CARRIER DYNAMICS OF THE TWO-DIMENSIONAL ELECTRON GAS FORMED IN THE OXIDE HETEROSTRUCTURE

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Dedicated to my Pather,

Mother, and Beloved Siblings

Declaration

The work presented in this thesis has been carried out by me under the guidance of Prof. Suvankar Chakraverty at the Institute of Nano Science and Technology, Mohali. This work has not been submitted in part or in full for a degree, diploma a fellowship to any other university or institute. Whenever contributions of others are involved, every effort has been made to indicate this clearly, with due acknowledgment of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

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In my capacity as the supervisor of the candidate's Ph.D. thesis work, I certify that the above statements by the candidate are true to the best of my knowledge.

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Abstract

"The number of transistors on a microchip doubled about every year": Gordon Moore predicted about transistors in 1965- called "Moore's Law". However, semiconductor chips will very soon be reaching their limit and will be unable to hold any additional transistors, implying future innovations will require a replacement material. Transition metal oxides (TMOs) are one of the potential candidates to replace conventional semiconductor devices. Due to electron correlation, the TMO displays an array of functionalities. The electron correlation in TMO constrains the number of electrons at a given lattice site and induces local entanglement of charge, spin, and orbital degree of freedom. This entanglement gives rise to various emerging phenomena like metal-insulator transition, ferroelectricity, spin-orbit coupling, superconductivity, etc. By making a heterostructure of such TMOs we can manipulate these functionalities along with creating new ones. The finding of highly mobile two-dimensional electron gas (2DEG) at the interface of two wide gap insulators LaAlO₃- SrTiO₃ (LAO/STO) marked a significant advancement in the field of TMO interfaces. The origin of conductivity at such oxide interfaces is still a topic of debate. The polar catastrophe, oxygen vacancy, cation intermixing, and cation off-stoichiometry are among the many models put out to explain conductivity. In this thesis, we mainly tried to investigate the nature and the shape of the conducting channel at the interface of two insulating oxides namely LaVO₃ and SrTiO₃ along with the dynamics of these carriers. In the later part, we have presented an entirely new type of quantum oscillation in the resistivity arising from the non-trivial spin texture in the momentum space as a consequence of the strong spin-orbit coupling present in the conduction channel at the interface of LaVO₃ and KTaO₃.

The research on perovskite oxide thin films, interfaces, and super-lattices demands the need for the atomically flat surface of the substrate to realize high-quality epitaxial thin films and atomically well-defined interfaces. In this thesis, we report the time exposure and pH dependence of Buffered NH₄F-HF (BHF) etching as well as the concentration dependence of ACID (HCl+HNO3 in 3:1 ratio) etching of the STO substrate. This study was performed for different orientations [(001), (110), and (111)] of STO single crystals.

To study the depth profile of the conducting channel at the interface of two perovskite oxides, we have grown LaVO₃ (LVO) thin film on TiO_2 terminated STO substrate in (001) orientation. We

have proposed a scheme, that combines the photoluminescence and time-correlated single-photon counting with transport measurements of resistivity to unravel the carrier distribution, the shape of the quantum well, energy subbands, and Fermi surfaces of the conducting interface of LVO and STO. The measurements further show that the conductivity at the interface of LVO/STO is arising because of a polar catastrophe. Electronic parameters, such as the carrier density, and the mobility, estimated from the electrical measurements, are in remarkably good agreement with those extracted from the spectroscopy with theoretical modelling providing a bridge between the two sets of data analysis. A similar analysis has been done for the conducting interface of LVO and KTaO₃ (KTO). For both interfaces, the full-width half maxima of the depth of the conducting channel at the interface are estimated to be around 10 nm by using spectroscopy techniques of photoluminescence and time-correlated single-photon counting: suggesting a quasi-2-dimensional nature of the conducting electrons.

To unravel the shape of the Fermi surface and its evolution with an applied magnetic field of an interface having strong spin-orbit coupling we have done temperature-dependent magnetotransport measurements at the LVO/KTO interface. In a quantum material when a charge carrier undergoes adiabatic evolution on a closed path, it captures signatures of non-trivial features present either in real or momentum space. We have observed Shubnikov-de Haas oscillation at the conducting interface of LVO/KTO in both perpendicular and in-plane configurations (B \perp E and B//E). This indicates the 3D nature of the Fermi surface at the interface. The oscillations produce a non-linear Landau fan diagram. This oscillation carries the signature of zero-field susceptibility arising from the non-trivial spin texture in the momentum space. In addition, we have observed a surprising dependence on quantum mobility when the electric field (E) and magnetic field (B) are applied in the plane of the interface. Quantum mobility depends on the relative orientation of E and B. The quantum mobility in the B//E configurations may open up new directions in the field of quantum oscillation observed in systems with non-trivial electronic and magnetic textures in the momentum space.

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Chapter 1: Introduction

1.1 Introduction:

Herbert Kroemer in his Noble lecture quoted "*Often, it may be said that the interface is the device*". From this quote, he pointed out that in many devices the functionality is not generated by the bulk material but rather from its heterostructure (or physics of the interface playing the role). Some examples of heterostructures are p-n junctions, transistors, Schottky contacts, interfaces between SiO₂ and Si, and many more. The devices become more complicated over time; for example, in 2007 it was estimated that 10^{19} transistors might be produced on a single microchip. Deep knowledge of surface properties and interfacial physics is needed in device miniaturization. By making the interface we are altering the bulk properties by inducing crystal reconstruction, changing the bond between ions, creating the defects, and breaking the symmetries. All of this can lead to a shift in the band structure and electronic state at the interface, allowing for novel electronic phases. By taking advantage of these properties we can make better future-generation devices. All of the above-mentioned properties are explained using single-particle physics with no interaction between the charge carriers.

Oxide has emerged as a new material with an eclectic range of distinctive properties in recent decades. Unlike conventional semiconductors, they show high electron correlation which further gives rise to emergent properties like ferromagnetism, superconductivity, ferroelectricity, multiferroicity, and many more. These properties can easily be tuned by external stimuli. This shows that oxides can be one of the potential candidates to replace conventional semiconductors in future-generation devices. In this thesis, we present work on the heterostructures of transition metal oxides (TMOs). So what is so promising about TMO interfaces?

1.2 <u>The system: Transition metal oxide and their heterostructures:</u> 1.2.1 <u>Transition metal oxide:</u>

The primary objective for material scientists is to discover new exotic electronic phases in materials. Recently, attention has shifted towards engineered materials such as heterostructures or superlattices, which are formed by interleaving two or more structurally or chemically dissimilar materials. In the quest for novel materials, transition metal oxides (TMOs) present an ideal platform for investigating exotic properties resulting from electron correlation. Electron correlation refers to the phenomenon where the motion of one electron is influenced by its neighboring electrons, leading to intriguing many-body phenomena. This correlation profoundly impacts the optical, magnetic, and electronic properties, ranging from insulator to metal-insulator transitions and even superconductivity. By constraining the number of electrons within the lattice, electron correlation induces entanglement of spin, charge, and orbital degree of freedom [1-3]. These unique properties of TMOs can be controlled and manipulated by adjusting various parameters, including temperature, pressure, creating interfaces, and doping. Consequently, TMOs and their heterostructures have been the subject of extensive theoretical and experimental research for an extended period. In order to comprehend the fundamental properties of TMOs, it is crucial to understand the structure and symmetry of the order parameters. Figure 1.1 shows that the TMOs typically exhibit a perovskite structure with the chemical formula ABO₃, where A represents an alkaline earth metal, B stands for a transition metal, and O represents oxygen. The transition metal within the TMO is surrounded by six oxygen atoms, forming an octahedron. This octahedron creates a crystal field that interacts with the transition metal ion.



Figure 1.1: Perovskite structure with A, and B cations (blue and green color spheres, respectively), and O is oxygen (red sphere).

Consequently, the initially five-fold degenerate 3d orbitals split into three-fold degenerate t_{2g} orbitals (xy, yz, and zx) and two-fold degenerate e_g orbitals (x²-y² and 3z²-r²). The octahedron's sensitivity to external stimuli, such as temperature or pressure, allows for straightforward manipulation of TMO properties by perturbing the octahedral structure. This perturbation within the octahedron gives rise to numerous exotic phenomena, including ferroelectricity and piezoelectricity[4].

The crystal symmetry is predicted by Goldschmidt-tolerance factor t given as,

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)}$$
(1.1)

Where, R_A and R_B are A and B ion radii, respectively and R_O is the oxygen anion radius. For a perfect crystalline cubic structure, the tolerance factor should be equal to 1. The divergence of t from unity gives rise to distortion in the lattice structure, for example for t<1, the ionic radius of cation A is smaller than cation B, which results in a tilted octahedron. This reduces the symmetry of the crystal and orthorhombic and tetragonal structures are formed. The change in symmetry is the essence of phase transition. For example, in the case of the insulator, the breaking of the spatial inversion symmetry (I) gives rise to spontaneous polarization resulting in ferroelectricity, or pyroelectricity. Broken time-reversal symmetry (T) is associated with magnetism. The superconductivity or superfluidity comes from breaking the gauge symmetry (G) associated with the wave function phase. The interplay between these symmetries and the electronic degree of freedom creates novel properties which cannot be obtained in the single-particle system.

1.2.2 The oxide interface:

Creating heterostructures and superlattices offers a significant advantage in developing novel properties that are not present in individual materials and enables precise control over their functionalities. The study of these heterostructures holds crucial importance from both technological and fundamental perspectives. A groundbreaking discovery in this field was the identification of a highly mobile (~10,000 cm²/Vs) two-dimensional electron gas (2DEG) at the interface of two wide band gap insulators, LaAlO₃ (LAO) and SrTiO₃ (STO), which sparked remarkable progress[5]. STO possesses a band gap of 3.2 eV, while LAO exhibits a band gap of 5.6 eV. Astonishingly, a metallic interface emerges between these two insulators with such large band gaps! Several models have been proposed to explain this phenomenon, including polar catastrophe, oxygen vacancies, structural distortions, and cation intermixing. The origin of conductivity remains a subject of debate among researchers.

Remarkable findings have been reported for the LAO/STO (001) interface, particularly by Ohtomo and Hwang, which shed light on its intriguing properties [**Figure 1.2** (**a**) and (**b**)]. Firstly, only the interface with an AlO₂/LaO/TiO₂ layer arrangement exhibits conductivity, while the interface with

an $AlO_2/SrO/TiO_2$ arrangement behaves as an insulator. Secondly, the interface only becomes conducting after the deposition of a thin film of LAO comprising at least three unit cells. Lastly, the electronic properties of the interface also depend on the oxygen partial pressure utilized during the film deposition [**Figure 1.2** (**a**) and (**b**)].



Figure 1.2: Schematic of a) AlO₂/LaO/TiO₂ and b) AlO₂/SrO/TiO₂ layer arrangement for LAO/STO interface, c) the resistance vs temperature plot for different oxygen partial pressure, d) mobility vs temperature plot for different oxygen partial pressure.

The origin of conductivity explained by Ohtomo and Hwang is the polar catastrophe. **Figure 1.2 a) and b)** is clearly showing that the interface formed at low oxygen partial pressure has low sheet resistance and high mobility, respectively. This is because, at low oxygen pressure, there is a chance of creating oxygen vacancy in the system which further enhances the conductivity. But high oxygen vacancy can also destroy the two-dimensionality of the conducting channel. They also found the interface became conducting after a critical thickness that is 4 unit cell (u.c.) in the LAO/STO case. It is also shown by other groups as sheet resistance vs thickness of film[6]. After that several other interface were reported like LaVO₃(LVO)/STO[7], LVO/KTaO₃(KTO)[6], EuO/KTO[8], GdTiO₃(GTO)/STO[9], and many more. The critical thickness for the film is 4 u.c. for almost all the interfaces except GTO/STO, there is no such critical thickness. The 2DEG shows a plethora of emergent properties such as magnetism, ferroelectricity, quantum oscillations, superconductivity, the coexistence of magnetism and superconductivity, colossal magnetoresistance, high spin-orbit coupling, Edelstein and inverse Edelstein effect, Rashba spin-orbit coupling are few to say [6, 10-15].

