THIN FILM HETEROSTRUCTURES

Abstract

Complex thin film heterostructures of transition metal oxides exhibit an astonishing diversity of physical properties. Some of these properties are high dielectric permittivity, piezoelectric, pyroelectric, and ferroelectric behaviors. Moreover, this class of materials holds promise for even more extraordinary applications, such as exploiting high-temperature superconductivity and colossal magnetoresistance. Recent progress in deposition techniques has led to oxide heterostructures with structural quality comparable to top-tier conventional semiconductors, elevating oxide electronics to unprecedented heights. Through these heterostructures, researchers can create artificial multifunctional materials, revealing intriguing phenomena at the interfaces where compounds with distinct structural and electronic properties come together to form an interface and give a route to new emerging physics. This newfound understanding grants access to previously unexplored physics arising at oxide interfaces, presenting a wealth of exciting opportunities.

Keywords: Transition metal oxides, heterostructure, multiferroic, oxide interfaces.

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I. INTRODUCTION

In recent decades, the scientific community has been captivated by the rapidly developing field of spintronics, which offers excellent opportunities for basic and applied research. Spintronics processes and transmits data utilizing the electrons charge and spin degrees of freedom [1]. Despite having various reports in three-dimensional semiconductors and metals, spintronics has recently begun to rapidly approach the field of complex oxide heterostructures due to the potential for novel multifunctionalities at the interface due to the strong interaction between orbital, spin, charge, and structural degrees of freedom.

Transition Metal Oxides (TMOs) are a class of materials which exhibit an extensive variety of novel functional properties. TMOs have several essential properties that are relatively rare in semiconductors or conventional metals and alloys, and as a result, they are widely used in the development of new electronic devices. Some of them are: i) using complex oxides solves the problem of materials oxidizing in electrical devices [1], ii) novel quantum states can be achieved in complex oxides as a result of the entanglement of multiple degrees of freedom such as spin, orbital, lattice, and charge [2], and iii) since TMOs are ABO_3-type compounds, the oxygen octahedra play a central role in these type of compounds, leading to the novel magnetic and transport and electrochemical properties and iv) Oxides exhibit several interfacial advantages. When different multifunctional oxides are combined, many artificial modifications occur, leading to a significant change in the chemical and physical properties of the system, thereby offering the opportunity to explore spintronic and electronic devices of the next generation with high functionality [1,3, 4].

Due to advancements in thin film growth techniques such as pulsed laser deposition (PLD) and molecular beam epitaxy (MBE), the growth and control of heterostructure interfaces on an atomic scale are now achievable. In order to utilise these oxide heterostructures in next-generation spintronic-based devices, numerous efforts have been made to comprehend their unique interfacial properties. Among them are high Tc superconductivity in an oxide layer [5], a conducting interface between two broad band gap insulators [6], and a colossal magnetoresistance effect in a manganite layer [7], etc. Since the layers of heterostructures are stacked one on top of the other, symmetry breaking at the interface would be very apparent, which could result in changes to the electronic and structural properties. Matsuno *et al.* (2016) reported the presence of skyrmion phase in $SrRuO_3/SrIrO_3$ heterostructures owing to the presence of interfacial Dzyaloshinskii-Moriya interactions caused by the broken inversion symmetry [8]. When there is a significant lattice mismatch between the two layers in our heterostructures, epitaxial strain may be induced at the interface, influencing the electronic degrees of freedom at the interfaces. The manipulation of Berry curvature and anomalous Hall effect in correlated materials by epitaxial strain and magnetic anisotropy at the interface of $SrRuO_3$ thin films was reported by Tian *et al.* in 2021 [9].

Due to the electrostatic interactions at the interfaces, there may be electrostatic coupling between layers when polar materials are present at the interfaces. The spin reconstructions at the interface may cause further interface frustration, which may result in the formation of new electronic and structural phases. If the chemical potentials of two materials are distinct, charge transfer may occur at the interface. In the field of semiconductor heterostructures, this phenomenon has been extensively utilized in a broad range of devices (example: Schottky diode, p-n junction diode, and 2 D electron gas based on high-mobility transistor, etc.). The doping level at the interface is altered in complex oxides due to the charge distribution across the interface. Ohtomo*et al.* reported for the very first time in 2004 that an exceptionally mobile electron gas exists at the interface of two wide band gap insulators, $LaAlO_3$ and $SrTiO_3$. Due to the inherent polar discontinuity at the interface, LaO+ donates a half electron per two-dimensional unit cell at the interface, forming 2D electron gas at the interface [6]. The length scale is a crucial consideration at the interfaces. A phenomenon may originate at the interface but need not be confined to the interface [3].

