devices during operation. Further developments in synthesis/growth of TMOs thin films will allow greater control of dynamic ionic defect profiles. In turn, it may be possible to exploit the different mobilities of cations and anions to engineer gradients in static and dynamic chemistry and carrier concentrations.

(3) Electrochemical reactions and ionic transport underpin the functionality of memristors, wide bandgap oxide semiconductors and electrochemical water splitting. When the bias voltage is applied for driving ionic motion, the irreversible/reversible redistribution of defects in TMOs thin films may occur. Consequently, the stability of defects in TMOs thin films is a key problem for the irreversible fatigue/degeneration of electronics and catalysts and needs to be addressed. One approach is to investigate static and dynamic ionic behaviour which will help us to understand the interaction between ionic motion and defects. Further progress, in both experimental and theoretical methodology, will be key for exploring and controlling the stability of defects in TMOs thin films for electronics and energy applications.

Conflicts of interest

The authors declare no competing financial interests.

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