Undoubtedly, STO serves as the workhorse of oxide electronics. Its close lattice constant to a wide range of perovskite oxides grants it the versatility to form epitaxial thin films and interfaces. However, recent research has shifted focus towards inducing a two-dimensional electron gas (2DEG) in more exotic parent materials. One potential candidate for this purpose is KTO, which stands out due to the presence of Ta, a 5d transition metal. The advantage of 5d transition metals lies in their substantial spin-orbit coupling, which gives rise to a multitude of exotic properties, including correlated topological insulators, spin-triplet superconductors, J=1/2 Mott insulators, and Rashba spin splitting. Consequently, 5d transition metals offer spintronic functionalities in conjunction with semiconductor properties, making them promising for future devices and technologies.

To realize practical applications, it is crucial to comprehend the interplay between quantum confinement, spin-orbit coupling, and electronic correlation. Notably, the charge carriers in KTO possess a mass nearly two orders of magnitude smaller than those in STO, indicating the potential for high mobility in devices fabricated from KTO. Furthermore, KTO exhibits a high degree of electron correlation, which further contributes to its diverse range of exotic functionalities[16, 17].

1.3 <u>Proposed models to explain the Origin of conductivity at the</u> <u>interface:</u>

In previous section we have introduced the heterostructure of TMO. In spite of all the exotic properties oxide heterostructure the origin of conductivity at the interface of two insulators is still a topic of debate. Various models have been proposed to explain the same are polar catastrophe/ electronic reconstruction, cation intermixing, structural distortion, and oxygen vacancy. In this section we have explained these models in detail.

1.3.1 Polar catastrophe or electronic reconstruction:

To understand the polar catastrophe first we should know that what polar and non-polar perovskite are. To make this clear we have taken the example of two perovskite materials first is the workhouse of oxide electronics $SrTiO_3$ and second is high dielectric constant insulator LaAlO₃. In the ABO₃ structure, oxygen has its valence -2 and for A and B, they exhibit valances like $A^{4+}B^{2+}$, $A^{3+}B^{3+}$, $A^{2+}B^{4+}$, and $A^{1+}B^{5+}$ such that the bulk remains neutral. For a perovskite structure, along <001> direction the alternating planes are AO and BO₂. Hence, in the case of $A^{2+}B^{4+}$ the alternating layers are neutral (example STO) however for other combinations the layers have charge (example LAO). The perovskite with neutral atomic layers is known as non-polar perovskite (STO) and the perovskite with charged layers is known as polar perovskite (LAO).

When we join such two different polarity materials the discontinuity arises at the interface. This discontinuity of polarity can create potential divergence at the interface, making the system unphysical. Let us take the example of STO and LAO, if we join these two perovskites there are two possible configurations of the atomic layer: AlO₂/LaO/TiO₂ or AlO₂/SrO/TiO₂. Unlike semiconductors with fixed ion valence, the complex oxides redistribution of ions is not the only option rather they can have mixed valence charge compensation. If the redistribution of charge costs lower energy than the redistribution of ions, in that case half of the electron (e/2) per unit cell is transferred to the interface. **Figure 1.3 a) and b)** is showing the interface before and after the electronic reconstruction.

The half of the electron makes the interface metallic and give rise to the conductivity. The model suggests that, a critical thickness of thin film is required to build up a sufficient electric field to change the valance of Ti ion. That critical thickness for LAO is 4 unit cell to make the LAO/STO interface conducting and is true for most of the other oxide interfaces like LaVO₃/STO, LaFeO₃/STO and so on. The polar catastrophe or the electronic reconstruction is the most accepted model because of experimental findings like the carrier density calculated from Hall measurements ~ 10^{14} cm⁻² which is very close to the predicted value that is ~ $3x10^{14}$ cm⁻².

From x-ray photoelectron spectroscopy (XPS) measurement also Ti⁴⁺ and Ti³⁺ peaks are observed for the interface confirming the mix valance of the titanium[18].

1.3.2 Oxygen Vacancy:

Although the polar catastrophe is the most widely accepted explanation, it has been noted that oxygen vacancy is also an origin of interface conductivity. The formation of oxygen vacancies in substrate and the thin film mainly occurs during thin film growth. PLD and MBE are the two main deposition techniques to fabricate the thin film and heterostructure of the TMOs. The detailed discussion about the PLD technique is given in **chapter 2** of this thesis.



Figure 1.3: Schematic of a) Before and b) After the electronic reconstruction at the interface of LAO and STO.

There are three basic factors that can produce oxygen vacancies during growth. First, the high temperature growth condition example in case of LAO/STO interface the growth temperature is 760 °C. This high temperature can produce oxygen vacancies in both the substrate and the thin film, resulting in conductivity at the interface. Second, the oxygen partial pressure during the deposition and cooling process. Fabrication of thin film in low oxygen pressure can cause oxygen vacancy in the interface. Third, the high energy ions, molecules, and electron generated in laser ablated plasma can cause oxygen vacancy in the substrate material. Oxygen vacancy due to high energy ions is mainly found in PLD-deposited interfaces. Another reason that can also cause

oxygen vacancy is the (Aluminum) Al, it has a very strong proclivity to attract oxygen, and even at 300 K may be one of the main reasons behind oxygen vacancy created in the interface. Oxygen vacancy introduces an intraband shallow donor level near the conduction band of the STO which is responsible for the conductivity[19]. Liu et al. have studied the role of oxygen vacancy in the LAO/STO (crystalline and amorphous) interface. According to their study in amorphous LAO/STO samples, the main origin of conductivity is oxygen vacancy. But in the case of crystalline samples, oxygen vacancy, and polar catastrophe are the reason for interface conductivity. To remove the oxygen vacancy annealing is done in the presence of oxygen after the deposition process. Sharma et. al reported that the oxygen off-stoichiometry can induce ferroelectricity in the LAO/STO interface[20]. Controlling and understanding the role of oxygen vacancy can be very useful in future device fabrications.

1.3.3 Structural Distortion:

One effective technique for creating and controlling novel capabilities is the fabrication of heterostructures and superlattices. Many physical parameters can be controlled by controlling the octahedral rotation. For example, the interface of PbTiO₃/SrTiO₃ where the structural coupling gives rise to stabilization of the improper ferroelectric phase allows the control of magnetism through controlling the octahedron rotation, magnetoelectricity, weak ferromagnetism, and so on[14, 21]. When we are joining the two structurally different materials/compounds the structural coupling occurs at the interface. In the case of LAO, the room temperature crystal structure is rhombohedral generally describe as pseudocubic having a lattice constant of 3.79 Å with a lattice angle of 90.087⁰[22]. According to reports, the critical thickness of the LAO thin film is ~3.8 nm to proportionate with the cubic STO crystal structure, LAO adjust the in-plane lattice parameter with the STO lattice constant 3.905 Å by octahedron rotation. From transmission electron microscopy (TEM) it has been shown that the octahedral rotation occurs upto 3 unit cells of the STO at the interface. This rotation give rise to the formation of ferroelectric dipole at the interface which further modified by cation intermixing[4, 5]. In 2011, Boschker et.al showed in their article that how the substrate surface (single termination in case of STO) orders the defect in thin film. They also demonstrated that not only the substrate crystal structure but film crystal structure also generate defects in the substrate material[23]. Structural distortion in the LAO/STO heterostructure can induce high piezoelectric response. This response is non-switchable saying that the ferroelectricity induced in the LAO/STO interface is not intrinsic. Structural distortion can affect the electronic properties of the interface. This structural distortion is crucial to study for better performance and controlled devices. By making distortion in the system we can control the charge carrier density which further can be used in advanced nanoscale devices[20].

1.3.4 Cation intermixing or Cation off-stoichiometry:

The fabrication of the heterostructure is crucial in designing devices with reproducible properties. For example, the controlled growth of III-V semiconductor heterostructures in the 1980-90s led to the invention of new novel devices and technologies. The TMOs and their interfaces are viable candidates for the next generation of materials replacing conventional semiconductors and their heterostructures. The properties of the interface are greatly dependent on the film composition. This field is not much explored, since we assume that the thin film growth in pulsed laser deposition system (PLD) is stoichiometric in nature. But a recent study of cation stoichiometry has reported in PLD-grown thin films like LVO[24], LAO[25, 26], SrRuO₃ (SRO)[27], BaTiO₃ (BTO)[28], PbTiO₃ (PTO), STO[29, 30], LaMnO₃ (LMO)[31], SrMnO₃ (SMO)[32], LaCrO₃ (LCO)[33]. The cation off-stoichiometry has proven to induce dramatic changes in the property of the system such as transport property[34], ferroelectricity[35] and so on. The laser energy/fluence is assumed to be a parameter in achieving cation stoichiometry by tweaking the threshold ablation energy of the cations present in the target material [24]. The study shows that the stoichiometric film deposition is exception from PLD systems. Breckenfeld et. al shown in their study that the stoichiometric films and La-rich films show the conventional results expected for two-dimensional electron gas system. The physics for these systems can be explained using electronic reconstruction. In case of La-deficient or Al-excess samples the conductivity is originating from cation off stoichiometry and the metallic nature might be coming from the substrate. For low oxygen partial pressure there is a crossover from off stoichiometry to oxygen deficiency, here the conductivity is substrate dependent[36]. In 2013 Sato et. al reported that by changing the laser parameters (such as spot area, laser fluence) we are actually disturbing the balance between atomic and electronic reconstruction. The cation off stoichiometry also changes the lattice parameter of the sample hence the transport and other interfacial properties [37]. The cation stoichiometry is the extrinsic effect and it is well known that the STO and LAO/STO (001) interface became conducting on extrinsic doping. Qiao et al. in 2013 shown that the off stoichiometry occurs mere

in PLD grown thin films than molecular beam epitaxy (MBE) system because of high energies of atoms and ions in laser ablated plasma[33]. In 2013 the nature communication report, shows that only LA-deficient/Al-rich samples can give rise to two dimensional electron gas (2DEG). The main origin of conductivity for such interface is polar catastrophe[38]. Defect and off stoichiometry in STO/substrate can also affect the interfacial properties in many ways. Defects in STO result in low performance devices, necessitating defect correction. Annealing is one method for reducing Ruddlesden-Popper-like defects that cause electron scattering and so limit charge mobility of the system[39]. It has also been pointed out that the B-site cationic defect is the primary source of magnetic ordering in complex oxides. Manipulation of magnetic ordering in the oxide interface has the potential to be extremely useful in future generation gadgets and technologies[40].

1.4 Origin of conductivity: Still debatable

Although different models have been suggested to explain the conductivity that arises at the interface none of them are fully accepted or explain all the physics behind the conductivity. In the case of LAO/STO heterostructure, there are two possible atomic layer arrangements: $AlO_2/LaO/TiO_2$ and $AlO_2/SrO/TiO_2$ as shown in **Figure 1.4**. The $AlO_2/LaO/TiO_2$ is n-type doped and $AlO_2/SrO/TiO_2$ is p-type doped.



Figure 1.4: Schematic of charge transfer in n- and p-type LAO/STO interface

Polar discontinuity arises at the interface of polar and nonpolar perovskite, to overcome this discontinuity $\frac{1}{2}$ of the electron transferred from the thin film to the interface. These electron forms mobile 2DEG at the interface which results in metallic nature. But conductivity is not observed in case of AlO₂/SrO/TiO₂ layer arrangement.

In the case of the $AlO_2/LaO/TiO_2$ layer arrangement, Ti is a transition metal that can exhibit multiple valances, but on the other hand, Sr cannot exhibit multiple valances hence the interface is insulating in nature. But conferring to the polar catastrophe model this should not be the case. The $AlO_2/LaO/TiO_2$ should have hole gas at the interface.