II. OXIDE HETEROSTRUCTURES

1. **3d/3d Heterostructures:** Combining TMOs of 3d block with another element of the 3d block can lead to several interesting properties due to the interplay of their electronic, magnetic, and structural characteristics. J. Hoffman*et al.* reported that combining $LaNiO_3$ and $LaMnO_3$ layers in a heterostructure results in interesting phenomena like the interfacial charge transfer, which can modify the electronic structure and lead to enhanced catalytic properties which finds potential applications in fuel cells and other energy-related devices [10]. Another study by S. Panda*et al.* reports that combining $LaFeO_3$ and $LaNiO_3$ layers allows for tuning the magnetic and electronic properties at the interface which holds promise for spintronic applications [11]. Novel quantum phases have been reported at the interface of high-temperature superconductors $YBa_2Cu_3O_7$ and $La_{2-x}Sr_xCuO_4$ [12].

   These examples illustrate the vast potential of 3d/3d transition metal oxides heterostructures in designing new functionalities and novel electronic properties, making them a hotbed for research in condensed matter physics and materials science. As the field progresses, more complex and tailored heterostructures are likely to emerge with even more exciting properties and applications.

2. **3d/4d Heterostructures:** 3d-4d TMOs heterostructures involve combining materials from the 3d and 4d transition metal blocks to create composite materials with unique properties. These heterostructures offer a platform to explore interfacial effects, quantum confinement, and tailored electronic and magnetic behaviors, resulting in potential applications in electronics, spintronics, and catalysis. Combining $LaNiO_3$ and $LaRuO_3$ layers in a heterostructure can lead to a metal-insulator transition and interfacial magnetism. The differing electronic configurations of Ni (3d) and Ru (4d) ions influence the electronic structure and magnetic properties at the interface, making it an exciting system for exploring spintronics and magneto-transport phenomena [13]. Another example includes the stacking of $LaCaMnO_3$ and $SrRuO_3$ layers. Their combination can lead to interesting magnetic and electronic properties such as stabilizing of high-Tc ferromagnetic phase and the results pave a promising approach towards the effective control of interfacial magnetism and new designs of oxide-based heterostructure [14].

3. **3d/5d Heterostructures:** 3d-5d TMO heterostructures provide an exciting platform to study the interplay between different transition metal elements at the interface. Study reveals that stacking the MnO_2 (3d) and IrO_2 (5d) layers enhances the chiral magnetism at the interface which has potential applications in energy conversion devices [15]. Some of the charge transfer effects have been explored at the interfaces of $CaMnO_3$ (3d) with $CaIrO_3$ (4d) layers which finds potential applications in spintronic based devices [16]. Since the last decade researchers have been intensely involved in the study of the versatility and potential of 3d-4d TMO heterostructures in designing materials with unique properties and functionalities. By controlling the combination and thickness of the constituent layers, researchers can tune the electronic, magnetic, and catalytic properties for specific applications in nanotechnology and materials science.

4. **4d/5d Heterostructures:** Complex oxides containing 4d and 5d transition metal elements have recently become a popular topic in condensed matter physics due to the intricate interplay between electron correlation (U) and spin-orbit coupling (SOC). For 4d and 5d ions, the SOC term can be as large as 0.2–0.4 eV, which is of the same order or larger than a number of other parameters such as Hund's coupling, the amplitude of electron hopping, and crystal field splitting. Consequently, there are numerous spin-orbit entangled degrees of freedom, as well as significant nontrivial interactions between them, which depend on the chemical bonding, lattice geometry, and d-electron configuration. Consequently, a number of uncommon electronic phases arise, such as correlated topological semimetals and spin-orbit aided Mott insulators. [17].

   One of the primary objectives in the area of spintronics based applications is to modulate the spin orbit coupling (SOC), which relates electron motion and spin and is responsible for the fascinating magneto-transport characteristics of itinerant ferromagnets. Some of the prominent examples of such SOC based phenomena are observed when 4d $SrRuO_3$ and 5d IrO_2 are stacked together to form heterostructures. These phenomena include anomalous Hall effect, topological Hall effect (THE) and spin Hall magnetoresistance (SMR), etc. The origin of the hump-like feature in the resistivity loops of the SRO-based heterostructures have recently been attributed to the two-channel AHE and the magnetic skyrmions induced THE [18]. In addition, the magnitude difference of anisotropic magnetoresistance signals in $SrRuO_3$-based heterostructures have been ascribed to the SMR based phenomena which would have profound applications in transmitting data avoiding any loss due to Joule heating.