According to the model for a given interface one of the two materials should be polar in nature, while the other should be non-polar. This is fail to explain the conductivity of the polar-polar interfaces such as LVO/KTaO₃ (KTO), LAO/STO (110), and LAO/STO (111).

1.5 <u>Outlook of the Thesis:</u>

The central focus of this thesis is to investigate the dynamics of charge carriers at the interface of transition metal oxides (TMOs). To achieve this, we have chosen two different heterostructures with the same thin film but different substrate materials: LVO/STO and LVO/KTO. **Chapter 1** provides an overview of the advantages of TMOs and their potential applications in next-generation electronics. The possible mechanisms behind conductivity at the interface of insulators are also discussed.

Chapter 2 delves into the fabrication and characterization techniques employed to study the interface. These techniques include Pulsed Laser Deposition (PLD) for thin film growth, Atomic Force Microscopy (AFM) for surface characterization, Pulse-Probe technique and Time-Correlated Single Photon Counting (TCSPC) for carrier lifetime measurement, and the Physical Property Measurement System (PPMS) for transport measurement.

Chapter 3 focuses on the methods used to obtain a single-terminated substrate surface via chemical processes. We explain how the etching time and etchant concentration can impact the substrate surface. Through our chemical route, we successfully achieved single-terminated STO surfaces in all three orientations.

In **Chapter 4**, we investigate the formation of quantum wells at the LVO/STO interface using spectroscopy and transport measurements. Interestingly, the results from both measurement methods align with each other. We also calculate parameters such as quantum well depth, spatial carrier distribution, energy subbands, and wave function for the interface. Additionally, we explore the effects of changing the substrate material to obtain exotic properties. Moving from STO to KTO in this thesis, we take advantage of the 5d transition metal, which exhibits significant spin-orbit coupling and offers a range of functionalities. Similar measurements were carried out for the LVO/KTO system, yielding comparable results. We observe that most carriers are concentrated within an 11 nm range from the interface towards the bulk of KTO.

Chapter 5 focuses on the LVO/KTO sample, where we investigate the behavior of carrier density and mobility as a function of film thickness. We select a sample with a critical thickness (4 u.c. for LVO/KTO) for conductivity measurements. In the LVO/KTO interface, we study quantum oscillations and observe oscillations in all directions when a magnetic field is applied perpendicular or in-plane to the sample. This suggests a three-dimensional Fermi surface. The Landau fan diagram in our case is nonlinear and can only be explained by a modified version of Onsager's equation. The non-linearity in the fan diagram is attributed to the zero magnetic field susceptibility in the system, which arises from the non-trivial spin texture in momentum space.

Chapter 6 concludes the thesis by summarizing its findings and discussing the future prospects of these findings in next-generation electronics and smart materials.

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Chapter 2: Experimental Techniques for Growth and Characterization

The study of complex oxides is driven by advancements in growth and characterization techniques, which offer unprecedented access to explore new insights and functionalities of these materials. Two commonly used techniques for growing thin films and heterostructures of transition metal oxides are molecular beam epitaxy (MBE) and pulsed laser deposition (PLD) systems.

In MBE, individual elements are heated and deposited on the substrate material within a high vacuum environment. However, growing high-oxygen-pressure complex oxides poses a significant challenge in MBE. On the other hand, PLD enables the growth of oxides over a wide range of oxygen partial pressures, ranging from high vacuum to high oxygen partial pressure (e.g., 1000 mbar). This capability reduces the occurrence of oxygen vacancies, which are often observed in other deposition techniques. PLD ensures nearly stoichiometric deposition of the target material onto the substrate surface, making it advantageous for achieving stoichiometric removal of material from the target surface.

PLD initially gained attention in the scientific community during the 1960s when it was used to grow various semiconductor and dielectric materials, including complex oxides like SrTiO₃ (STO) and BaTiO₃ (BTO)[1, 2]. However, it gained significant recognition in the 1980s after its successful application in the growth of high-temperature superconductors (Y-Ba-Cu) by D. Dijkkamp and T. Venkatesan in 1987[3]. PLD utilizes an ultraviolet KrF excimer laser, typically operating at 248 nm with a pulse duration of 20-35 ns, to ablate the target material. As a result, PLD is an ideal technique for growing complex/multi-component materials with high melting points, such as ceramics and high-Tc cuprates[4, 5].

Simulations suggest that the optimal growth rate in PLD should be close to 1 Å per pulse. The slow growth rate provides better control over the layer-by-layer deposition of superlattices or thin films. Additionally, in situ, monitoring of layer-by-layer growth using techniques like reflection high energy diffraction (RHEED) enables thickness-controlled growth of thin films and

heterostructures within the PLD chamber. For a more comprehensive understanding of PLD, we recommend referring to the book by Eason[6].

This chapter will first discuss the fabrication technique, PLD, and then explore the characterization techniques used to monitor the properties at the interface and surface of the samples, primarily focusing on transition metal oxides and their heterostructures.

2.1 <u>Thin Film Fabrication:</u>

The thin films and their heterostructures are grown for this thesis work using the *mobile combilaser molecular beam epitaxy (MC-LMBE)* (PLD) technique. This is a simple thin film fabrication technique as shown in **Figure 2.1**. This high-performance laser MBE system has an ultimate high vacuum pressure of 10⁻⁹ torr, having the advantage of both conventional MBE and PLD, simultaneously, because the deposition is done using pulsed laser ablation in an ultra-high vacuum (UHV).



Figure 2.1: Schematic of pulsed laser deposition system.

The system is equipped with other things like a substrate heater, multiple target holder, rotator, pyrometer, Infrared (IR) laser source, reflection high energy electron diffraction (RHEED) gun, background processing gasses (such as O/Ar/He), and different gauges to monitor the pressure (ion gauge and thermocouple gauge for low- and high-pressure measurement, respectively) as shown in **Figure 2.1**[7].

The pressure inside the chamber is maintained by turbopumps followed by rotary pumps. Because of the exact control of heat input, time efficiency, and self-quenching process, an IR laser was employed for substrate heating. The temperature of the substrate is measured by the attached pyrometers (typically of 2 mm diameter). The additional benefit of using laser heating is that we can obtain a temperature gradient that helps in combinatorial temperature deposition (i.e., we can grow thin film at different substrate temperatures at the same time on a single substrate using this temperature gradient heating method).





Load-Lock Chamber



Plume formation during the deposition in the main Chamber

Figure 2.2: a) The real-time image of the pulsed laser deposition system in INST Mohali, b) showing the load-lock chamber image, and c) the plume formation during the deposition process.

This PLD system is also equipped with a load-lock chamber for easy transfer of substrates and targets using a transfer rod without breaking the vacuum of the main deposition chamber (shown in **Figure 2.2**). Inside the deposition chamber, there are two motor-driven masks of different sizes (long and short masks) that are suitable for combinatorial deposition and heteroepitaxial thin film growth. The system consists of high-performance RHEED without any special instrumentation. The intensity of oscillations is interpreted using an elastic model will be discussed in the next section. The target is ablated using a KrF excimer laser having a wavelength of 248 nm and pulse duration of 20 ns with a variable repetition rate (usually we use 2Hz to 5Hz). The material ablated by a laser pulse can be deposited into a thin film in a controlled manner. The target ablation using the external source-the laser, makes the instrument one of the versatile growth technique. In an

article published in Nature in 1985 by Kroto, Heath, O'Brien, Curl, and Smalley, they discovered a new phase of graphene by examining the product created during laser ablation of graphene. That new material was "Buckminsterfullerene" (C_{60}), which turn out to be the new frontier in the carbon nanomaterial family and led to the Nobel Prize in chemistry[8].

The major criticism about PLD is- the ejection of macroparticles due to thermal shock. In this next section, we try to understand the laser-material interaction.

2.1.1 Laser-material interaction:

The laser ablation depends on various factors like the laser properties, optical and thermodynamic properties of the target material. When the laser strikes the target material's surface, absorption occurs, converting the electromagnetic radiation into electronic excitation energy, which is then converted into thermal, chemical, and mechanical energy. This mechanical energy triggers the formation of plasma, excitation, exfoliation, and ablation. The plume shown in **Figure 2.2** consists of atoms, molecules, electrons, ions, clusters, and even micron-size particulates. The plume has a highly directed, dense shape that rapidly expands in the vacuum chamber to form a jet of material that is oriented normally towards the target. The nature of the plume limits the PLD to fabricate large-size wafers[9].

The ablation and plume formation takes place in a few tenths of a nanosecond. To understand the phenomenon of laser-material interaction, let's split the evolution of plume formation of material into different stages. First, the absorption of the (here, the KrF laser) laser by the target material, the absorption is defined as,

$$I = I_0 e^{-\alpha x} \tag{1}$$

Here, $1/\alpha$ is the absorption length, which is ~100 nm for most of the oxide materials (the wavelength of the laser is 248 nm). In this process the electrons are excited in higher states and thermalized. Second step is the conduction of heat into the bulk of the material and then melting of the target material. The thermal diffusion length is given as,

$$\lambda_{th} = 2(\alpha_{th}\Delta t)^{\frac{1}{2}} \tag{2}$$

Here, α_{th} is defined as the thermal diffusivity ($\alpha_{th} = K/\rho c$, where, K is the thermal diffusivity, ρ is the mass density, and c is the specific heat) and Δt is pulse duration. In this step, the temperature

of the surface of the target material increases for the evaporation process. In the next step, the actual vaporization of the target material occurs, in this step, multiphoton ionization of the gas phase generates the plasma. In this process, the temperature of the material surface exceeds its boiling point temperature. Finally, the excitation of plasma, here the further ionization excites the free electron results in Bremsstrahlung absorption in which the hot pulse, nearly 2000 K, expands in a well-directed manner[7].

What is the threshold energy density to generate the plume? Let's start with the comparison of $1/\alpha$ and diffusion length (λ_{th}). In general, for complex oxides, the diffusion length is longer than the absorption length, especially in the case of UV lasers. The laser-affected area is directly proportional to the diffusion length times spot size. By calculating the area we can calculate the minimum energy required for sublimation of the target material. The total energy required is the sum of energy needed to bring the target to its melting point, the energy needed to bring the material from the melting point to its boiling point, and vaporization energy. The typical energy density for a laser for 2 J/cm² fluence and 20 ns pulse duration is 10^8 W/cm², enough to ablate almost all the materials. The shape of the plume can define as a function of $\cos \theta$ and $\cos^n \theta$ with a range of n from 4 to 14. The $\cos \theta$ type distribution happens because of conventional thermal evaporation, which leads to nonstoichiometric deposition. Whereas, $\cos^n \theta$ is a sharply lobed distribution of evaporate. The plume species in this kind of distribution have thermal velocity near 10^4 m/s and ~40 eV kinetic energy. This large kinetic energy is the main advantage of the PLD technique, which helps in activating reactions like the dissociation of O₂[10].

Coming to the biggest detractor for the PLD system is the ablation of micro-sized solid particulates. "Splashing" is one of such effects, it occurs due to various reasons like low density of target or subsurface boiling. It happens when the time necessary to convert energy into heat is less than the time required to evaporate a surface layer with a thickness on the order of the skin depth. In that case the subsurface layer is superheated before the surface becomes vapor, and micron-sized molten globules can be ejected from the system[7, 10].

2.2 <u>Surface and Structural Characterization Techniques:</u>

Prior to any type of measurement, confirming the quality of the surface and structure of the samples is critical. The RHEED technique helps us in monitoring the real-time kinetics of thin film

deposition. The surface morphology analysis before and after deposition was carried out using atomic force microscopy (AFM). In this section, we will discuss these techniques in detail.

2.2.1 <u>Reflection High Energy Refraction (RHEED):</u>

To achieve atomically perfect and epitaxial heterostructure of complex oxides, a layer-by-layer (also known as Frank-Van der Merwe growth) is highly desired. In layer-by-layer growth mode, first, the atoms grow in two dimensions to cover the substrate surface, then the subsequent layers grow, this provides full coverage of atomically arranged thin film deposition. The main criteria to obtain layer-by-layer growth is that the free energy of the thin film surface and the interface should be equal to the substrate surface, hence it requires well optimizations of parameters like substrate temperature, partial pressure of background gas, fluence of laser, and distance between the target and the substrate[11].



Figure 2.3: RHEED set up include an electron gun, sample, and fluorescent screen

The PLD equipped with the RHEED gun which is also known as laser-MBE has become one of the most commonly used techniques to grow high-quality thin film and heterostructures. The RHEED gun is used to monitor the *in-situ* real-time kinetics of thin film growth. **Figure 2.3 a)** is showing the basic working principle of the RHHED gun. A high-energy electron gun (typically 8-50 keV and voltage 30 kV max) is incident at a very small angle on the substrate surface (normally less than 3⁰). The low glancing angle makes the instrument surface sensitive, because at this angle the electrons only interact with the few topmost atomic planes of the sample. The elastically scattered electrons are captured by a phosphorescent screen behind the sample to create the diffraction pattern, which contains information about the surface morphology as shown in **Figure 2.3 b**). The diffraction characteristic in reciprocal space often exhibits infinite rods perpendicular to the surface arising from the 2D periodic lattice points at the surface in real space for the atomically precise terminated samples. When the Ewald sphere intersects these rods constructively, we see the Ewald construction as spots on the screen. As soon as the thin film starts

depositing over the substrate surface the intensity of the electron beam starts decreasing due to scattering of electrons. The scattering occurs due to the increased roughness at the sample surface.



Figure 2.4: Elastic scattering model of RHEED intensity oscillation in 2-dimensional epitaxial growth.

However, the intensity of the electron beam starts increasing with the coverage of the sample surface and reaches its initial value when one full atomic layer is deposited over the substrate surface. **Figure 2.4** is showing how the intensity of electrons decreases and increases with the coverage of film material over the substrate surface. This increasing and decreasing intensity of the electron beam gives a temporal change in the brightness of the specular spot, hence the oscillation. By counting the oscillations we can calculate the number of layers deposited on the substrate surface. This gives us precise control over the thickness of the thin film[11, 12]. Due to its easy installation in any vacuum system, RHEED became not only important in research but also used in device fabrication for industries as well.

2.2.2 Atomic Force Microscopy:

The AFM was used to analyze the surface morphology of the substrate surface before and after the thin film deposition. We have used Bruker Multimode-8 Atomic Force Microscopy (AFM) in tapping mode to see the topography and roughness of the sample at room temperature in ambient

conditions. The SiN tips having a force constant of 40 N/m were used for both tapping and contact mode AFM.



Figure 2.5: Schematic of lateral force microscopy.

For the compositional study, we used Lateral Force Microscopy (LFM). For topographical information, LFM records the vertical deflection and for the frictional force information, it monitors the torsion in the cantilever in the lateral direction. The torsion magnitude is depending on the frictional coefficient between the AFM tip and the sample, scan direction, surface topography, and the cantilever's lateral spring constant. LFM measures displacement in both lateral and vertical directions simultaneously for topographical and frictional image recording. For that, it uses a photo-sensitive photo-detector with a quad-cell (or four domains) in general topographical imaging AFM only used "bi-cell". As shown in **Figure 2.5 a**), the signal difference between upper cells and lower cells will give the topographical image.

Topographical image = (a+c)-(b+d)

Similarly, the frictional image is given by the difference between the left cells and the right cells,

Frictional image = (a+b)-(c+d)[13]

2.3 Optical measurements:

2.3.1 <u>Photoluminescence spectroscopy:</u>

For photoluminescence (PL) measurement, we used the optical spectroscopy. PL spectroscopy is an analytical technique used to measure emission and excitation spectra, and luminescence lifetime. In this technique, the sample is excited using high-energy photons (usually higher than the band gap energy of the sample), and the excess energy is released from the sample in the form of light which is monitored in different modes such as excitation. Emission, and luminescence decay lifetime.



Figure 2.6: Jablonski diagram shows the possible relaxation processes in a molecule after the molecule has absorbed a photon.

Working principle: In PL spectroscopy, the molecule of the sample is first excited (by absorbing the incident photon having energy higher than the band gap of the sample species) from its ground/equilibrium state to one of the vibrational energy states in the excited electronic state. The collisions in the vibrational levels trigger the molecule to lose its energy and drop to the lowest vibrational level of the excited electronic state. The molecule then drops to the vibrational level of the ground state/equilibrium state by emitting photons. The molecule drops in different vibrational states and emits different energy photons. To understand this process people use the Jablonski diagram as shown in **Figure 2.6**. The PL spectra are sensitive to many factors like temperature, pressure, pH, polarity, viscosity, hydrogen bonds, and so on [14-16].

2.3.2 <u>Photoluminescence lifetime measurement:</u>

The common and well-established technique to measure the luminescence lifetime is timecorrelated single photon counting (TCSPC). It also became useful in some other optical measurements like photon migration measurement, time of flight measurement, and so on.



Figure 2.7: Schematic of TCSPC-fast stopwatch with two inputs.

The working principle of the TCSPC is the detection of single photons and the measurement of their arrival time with respect to the reference light source. It is a statistical measurement method that requires a highly repetitive light source to collect enough photon events for the required precision of the data. It can be compared with a fast stop watch with two inputs, the clock starts with the START signal pulse and stops with the STOP signal pulse. The time measured for one START-STOP sequence will be represented as one data point on the histogram. For a highly repetitive light source millions of data points are collected for a short period of time. The resulting histogram data will give the PL intensity vs time graph. For correct data collection, it should be ensured that not more than one photon is counted for a single flash of light. For that reason, the photon rate is kept low in comparison to the rate of the excitation lamp (usually <2%)[17, 18].

2.4 Electrical and Magnetic transport measurement:

The electrical and magnetic transport properties were measured using a physical property measurement system (PPMS, from Quantum design, ± 14 T). Figure 2.8, shows the real-time image of the physical property measurement instrument in INST Mohali. The electrical contacts for measurement were made by wire bonder from West Bond, with Al wire of diameter 0.5 μ m.

For I-V characteristics of the sample give the nature of contact e.g., a straight line depicts ohmic contact. The temperature and magnetic range of the measurement is 1.8 K to 400 K and +14 T to -14 T, respectively.



Figure 2.8: Physical property measurement instrument at INST Mohali

The electrical transport option (ETO) module and VSM module are used for both electrical and magnetic transport measurements, respectively. The carrier density and mobility of the samples were calculated from the Hall measurement. The angle-dependent measurement (varying the angle between the magnetic field and the sample surface) was done using a horizontal rotator.

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Chapter 3: Realization of Atomically Flat Single-Terminated SrTiO₃ single crystal in different crystallographic orientations

3.1 Introduction:

In this chapter, we have presented a protocol for obtaining atomically flat, single-terminated $SrTiO_3$ (STO) substrates in three orientations: <001>, <110>, and <111>, using the chemical etching method. Over the last few decades, transition metal oxides (TMOs) have garnered significant attention among researchers due to their wide range of properties in condensed matter and material sciences. These materials exhibit diverse functionalities, including metal-insulator transitions and superconductivity.

In 2004, Ohtomo and Hwang demonstrated the discovery of a two-dimensional electron gas (2DEG) at the interface of two large band gap insulators, LaAlO₃ and SrTiO₃. Their study highlighted how the carrier density decreases with the insertion of a SrO layer prior to the deposition of LAO. Nakagawa et al. further explored the importance of substrate surface termination in 2006[1]. SrTiO₃ (STO) is a noble transition metal oxide with a large dielectric constant[2], quantum paraelectricity[3], and a simple cubic structure with a lattice parameter of 3.905 Å. It is widely used as a substrate for creating heterostructures and fabricating thin films [4-6].

The chemical formula of perovskite oxide is ABO₃, where A represents the rare earth metal, B represents the transition metal, and O represents oxygen. In the <001> direction, perovskite is stacked with alternating atomic layers of AO and BO₂, where O has a valence of -2. The cations A and B can have valences of $A^{+1}B^{+5}$, $A^{+2}B^{+4}$, $A^{+3}B^{+3}$, or $A^{+4}B^{+2}$, ensuring the bulk remains electrically neutral. A polar discontinuity arises at the interface when perovskites of different charge families are connected. For example, in the case of the LAO/STO interface, STO in the (001) direction consists of alternating atomic layers of $Sr^{+2}O^{-2}$ and $Ti^{+4}O_2^{-4}$, while in LAO, the layers are La⁺³O⁻² and Al⁺³O₂⁻⁴. This results in two possibilities: TiO₂/LaO/AlO₂ and

SrO/AlO₂/LaO. The interface is conductive only in the first case, highlighting the significance of the surface termination of the substrate material.

Achieving an atomically flat, single-terminated substrate surface is a critical requirement for epitaxial heterostructure formation with atomic control in transition metal oxides. The topmost layer of the oxide surface significantly influences the properties of the thin film and the resulting heterostructure [4, 7, 8]. For the interface to be conductive, STO needs to be TiO₂ terminated.

In addition to the STO (001) orientation, interfaces based on STO (110) and STO (111) orientations have exhibited intriguing properties such as high mobility and superconductivity[9-12]. Unlike STO (001), STO (110) and (111) have high surface energy, making it challenging to achieve single-terminated surfaces. Therefore, these orientations require different surface treatments under specific conditions [13]. Reports are available for surface termination for all orientations for STO[13, 14].

3.2 <u>Realization of the atomically flat single terminated surface of</u> <u>SrTiO₃ (001), (110), and (111) substrate by chemical etching:</u>

In this section, we will explain the structure and lattice parameter of STO in all three orientations (that are <001>, <110>, and <111>). After explaining the STO structure, we will discuss the different chemical etchants used in this thesis work to get a single terminated step-terrace-like structure.

3.2.1 <u>SrTiO₃ in <001>, <110>, and <111>:</u>

STO has been the most studied perovskite material because of its unique properties like quantum paraelectricity, cubic perovskite structure, high dielectric constant[15, 16], and many more. It has been the best choice for substrate material for thin film and heterostructure fabrication due to its lattice parameter (3.905 Å), which is very close to many perovskite oxides. The crystal structure of simple cubic STO is shown in **Figure 3.1** (left panel). The right panel of **Figure 3.1** is

representing the atomic layers of STO in different orientations. The interplanar distance for STO (001), (110), and (111) are 3.905 Å, 2.76 Å, and 2.25 Å, respectively[14].

3.2.2 <u>Chemical etchant:</u>

These are mainly divided into two major categories 1.) Deionized (DI) water etching and 2.) Chemical etching (also known as wet etching). Chemical etching is done using different etching agents, some of them are HCL+NH₄Cl, HCl+HNO₃, Buffered NH₄F-HF (BHF), and so on. After etching, the surface morphology is confirmed by various characterization techniques like atomic for AFM, ion scattering, and photoelectron scattering.



Figure 3.1: (Left panel) the crystal structure of the STO (001) unit cell, where Sr is at the corners of the unit cell and Ti lies at the center of the cube. Each Titanium atom is surrounded by 6 oxygen atoms. The right panel is representing the stacking of the atomic layers of STO in a different orientation. The distance between two atomic layers is 3.905 Å, 2.76 Å, and 2.25 Å in (001), (110), and (111) orientations, respectively.

In this thesis, we have used AFM to characterize the surface morphology of the STO (001), (110), and (111) substrates and realized single terminated step-and terrace formation at the surface of STO (001), (110), and (111) single crystals by thermal treatment followed by chemical etching method. In the chemical etching method, we have used the BHF etching and ACID etching (HCL+HNO₃ in *3*:*1*). The concentration or pH value of the etchant and etching timing are the two main parameters that affect the termination and morphology of the substrate surface.