III. EMERGENT PHENOMENA AT THE INTERFACES

When complex oxides are brought together, various intriguing phenomena emerge at the interfaces as a result of charge transfer, orbital ordering, and other transformations. These intriguing properties may result from the diverse interfacial modifications caused by the complex entanglement of four degrees of freedom such as lattice, orbital, spin, and charge. Some of them are discussed as:

1. **Manipulation of Various Properties at the Interfaces:** Heterostructures incorporating perovskite manganites provide a fascinating demonstration of the diverse interfacial phenomena and their potential for precise manipulation of magnetism and electronic transport at the nanoscale in complex oxide materials. These structures offer a unique platform for generating novel magnetoelectric couplings, where charge transfer occurs upon depositing $LaMnO_3$ (LMO) on $SrMnO_3$ (SMO) or vice versa. This transfer leads to in-plane ferromagnetism with aligned spins (and potentially orbital ordering) at the interface. In addition to that, the electric dipole moment arises from SMO to LMO.

   The interface effectively breaks both the time-reversal and space-inversion symmetries, thus, enabling a magnetoelectric coupling (ME) between both the magnetization and polarization [19]. As per Rondinelli *et al.*, when a dielectric is interfaced with a spin-polarized metal, magnetoelectricity mediated by carriers can occur. An external electric field prompts the accumulation of spin-polarized charge, subsequently inducing a magnetic response [20]. A pivotal concept for comprehending and engineering these interfaces lies in the interplay or frustration between different physical parameters and mechanisms. In order to minimize these frustrations, materials repeatedly undergo significant changes, leading to the emergence of entirely new behaviors.

2. **Charge Transfer at Interfaces:** If the interface of the materials is not chemically abrupt then charge gradients as well as a non-uniform doping profile can occur. This results in differing electronic concentrations in the atomic planes of the layered compounds. In the case of high-temperature superconductors (HTSC), the critical transition temperature T_c is determined by the carrier density in the CuO_2 planes [21]. Polar discontinuities can also facilitate charge accumulation at interfaces. Based on this theory, the observation of the metallic state in the $LaAlO_3/SrTiO_3$ (LAO/STO) based heterostructures in 2004 [6] was interpreted. Both the substances (LAO and STO) are band insulators with bandgap of 5.6 eV and 3.2 eV, respectively, however, when thin film of LAO is deposited on the (001) oriented STO substrate in the controlled layer by layer manner, the interface will become metallic when the thickness of the film surpasses 3- unit cells.

   The LAO/STO interface and related systems represent a highly dynamic area of research. While fundamental questions concerning the source of carriers, their carrier density, the precise characteristics of the confining potential, and the influence of electronic correlations [22] are still unresolved, scientists are actively exploring potential applications and seeking methods to manipulate the captivating properties of this system.

IV. CONCLUSION

In recent times, significant advance in the oxide based thin film growth techniques has made it possible to create top-notch heterostructures comprising complex transition metal oxides, leading to a new frontier in exploring the captivating physics of phenomena emerging at the interfaces. In this chapter, we have made an effort to shed light on some of the novel properties exhibited by such interfaces, encompassing a wide spectrum from unconventional electronic transport and magnetism to intricate connections between structural instabilities and fundamental concepts of epitaxial strain, electrostatic coupling, charge transfer, symmetry breaking, and the competition and frustration between distinct phases and the order parameters that underlie the intricate physics of various phenomena emerges at the interface. Although the numerous examples provided showcase the enormous potential of oxide interfaces for the discovery of novel behaviors, one must always be mindful of the complexities inherent to these nanoscale systems.

This is an exciting period for the community of oxide materials since the searching for the various novel properties of oxides materials is no longer confined to the laboratory. Significant advancements in first-principles and model calculation techniques, as well as enhanced computational power, have enabled the discovery of the Higgs field. With advancements in theoretical capabilities, researchers now have unparalleled predictive abilities, enabling them to guide and offer real-time feedback to experimental endeavors. Numerous fascinating predictions, such as the possibility of HTSC in $LaNiO_3/LaAlO_3$ superlattices [23] and the existence of novel ME coupling at oxide interfaces, eagerly await experimental validation.

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