We have varied both parameters to optimize the step-terrace structure formation (or removal of SrO particles) on the surface of STO single crystal.

3.2.3 The flow chart to get the single terminated STO in different orientations:

The crystal structure and morphology of the substrate depend on the polishing method used. Generally, there is corrugation of up to 2 unit cells present in the non-terminated substrates. Mechanical polishing led to defects on an atomic level. The defect-induced surface with impurities like carbon and organic compounds affects the interface and hence the interfacial properties. In **Figure 3.2** we have shown the flow chart to get the single terminated step-like structure on the STO surface. In commercially available STO substrate the surface is mixed terminated as shown in **Figure 3.2 a**). To achieve desired surface morphology, we took one side mechanically polished mixed-terminated commercially available 10×10 mm STO single crystal.



Figure 3.2: The flow chart to get a step-terrace-like structure for STO substrate. a) Represents the mixed terminated surface of the commercially purchased STO substrate. b) The heating geometry. c) The agglomerated SrO particles on the STO surface after high-temperature annealing. d) The STO surface after chemical etching. e) The clean step-like structure on the STO surface after annealing the etched substrate.

Firstly, we cleaned the as-received STO substrates with acetone and ethanol each, respectively, for 10 min in an ultrasonic bath, to remove the hard metal and unwanted particles present on the surface. We anneal the cleaned substrate at a high temperature (>900^oC) in the geometry shown in **Figure 3.2 b**), where two STO substrates are placed over one another facing the shiny surface to reduce the chances of oxygen vacancy. The annealed substrate has agglomerated SrO particles on the surface as shown in **Figure 3.2 c**). The SrO particles are then removed by the chemical etchants we have described in the previous section to get a clean single terminated surface (**Figure 3.2 d**)). The etched STO samples are then again annealed for recrystallization. **Figure 3.2 e**) is showing the final step terrace-like structure obtained for the STO surface.

3.3 <u>Results and Discussion:</u>

To study the surface morphology, we have taken the surface image of as-received STO single crystals using tapping mode AFM. The surface contained mixed termination of atomic layers, nonpolar SrO and TiO₂ in case of STO (001), SrTiO₄⁺ and O₂⁴⁻ polar layers for STO (110), and STO (111) is stacked as SrO_3^{4-} and Ti^{4+} polar atomic layers[14]. The schematic of the as-received substrate is shown in Figure 3.3 a) left panel, the dark and light blue colors are defining two different atomic layers. Figure 3.3 (b), (c), (d) (left panel) is representing the AFM of the asreceived STO (001), (110), and (111). The roughness of the sample suggests the presence of small corrugation at the surface due to the presence of mixed atomic layers. This roughness or corrugation is not suitable for thin film deposition, to improve the surface quality, hightemperature annealing in an oxygen environment was done followed by chemical etching. We have annealed the substrates at different temperatures, the optimized annealing temperatures are 950°C for 4hours, 900°C for 2 hours, and 1000°C for 2 hours for STO (001), (110), and (111), respectively. The substrates with different orientations have different surface energy, thus, requiring different annealing temperatures. The heating at a high temperature increased the kinetic energy of the atoms, hence the agglomeration of the particles took place at the surface, as shown in Figure 3.3 a) right panel. The right panel (Figure 3.3 a)) shows the schematic of the surface of annealed STO substrate. The right panel of Figure 3.3 (b), (c), and (d) is representing the AFM image of annealed STO (001), (110), and (111) substrate in which the particles were agglomerated on the STO surface.

In 1994, Kawasaki et. al. [17] demonstrated a chemical (using BHF) route of etching to achieve a single terminated substrate surface. The best step termination achieved in their case was at pH \sim 4.5, but the surface contains etch pits. They assumed the polishing and crystal defects are responsible for the formation of the pits.



Figure 3.3: a) (Left panel) the schematic of the as-received mixed terminated STO substrate, (right panel) the schematic of the annealed substrate. b) (Left panel) AFM image of as-received STO (001) substrate having roughness 0. 242 nm, (right panel) AFM image of annealed STO (001) showing agglomerated SrO particles. c) (Left panel) The AFM image of as-received STO (110) substrate having a roughness of 0.125 nm, (right panel) AFM image of annealed STO (110). d) (Left panel) The AFM image of as-received STO (111) substrate having a roughness of 0.102 nm, (right panel) AFM image of annealed STO (112) nm, (right panel) AFM image of annealed STO (110). d) (Left panel) AFM image of annealed STO (111).

The work is followed by Koster et. al., Hallsteinsen et. al., where they obtained the single terminated STO (001), and (111) substrate, respectively by firstly formation of Sr-hydroxide complex followed by BHF treatment[18, 19]. The method helps to remove etch pits formed in former case. The pit formation deteriorates the thin film quality and also degrades the properties. In 2012 Wang et al reported the single termination of STO (110) using molecular beam epitaxy with minimum deviation from cation-stoichiometry of < 0.5% [20]. In this work, we have studied the etching of the STO surface using BHF and ACID by varying the pH value and time of etching.

3.3.1 BHF etching:



Figure 3.4: a-b) The STO (001) surface after etching with 1% and 2% BHF solution, respectively. e) The upper panel shows the schematic of the step-terrace structure on the STO surface, and the lower panel represents the height profile of the 2% BHF etched STO (001) surface. c-d) The STO (001) surface after etching with 3% and 4% BHF solution, respectively. Similarly, f-i) The STO (110) surface after etching with 1%, 2%, 3% and 4% respectively, j) upper panel represented the schematic of the step-terrace structure on the STO surface, the lower panel presents the height profile of STO (110). (k-n) The STO (111) surface after etching with 1%, 2%, 3% and 4% respectively, o) upper panel represented the schematic of the step-terrace structure on the STO surface after etching with 1%, 2%, 3% and 4% respectively, o) upper panel represented the schematic of the step-terrace structure on the STO (111).

To make a BHF solution, 4g of NH₄HF₂ (powder, Fisher Scientific, NH₄HF₂ = 57.04) was taken into a glass beaker and mixed with 6ml of deionized (DI) water to make a 40% solution. A clear solution was obtained by heating the mixed solution at 60° C using a magnetic stirrer for 30 minutes to 1 hour. The above solution was transferred to the Teflon beaker in a warm state only otherwise, the solution start forming crystals of NH₄HF₂. To obtain BHF solution 1 ml of HF (about 40% HF, Fisher Scientific, HF=20.01) was added to the 40% NH₄HF₂ solution. The pH of obtained BHF solution can be varied by diluting it with DI water. We added 1 ml of BHF solution to 99 ml of DI water to obtain 1% BHF solution and the pH value was measured. Using the same technique, we prepared different concentrations of BHF solutions varying from 2%, 3%, 4%, and so on, thus, having different pH values.

The pH value and the etching time are the main parameters that control the surface morphology and stoichiometry of the substrate. The substrate was rinsed with DI water after etching and then dried using nitrogen gas. **Figure 3.4 a**) was showing the AFM image of the STO substrate after being etched with 1% BHF solution. In our case, the best step-terrace structure is observed for a pH value of ~ 3.30 (2% BHF solution) as shown in **Figure 3.4 b**). The upper panel of **Figure 3.4 e**) is the schematic figure for step-terrace-like structure formation on the STO surface after etching, and the lower panel of **Figure 3.4 e**) represents the height profile of the 2% etched substrate. The height profile shows that the steps formed have an average height of 0.398 nm which is very close to the lattice parameter of the STO (001) (0.3905°A) single crystal. If we increase the pH of the solution, the formation of the pit starts at higher pH values as seen in **Figure 3.4 c-d**). When the pH of the BHF solution is increased, there is an increase in the roughness of the surface. The pit formation starts on the surface when etched with a high concentration (3% and 4%) of BHF solution deteriorating the substrate as shown in Figure 3.4 d). A similar result was shown for STO (110) (middle panel of Figure 3.4 (Figure 3.4 (f-j))), and STO (111) (Lower panel of Figure 3.4 (Figure 3.4 (k-o))). As BHF is a highly reactive chemical, a high concentration of the BHF in the solution damages the surface of the STO single crystal, and hence the pits are formed. To optimize the etching time for BHF treatment, we performed etching at a different time at the same pH value. For the 2% solution (\sim 3.30), we had done an etching at different times for all orientations of the STO substrate. In Figure 3.5, we have shown the selective time AFM images for STO (001), (110), and (111), respectively. The best step-like structure was obtained for 30sec, 40sec, and 60sec etching times for STO (001), (110), and (111), respectively as shown in Figure 3.5 (a, c, and e). The different etching time for different orientation indicates the different surface relaxation energy of crystal in different crystallographic axis. The surface relaxation energy (-1.66 eV) for Titerminated STO (111) is five times larger than the SrO₃ terminated surface (-0.35 eV), similarly for STO (110) the surface relaxation energy for Ti terminated surface is -5.78 eV which is larger than the Sr-terminated layer (-0.86)[21, 22]. From the AFM images (Figure 3.5 (b), (d), (f)), we observed that as we increase the etching time the reaction time increases with the substrate surface. For higher etching time the steps started deforming (stacking of multiple steps) and there was a commencement of pit formation observed at the substrate surface.

Figure 3.5 (f) represents the stacking of steps for STO (111) for 90 sec of etching time with a roughness of ~0.408 nm. The best etching time and pH value for step-terrace-like structure formation on STO (001), (110), and (111) substrate surface by BHF is 30 sec, 40 sec, and 60 sec with 3.30 pH value, respectively.

3.3.2 ACID etching:

For ACID etching we have prepared a solution by adding HCL (fuming 37%, Merck) to HNO₃ (69%, Merck) in a 3:1 ratio. The solution was diluted using DI water. We used the following three concentrations to etch the STO (001) substrate, 5%, 50%, and 100%. For 5% ACID solution, 5ml of ACID was mixed with 95ml of DI water, and similarly for 50% and 100% solution. From **Figure 3.6** (a), we observed that for 5% ACID solution, the SrO particles remained on the surface of the STO (001) substrate. Hence, we increased the concentration of the solution from 5% to 50%, for

the 50% solution there were still some particles that remained on the surface of the STO (001) substrate, as shown in **Figure 3.6** (b).



Figure 3.5: (Upper panel) a-b) the time-dependent etching of the STO (001) surface for 30 sec and 60 sec, respectively. (Middle panel) c-d) the time-dependent etching of STO (110) surface for 40 sec and 60 sec, respectively. (Lower panel) e-f) the time-dependent etching of STO (111) surface for 60 sec and 90 sec, respectively.

The best step-terrace-like structure was obtained for 100% ACID solution with a 10 min etching time (**Figure 3.6** (c)). **Figure 3.6** (d) is representing the height profile of the step-terminated STO (001) surface shown in **Figure 3.6** (c). From the height profile, we can observe that an average

height of ~0.4 nm step-terrace-like structure is obtained for STO (001) substrate. The height of the step is close to the lattice constant of the STO crystal. Similar results were obtained for both STO (110) and (111) (**Figure 3.6 (g-i)** for STO (110) and **Figure 3.6 (m-r**) for STO (111)).



Figure 3.6: (Left panel) a-c) The STO (001) surface after etching with 5% and 50%, and 100% ACID solution, respectively. d) Represents the height profile of the 100% ACID etched STO (001) surface. e-f) The STO (001) surface after etching with 100% ACID solution with etching time 10min and 20min, respectively. (Middle panel) g-i) The STO (110) surface after etching with 5% and 50%, and 100% ACID solution, respectively. j) Represents the height profile of the 100% ACID etched STO (110) surface. k-l) The STO (110) surface after etching with 100% ACID solution with etching time 10min and 20min, respectively. (Right panel) m-o) The STO (111) surface after etching with 5% and 50%, and 100% ACID solution, respectively. p) Represents the height profile of the 100% ACID surface after etching with 5% and 50%, and 100% ACID solution, respectively. p) Represents the height profile of the 100% ACID etched STO (001) surface. q-r) The STO (001) surface after etching with 100% ACID solution with etching time 10min and 20min, respectively.

We have also studied the effect of etching time on the morphology of the substrate surface. In the time-dependent study (**Figure 3.6 (e-f), (k-l), (q-r**)), we observed that as we increase the etching

time, the steps start deteriorating, and also the increase in roughness was observed, hence no longer a smooth surface. From this, we conclude that for our sample both ACID and BHF etching are most efficient at 100% and 2% concentration with an etching time of 10 min and 30 sec, respectively.

We have also done Lateral Force microscopy (LFM) measurements to confirm the surface termination of STO substrates.



Figure 3.7: LFM image and LFM line profile of STO (001) after ACID a), and BHF etching b). The inset is showing the height profile of the corresponding.

Figure 3.7 a) and b) is showing the LFM images and LFM line profile of the STO (001) substrate after ACID and BHF etching. The uniform frictional response in LFM topography implies single termination of STO substrates. The inset of **Figure 3.7 a) and b)** is showing the height image of the corresponding LFM images. **Figure 3. 8** is the summary showing all summarized results obtained for both BHF and ACID treatment. From **Figure 3. 8 a)** we can see the roughness is

lowest for 2% concentration BHF etched substrate, similarly for ACID etching the roughness is lowest for 100% (**Figure 3. 8 b**)).



Figure 3. 8: Roughness of Substrate surface as a function of concentration for BHF etching a), and ACID etching b).

3.4 <u>Conclusions:</u>

In conclusion, we have successfully optimized the concentration of the BHF solution and etching time to achieve a step-terrace-like structure on the STO substrate. The optimal pH for etching was found to be 3.30 for a 2% BHF solution. Solutions with higher pH values resulted in the formation of pits on the surface. The formation of step-terrace structures also depended on the etching time, with durations of 30 seconds, 40 seconds, and 60 seconds for STO (001), (110), and (111) orientations, respectively, in the BHF solution.

We also explored the ACID etching method, finding that the best concentration was 100% with a 10-minute etching time. By comparing the results of both etchant treatments, we can conclude that

BHF etching offers more controlled and superior surface treatment compared to ACID treatment. The pH control in BHF etching is much easier, while ACID treatment lacks reproducibility due to uncontrolled pH values.

These optimization techniques are not limited to STO alone and can be extended to other perovskite oxides. It would be particularly interesting to conduct similar studies on the newly emerging oxide material, "KTaO3"[8].

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Chapter 4: Probing conducting interfaces by combined Photoluminescence and Transport measurements

4.1 Introduction:

In this chapter, we delve into the study of carrier dynamics at the LVO/STO interface using both transport and spectroscopy measurements. Our investigation encompasses the calculation of carrier density, spatial distribution, energy subbands, eigenfunctions, and potential-well depth. Remarkably, the results obtained from both types of measurements exhibit a significant overlap.

A "two-dimensional electron gas" (2DEG) refers to a model system comprising non-interacting or weakly interacting highly conducting electrons that are free to move within two dimensions while being confined in the third dimension. The concept of 2DEG commonly arises in transistors fabricated with semiconductors, particularly metal-oxide-semiconductor-field-effect transistors (MOSFETs)[1]. Additionally, electrons confined within a quantum well at the heterojunction of two semiconducting materials also behave as a 2DEG at the interface[2]. Such heterojunction-based 2DEGs exhibit higher mobilities compared to those observed in MOSFETs. These interfaces offer intriguing physical properties and hold potential for applications in modern electronics industries [3-5].

Perovskite oxides have garnered attention as potential alternatives to conventional semiconductors due to their emergent properties, including superconductivity[6, 7], magnetism[8], coexisting magnetism and superconductivity[9], optically induced ferroelectricity[10], multiferroicity[11, 12], persistent photocurrent[13-15], photoinduced demagnetization and metal-insulator transition[16], Rashba spin splitting[17], Shubnikov–de Hass oscillations[18], and more. Combining these functionalities with 2DEG behavior may open new avenues for integrated laboratory-on-chip devices [19, 20].

In a seminal paper, Ohtomo and Hwang demonstrated the emergence of a high-mobility twodimensional conducting layer at the interface of two band insulators, LaAlO₃ (LAO) and SrTiO₃ (STO) [3]. Subsequently, these interfaces exhibited additional intriguing properties, although many fundamental questions surrounding them remain unresolved to this day. Various proposed mechanisms, such as polar catastrophe or electronic reconstruction, cation intermixing, oxygen vacancies, and cation stoichiometry, attempt to explain the origin of conductivity at the interface. However, none of these mechanisms has been fully accepted, and the precise origin of the 2DEG at the interface of insulating oxides remains a subject of debate [21, 22]. Among the various proposed models, the polar catastrophe model is widely accepted. In a perovskite oxide ABO₃, the atomic stacking occurs in the (001) direction and consists of AO and BO₂ layers. These layers can be either charged neutral, as in STO [(SrO) = 0 and (TiO₂) = 0)], or charged $\pm 1/-1$, as in LAO $[(LaO) = +1 \text{ and } (AlO_2) = -1)]$. When two such perovskites are joined, a polar discontinuity arises at the interface, leading to a diverging electrostatic potential. This potential divergence can be resolved by transferring a charge of 0.5 electrons to the interface, which is known as the polar catastrophe model. This model has two important consequences: (1) A critical film thickness is required to achieve a conducting interface, and (2) the interface should be doped with half an electron per unit cell. However, it has been reported that the interfacial carrier concentration at the LAO/STO interface is much lower than predicted by the model, despite the need for a critical thickness to achieve a conducting interface. On the other hand, in the GTO/STO (GTO: GdTiO₃) heterostructure, the interface is doped with 0.5 electrons per unit cell, as predicted by the polar catastrophe model, without requiring a critical thickness of GTO for interfacial conductivity [23]. In contrast, the LVO/STO interface fulfills both characteristics of the polar catastrophe model: it necessitates a critical thickness of LVO thin film to achieve a conducting interface and is doped with 0.5 electrons per unit cell. The n-type interface in LAO/STO consists of two band insulators, while both LVO and GTO are Mott insulators. Interestingly, the interfacial electron orbitals in all three heterostructures predominantly exhibit xy characteristics. Conversely, within the STO substrate, the orbitals are predominantly of the yz/xz character for all these heterostructures. [23, 24]. Furthermore, the growth condition of the LAO thin film is typically reducing (around 750°C), whereas for LVO, it is typically 600°C. Additionally, aluminum (Al) has a higher affinity for oxygen than vanadium (V). As a result, the possibility of an oxygen vacancy in the STO component of the LVO/STO heterostructure is much lower compared to the STO component of an LAO/STO heterostructure, highlighting the importance of using LVO instead of LAO as the film layer.

A captivating yet understood topic is the distribution and origin of the conducting layer. It has been reported that the majority of conducting electrons are concentrated within a range of 7–10 nm near the interface on the STO side, while a long tail of carrier density extends up to 1 μ m inside the STO substrate [25-27]. Understanding the carrier density distribution, confinement potential shape, and electronic subband quantization has gained increasing attention due to the possibility of the existence of "Rashba spin-splitting" bands in the two-dimensional electron gas (2DEG) at the conducting interface of perovskite oxides [17, 18, 28-30]. Amplifying the shape of the confinement potential becomes crucial to generate an internal electric field at the interface. This electric field, in the rest frame of a relativistic electron, transforms into a magnetic field that interacts with its spin, resulting in a significant Rashba spin-split band.

In this chapter, we investigate the depth profile of conducting carriers at the interface of LVO and STO by analyzing room-temperature photoluminescence (PL) lifetime measurements. Utilizing a theoretical model, we determine the shape of the confinement potential well and the energy subbands present at the interface. By combining the theoretical model with the PL lifetime data, we are able to estimate the carrier density and effective masses of the conducting electrons. Remarkably, these estimates closely align with the values obtained from electric transport measurements, demonstrating a strong agreement between the two approaches.

4.2 **Experimental section:**

As already explained in Chapters 1 and 2, the importance of surface termination of the STO substrate for the conductivity of the interface. To make the interface conduct single termination is required. In this section, we explain the process for getting a single terminated substrate, the thin film deposition, and then the measurement details.

4.2.1 The realization of single terminated STO substrate:

In Chapter 3, we explained the route to get a single terminated step-terrace-like structure for STO substrate by chemical etching method. We used the standard method to get TiO_2 terminated STO substrate. First, we annealed the substrate at 950 $^{\circ}C$ for four hours in the presence of oxygen. The annealed substrates are then treated with the chemical etchant (BHF) followed by post-annealing at 950 $^{\circ}C$ for two hours. A smooth step-terrace-like structure was obtained and the single termination is confirmed by the LFM measurement[31].

4.2.2 The fabrication of LVO/STO interface:

The LVO/STO heterostructure was grown employing a pulsed laser deposition system using LaVO₄ polycrystalline ceramic pellet as a target material. The KrF excimer laser of the fluence of 2 J/cm² at a repetition rate of 2 Hz was used to ablate the target. The LVO thin film of thickness 150 nm was deposited on top of the TiO₂ terminated (001) STO at 600 0 C in 1 × 10⁻⁶ torr oxygen partial pressure[17, 32]. For transport measurements, we have used the physical property measurement technique (PPMS, quantum design, ±14 T, and temperature range 1.8 K to 400 K). The electrical connections were made using 50 µm diameter Al wire by an ultrasonic wire bonder (West Bond).

4.3 <u>Results and Discussion:</u>

The schematic of the heterostructure is shown in **Figure 4.1** (a). The resistivity of the interface is measured as a function of temperature which suggests the metallic nature of the interface down to 3 K [see **Figure 4.1** (b)]. We have checked the top-down conductivity of the system and found that it is electrically insulating within our measurement limit. We have also ensured that the film is insulating by measuring the conductivity between the top of the film surface and the interface. It is worth mentioning that below around 5 K there is a small upturn in the resistance. A similar effect was reported by Hotta et al. and was explained by the localization mechanism arising from the defects present in the system[32, 33].



Figure 4.1: (a) Schematic of the LVO/STO heterostructure showing the alternative charged layers of LVO and neutral layers of STO that gives rise to 2DEG at the interface and (b) 2D resistivity of the LVO/STO sample. The inset shows the low-temperature (3-K) Hall measurement, and (c) shows the room-temperature PL measurement of the undoped (001) STO single crystal and the LVO/STO heterostructure.
We first focus our attention on **Figure 4.1 (c)** which shows the PL spectra of an undoped STO single crystal and n-type LVO/STO heterostructure at room temperature. The excitation photon energy and the excitation density used are 3.54 eV and 0.028 mJ/cm², respectively. The PL peak is at 2.9 eV for the undoped STO whereas the LVO/STO heterostructure is characterized by a broad peak at 2.8 eV (blue PL) which is similar to the previously reported electron-doped SrTi_{1-x}Nb_xO₃ and n-type LAO/STO heterostructures [27, 34-36]. The broad PL peak for nondoped STO signifies the polaron (electron-phonon coupling) formation, defects states, or the impurity present in the system[36]. The origin of the similar broad peak in LVO/STO is, thus, mainly from the STO substrate. The blue PL observed for the LVO/STO heterostructure is because of the two-carrier radiative recombination of photogenerated electrons and the holes. The dynamics of photogenerated carrier density n(t) [or p(t)] and the PL intensity I(t) are governed by the following rate equations [27, 36, 37]:

$$\frac{dn}{dt}(t) = -An(t) - B_{rad}n(t)p(t) - C[n^2(t)p(t) + n(t)p^2(t)],$$
(1)

$$I(t) = B_{rad}n(t)p(t),$$
(2)

Here A, B_{rad} , and C are the nonradiative photogenerated single carrier (electron or hole) trapping rate, two-carrier radiative recombination coefficient, and nonradiative Auger recombination rate, respectively. The Auger recombination is a three-carrier (electron-electron-hole and hole-holeelectron) nonradiative recombination where the energy from the electron-hole recombination is transferred to another electron (hole) which is used to excite the electron (hole) to higher states in the same band instead of releasing photons.

When we shine a light on undoped STO, electrons and holes are generated. These photogenerated electrons and holes are identical (n(t) =where), here n(t)/p(t) represents the number density of electrons (holes) at time t) in number. In the conducting LVO/STO interface the number of doped electrons (N_e) is much greater than that of the photogenerated electrons (N_e >> n: N_e + n ~ N_e). It is reported that at room temperature the radiative recombination is very small for undoped STO[38]. The term "B_{rad} n(t)p(t)" could be neglected from Eq. (1) as it is significantly small in comparison with the other two terms. This leads to the fact that the PL is dominated by the Auger recombination of doped electrons and photogenerated holes [27, 35, 36]. For the conducting

LVO/STO interface, Eqs. (1) and (2) are now modified to (with the approximation: $n^2(t)p(t) + p^2(t)n(t) = [N_e + n(t)]^2p(t) + p^2(t)(N_e + n) \sim N_e^2p(t) + p^2(t)N_e$: for $N_e >> n$),

$$\frac{dp}{dt}(t) = -Ap(t) - CN_e^2 p(t), \qquad N_e \gg n.$$
(3a)

Integrating both sides of Eq. (3a) we get

$$p(t) = exp - (A + CN_e^2)t,$$
(3b)

$$I(t) \propto B_{rad} N_e p(t). \tag{4}$$

From Eq. (3b), the photogenerated carrier/hole decay is exponential with a decay rate $(A + CN_e^2)$. The photogenerated carrier/hole decay rate is dependent on the intrinsic carrier density. In addition, the PL decay has a direct relationship with the photogenerated carrier decay [Eq. (4)], hence, the intrinsic carrier density of the sample can be calculated using PL decay.



Figure 4.2: PL dynamics of Bare STO under excitation wavelength of (a) 375nm laser, (b) 405nm laser monitored at 426nm. PL dynamics of LVO/STO under excitation wavelength of (c) 375nm laser, (d) 405nm laser monitored at 426nm.

To study the PL decay dynamics we have done time-correlated single photon counting (TCSPC) measurements for Bare STO and LVO/STO interface using two different wavelength laser diodes

having wavelengths 375 nm and 405 nm. The optical penetration depth is very sensitive to the excitation wavelength of the used laser[39]. The penetration depth for the laser 375 and 405 nm is \sim 300 nm and >10 µm, respectively, hence, by using laser 375 nm, electron dynamics around 100 nm below the interface can satisfactorily be monitored, and the laser 405 nm is monitoring the bulk of the sample[27, 39].

Figure 4.3 (a) and (b) represent the PL dynamics of the undoped (001) STO and the LVO/STO heterostructure for different excitation wavelengths (375 and 405 nm) monitored at 2.9 and 2.8 eV, respectively. It can be clearly seen from **Figure 4.3** (a) and (b) that the PL decay rate for undoped STO is slower than that of the LVO/STO interface. We have also compared the decay kinetics of STO and LVO/STO at the same wavelength laser as shown in **Figure 4.3** (c) and (d). The decay rate of nondoped STO at 405 nm is slower than at 375 nm and signifies the low carrier density in the bulk of the sample in comparison to the surface.



Figure 4.3: PL dynamics of (a) undoped STO and (b) LVO/STO heterostructure under the excitation wavelengths of 375 and 405 nm monitored at 426 and 442 nm, respectively. The solid curves represent the theoretical fitting of PL dynamics using Eq. (6). PL dynamics of (c) Bare STO and LVO/STO heterostructure under excitation of 375nm laser monitored at 426nm, (d) Bare STO and LVO/STO heterostructure under excitation of 405nm laser monitored at 426nm.

Similar behavior is already reported that shows a nonexponential behavior and is explained in terms of the inhomogeneous distribution of carriers in the nondoped STO[38]. The faster decay in the LVO/STO heterostructure is due to the Auger recombination of the 2DEG originating at the interface and the photogenerated holes [35, 38, 40]. From **Figure 4.3** (b), a nonexponential behavior of the PL decay curve in the LVO/STO sample is observed, which suggests that the charge carriers near the interface are inhomogeneously distributed in space. The decay rate is faster for the lower excitation (375 nm) wavelength corresponding to the least penetration of light, suggesting that most of the carriers are accumulated at the interface of the LVO/STO heterostructure. We have tabulated the decay constants of bare STO and the LVO/STO interface for both 405 and 375 nm light in **Table 1**.

From Eq. (4) the temporal variation of the PL intensity is given by

$$I(t) \propto B_{rad} \int_0^\infty N_e(z) p(z, t) dz.$$
(5)

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Excitation	τ 1(ps)		τ 2(ps)		τ₃(ps)		$ au_{ m ave.}(m ps)$	
Laser	Bare	LVO/STO	Bare	LVO/STO	Bare	LVO/STO	Bare	LVO/STO
Wavelength	STO		STO		STO		STO	
375 nm	96.158	77.692	683.927	446.73	4.341	3.428	153.30 1	91.035
	(96.5 %)	(98%)	(2.5)	(1.8%)	(1%)	(0.2%)		
405 nm	129.81 9	103.338	1335.9	833.487	9.182	7.278	244.46 2	193.861
	(97%)	(96.2%)	02 (2%)	(2.6%)	(1%)	(1.2%)		

Average life time calculated from equation,

$$\tau_{ave.}(ps) = \frac{\tau_1 A_1 + \tau_2 A_2 + \tau_3 A_3}{A_1 + A_2 + A_3}$$

Here, p(z, t) is calculated from Eq. (3a), $p(z, 0) = p_0 exp(-\alpha z)$, where $1/\alpha$ is defined as the optical penetration depth. To solve Eq. (5) we have used $N_e(z) = N_0 exp(-\beta z)$, where $1/\beta$ is the depth of the carrier distribution as the spatial distribution of the charge should be a smooth function of the distance that will decrease as you go away from the interface. The simplest and most obvious choice is exponential dependence. The previous reports have also used an exponential special variation of charge [27, 36, 38, 41].

By substituting all values in Eq. (5) we get the PL intensity as,

$$I(t) \propto \frac{\kappa}{\beta} e^{-At} \left[1 - \operatorname{erf} \left(N_0 \sqrt{C} t \right) \right], \tag{6}$$

Here, $\operatorname{erf}(N_0\sqrt{C}t)$ is an error function of its argument. The values of the constants $A = 1.7 \times 10^6$ s⁻¹ and $C = 1.3 \times 10^{-32}$ cm⁶ s⁻¹ are taken from the previously calculated values for undoped STO[35, 38, 40]. The existence of surface carriers in nondoped STO is already reported with a typical value of N₀ ~ 10¹⁸ cm⁻³ [35, 38, 42]. The N₀ obtained from our fitting of nondoped STO data [**Figure 4.3** (a)] is ~1.07 × 10¹⁸ cm⁻³ and is in good agreement with previous reports.



Figure 4.4: (a) Calculated spatial profile of the carriers at the interface perpendicular to the surface, (b) calculated potential energy as a function of depth from the surface, and (c) the confinement potential $V_P(Z)$ calculated from Poisson's equation and $V_M(Z)$ the Morse potential as a function of depth (Z) from the interface (Z = 0, Z > 0 is the STO side and Z < 0 is the LVO side). The dotted lines show the energy subbands of the potential well with the calculated wave function for the given energy level, and the inset represents the projection of the same in K_x (or the K_y)-E plane, the two Fermi momentum vectors corresponding to two conducting channels as well as the Fermi level are also indicated.

To estimate the value of N_0 and $1/\beta$ for the LVO-STO interface we have fitted the experimental data of **Figure 4.3 (b)**.

The best fit is obtained as $1/\beta = 10$ nm and $N_0 = 2.21 \times 10^{20}$ cm⁻³ for the LVO-STO sample [**Figure 4.3** (b)] for which the total carrier density obtained from the spatial integration of N_e (Z) is ensured to match well with that obtained from Hall measurements. The potential energy profile [V_P(Z)] near the interface as a function of depth is calculated from Poisson's equation given as[43]

$$V_P(Z) = -\frac{eN_0}{\epsilon(0)\varepsilon_0} \left(\frac{e^{-\beta z}}{\beta^2}\right),\tag{7}$$

and is drawn in **Figure 4.4** (b). As it turns out, the potential distribution can be well approximated by the Morse potential $[V_M(Z)][44]$,

$$V_M(z) = D_e \left(e^{-2a(z)} - 2e^{-a(z)} \right).$$
(8)

Where D_e represents the depth of the potential well. The value of the ϵ used in Eq. (7) is 400. In Eq. (8), a represents the width of the potential well formed at the interface (a = $1/\beta = 10$ nm). Figure 4.4 (c) shows the potential-energy profile generated from the Poisson relation Eq. (7) and the Morse potential Eq. (8). The eigenvalues and eigenfunctions of the Morse potential are exactly solvable[45]. This fact is utilized to find out the energy eigenvalue and the wave function for this confinement potential by using the Morse potential approximation. The calculated energy eigenvalues and wave function for the LVO/STO system are shown in Figure 4.4 (c). To calculate the energy eigenvalues, we have used the effective mass of STO 1.5 m_e . The wave function quickly vanishes as we go away from the interface, especially for lower subbands. The spatial distribution of the intrinsic carrier as a function of depth from the interface is plotted in Figure 4.4 (a) which indicates that most of the intrinsic conducting carriers are concentrated within a few nanometers near the LVO/STO interface. The total calculated carrier density $\sim 2.21 \times 10^{14}$ cm⁻² is very close to the carrier density $(3 \times 10^{14} \text{ cm}^{-2})$ predicted from the polar catastrophe model[46]. A similar carrier density also may be obtained in oxygen vacant STO-based interfaces. But in the present case, we have ensured that the level of oxygen vacancy in the present system is below the detection limit and, hence, extremely low. The Hall measurement was performed to elicit the nature and amount of the charge carrier present in the system. We have applied current along the x axis, a magnetic field is applied along the z axis, and the Hall resistance is measured. The sign of the Hall resistance suggests that the carriers are of n type. The inset of Figure 4.1 (b) shows the Hall data at 3 K, having a nonlinear nature. Similar nonlinear behavior was also reported previously for the LVO/STO interface[32, 33]. This nonlinear nature of the curve indicates the presence of two types

of electrons and, hence, the existence of two-band conduction in this system [33, 47, 48]. In the two-band model, two conduction channels are corresponding to two groups of charge carriers with mobilities μ_1 and μ_2 and charge carrier densities n_1 and n_2 . In the two-band model, the Hall and longitudinal resistances are written as

$$R_{xy}(B) = \frac{B}{e} \frac{n_1 \mu_1^2 + n_2 \mu_2^2 + (n_1 + n_2)(\mu_1 \mu_2 B)^2}{(n_1 \mu_1 + n_2 \mu_2)^2 + (n_1 + n_2)^2(\mu_1 \mu_2 B)^2}.$$
(9)

This equation has four unknown parameters but could be rewritten as an effective two-free parameter equation by using the fact the longitudinal resistance (R_{xx}) in the absence of any applied magnetic field is given by

$$R_{xx}(B=0) = \frac{1}{e(n_1\mu_1 + n_2\mu_2)}.$$
(10)

The best fit is for carrier densities $n_1 = 0.54 \times 10^{14}$ and $n_2 = 1.7 \times 10^{14}$ cm⁻² with mobility values of $\mu_1 = 500$ and $\mu_2 = 2000$ cm²V⁻¹s⁻¹, respectively. A detailed description of this analysis is given in Ref.[33]. The effective masses for the energy subband calculated from these data are 2.1 m_e and 0.67 me. The effective masses are calculated from the mobility by using scattering time 7×10^{-13} s[49, 50]. The effective mass of the carriers is similar to that reported for LAO/STO systems (~ 2.5 m_e and ~0.5 m_e)[50-53]. We have adopted the following scheme to draw the electronic bands [Figure 4.4 (c) inset] of this system. From the two-band fitting of Hall data, the carrier density of the individual conducting channel was calculated. By using the mass of the majority carriers the curvature of that parabolic band was determined, and the carrier density was used to find out the Fermi velocity and the Fermi level of the system. Keeping the Fermi level fixed for the second conduction channel and estimating the Fermi velocity from the carrier density of the minority carrier, the second parabolic band is drawn. For both channels the energy value at K = 0 is determined by the energy eigenvalue estimated from confinement potential. It is pleasantly surprising to note that the effective mass of the second channel ($m_2^* = 0.6 \text{ m}_e$) matches excellently with that estimated from the Hall measurement ($m_2^{\prime*}=0.67$ m_e). The parabolas in the Figure 4.4 (c) inset represent the two types of carriers, namely, light and heavy carriers. This is very similar to the Ti 3d t_{2g} band splitting in the STO at the interface of the LAO/STO heterostructure[54, 55].

4.4 Moving from SrTiO₃ to KTaO₃:

In material science we always look for materials with exotic properties for better future technologies. STO is a well explored material with wide range of functionalities however, in search of better performance we found KTO as an ideal material to explore. KTO exhibits all the properties shown by STO with additional features like high spin-orbit coupling, low effective mass, and correlation physics[56]. The spin-orbit coupling strength of KTO (400 meV) is almost 25 times higher than STO.

To see the effect of substrate on carrier dynamics we have deposited 150 nm thick film of LVO on Ta terminated KTO (001) single crystal. The termination was obtained from hot deionized water etching treatment. A similar measurement has been done with LVO/KTO sample.



Figure 4.5: a) PL of bare KTO (001) substrate and LVO/KTO heterostructure. b) The PL decay dynamics of KTO (001) substrate and LVO/KTO heterostructure at an excitation wavelength of 375 nm and measured at 412 and 403 nm, respectively (the inset showing the carrier density distribution perpendicular to the interface as a function of distance (z = 0 at the interface) toward KTO (001) substrate as shown in the schematic also).

Figure 4.5 a) is showing the comparison of the PL peak of LVO/KTO and KTO samples. The PL peak of the KTO (001) substrate is at 2.98 eV and for LVO/KTO heterostructure the peak is at 3.06 eV, the blue PL of the LVO/KTO interface suggests that the system is electron-doped. The resulting PL is due to the radiative recombination of the photogenerated holes and the doped electrons and hence can provide an estimate of the carrier density and their distribution at the interface of LVO/KTO[57]. **Figure 4.5 b)** presents the PL decay dynamics of the carriers at the interface and suggests that the PL decay dynamics are dominated by the nonradiative Auger recombination[27, 57]. The temporal variation of PL for the large spatial distribution of carriers is expressed by Eq. 5 as discussed in the previous section. By using Equation 6, we have fitted the PL decay curve, and from that, we get the carrier density at the interface $\approx 1.95 \times 10^{14}$ cm⁻². Although the tail of the carrier density distribution continues up to 25 nm, the full-width half maximum of the conducting channel is around 10 nm. Hence, this conducting channel could be considered quasi-2-dimensional. Further, analysis was done using transport measurements described in one of our works [58].

4.5 <u>Conclusion:</u>

In summary, our study presents a method that combines optical spectroscopy with electrical transport measurements and a theoretical model to map out the carrier density distribution, quantum well structure, and related energy subbands at a conducting interface. Through experiments on the LVO/STO conducting interface, we find that the potential near the interface can be well approximated by the Morse potential. The carrier distribution is predominantly concentrated within a few nanometers near the LVO/STO interface, indicating a nearly two-dimensional nature of this electronic system. This confinement leads to the formation of electronic subbands, which we analytically solve using the Morse potential approximation. The total carrier density obtained from this distribution is 2.21×10^{14} cm⁻², in close agreement with the carrier density of approximately 3×10^{14} cm⁻² predicted by the polar catastrophe model and deduced from Hall data analysis.

By fitting the observed nonlinear Hall data with the two-band theory, we estimate the mobility of the two conducting channels to be 500 and 2000 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, with corresponding carrier densities

of 0.54×10^{14} cm⁻² and 1.7×10^{14} cm⁻², respectively. Remarkably, the effective masses estimated from electrical transport measurements (m'_1 : 2.1 m_e and m'_2 : 0.67m_e) and optical spectroscopy (m_1^* : 2 m_e and m_2^* : 0.6 m_e) exhibit excellent agreement. Our method provides a valuable approach to investigating the electronic distribution, confinement potential shape, and electronic structure of conducting interfaces. It is not limited to specific systems and can be extended to other conducting interfaces as well.

Furthermore, we conducted a similar measurement for the LVO/KTO system, which revealed that the conducting channel is not strictly two-dimensional but exhibits a quasi-2D nature. Understanding the quantum well and its associated energy subband structure is crucial in comprehending intriguing physical phenomena arising from the "Rashba interaction," such as the planar Hall effect and the nontrivial Berry phase, observed at conducting oxide interfaces with strong spin-orbit coupling.

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Chapter 5: Signatures of the non-trivial spin texture in momentum space and angular dependence of quantum mobility at the KTaO₃-based conducting interface: Aperiodic Shubnikov de-Haas Oscillations

5.1 Introduction:

The discovery of a two-dimensional electron gas at the interface of two high band gap insulators, LAO and STO, has opened up exciting possibilities in the field of oxide electronics [1]. This finding not only holds significant technological implications but also sheds light on fundamental physical phenomena. Extensive research has been conducted on the interface, revealing intriguing phenomena such as superconductivity [2], gate-tuned superconductivity[3], magnetism[4], photoconductivity[5], Rashba spin-splitting[6], and the coexistence of magnetism and superconductivity[7].

More than a century after the discovery of Quantum mechanics, quantum materials continue to captivate us with their remarkable physical properties. These properties not only deepen our understanding of fundamental physics but also offer potential for future spin-electronics devices [8-14]. One particularly fascinating aspect of quantum materials is the concept of a geometrical phase. When a quantum particle undergoes adiabatic evolution on a closed path, either in real or momentum space, it accumulates a geometrical phase known as Berry's phase. This phase serves as a signature of the non-trivial nature of the space it traverses [15].

If a magnetic Skyrmionic lattice exists in real space, a conducting charge moving through that spin texture acquires Berry's phase, which is manifested in Hall measurements as the topological Hall effect [16]. On the other hand, if a conducting charge carrier rotates in a cyclotron orbit in k-space, enclosing a Dirac point, it accumulates Berry's phase that manifests in Shubnikov de Haas oscillations (SdH) observed in longitudinal magnetoresistance measurements [17].

However, beyond these established concepts, a question arises regarding the manifestation of a combination of non-trivial spin texture and a non-trivial electronic structure, specifically the presence of a Dirac point in momentum space.

5.1.1 What is Shubnikov de-Hass Oscillation?

Shubnikov de-Haas oscillation is the oscillation in conductivity at a high magnetic field and low temperature. This macroscopic phenomenon is the manifestation of the quantum mechanical nature of the matter.

Physical process behind the oscillations: At low temperature and high magnetic field the electrons in metal, narrow band semiconductor, and semimetal behave like simple harmonic oscillators. The period of oscillation changes proportionally with the magnetic field. The energy levels of the harmonic oscillator (or the Landau levels) are separated by the cyclotron energy and the cyclotron energy is directly proportional to the magnetic field value. So, as we increase the magnetic field the gap between the energy levels increases too. As the energy levels pass through the Fermi level it depopulate as the electrons become free for conduction. This results in periodic oscillations in the transport (for example conductivity and magnetization) and thermodynamic properties of the material. The oscillations contain a wealth of information about the band structure and the geometrical properties of the Bloch state. For a trivial band structure, Onsager's quantization rule is defined as,

$$\Delta \frac{1}{B} = \frac{2\pi e}{\hbar c} \frac{1}{S_e(\varepsilon_f)} \tag{1}$$

Here, e is the electronic charge, \hbar is the reduced Planck's constant, c is the speed of light, and S_e is the cross-sectional area of the extremal orbit on the Fermi surface in the plane perpendicular to the applied magnetic field direction. This suggests that by changing the direction of the magnetic field we can calculate the dimensionality of the Fermi surface. For non-trivial band structures, Eq. (1) further modifies to,

$$S_e = 2\pi \left[n + \frac{1}{2} + \gamma(\varepsilon, B) \right] \frac{2\pi B}{\varphi_0}$$
(2)

Here, $\varphi_0 = h/e$ is the quantum flux, n is the Landau level index, γ represents the appropriate offset to $\frac{1}{2}$ that corrects the Onsager's rule. The term γ includes the magnetic moment of the Bloch

states and the Berry phase (an important topological characteristic of the band structure). To calculate the Berry phase from Shubnikov de-Haas oscillations one should do the linear fitting of the Landau index to the inverse of magnetic field (B) and the intercept on the y-axis will provide the information about the Berry phase. It was quite successful for graphene and other topological materials but the theory fails for the surface model of 3-dimensional topological insulators. The value of the Berry phase deviates from the π value suggesting some additional term in Onsager's quantization rule which can change the linear relation between the n and 1/B.

Nio and Gao in their paper modified Onsager's rule by adding higher some-order terms (magnetic response functions especially magnetic susceptibility). The modified Onsager's equation is,

$$nB = \frac{\varphi_0 S_e}{4\pi^2} + \left[\frac{\Gamma(\mu)}{2\pi} - \frac{1}{2} + \varphi_0 < m > D\right] B + \frac{B^2 \varphi_0}{2} \frac{\partial \chi}{\partial \mu} + O(B^3)$$
(3)

Here, $\Gamma(\mu)$ is the Berry phase, D is the density of states, f is the Fermi functional at zero temperature, $\langle m \rangle$ is the average value of magnetic moment m over the Fermi surface, and χ magnetic susceptible. From Eq. (3) we can calculate the Berry phase and magnetic moment but more importantly, Eq. (3) shows how the magnetic susceptibility is affecting the formation of the Landau level.

5.1.2 Application: Extraction of magnetic response functions

In the previous section we discussed the deviation of the Berry phase calculated from Shubnikov de-Haas oscillations, from π value for the surface model of 3D topological insulators. This happens due to imperfection in linear band dispersion for the surface model of 3D topological insulators [17-24]. But in the case of Eq. (3), it is independent of any specific feature of the band structure. This implies that the Beery phase calculated from Eq. (3) is more accurate. We can also calculate other magnetic response functions from that like magnetic moment and magnetic susceptibility[25].

In this chapter, we present a new perspective on the Shubnikov-de Haas (SdH) oscillation occurring at the conducting interface of LaVO₃-KTaO₃ (LVO/KTO: LVO thin film grown on KTO substrate). Our findings reveal profound insights into the nontrivial characteristics of both the electronic structure and the magnetic spin texture in momentum space.

Particularly noteworthy is the observation of a non-linear relationship between 1/B (inverse of the magnetic field) and the Landau index (n). To explain this behavior, we introduce a B-linear dependence multiplied by a susceptibility term, which arises from the nontrivial spin texture in momentum space[25, 26]. Furthermore, we have made an observation of a constant Berry phase π , indicating the presence of a Dirac cone-like feature in the electronic structure [17, 27-29]. Additionally, a surprising revelation emerged as we found that quantum mobility exhibits a cosine squared dependence on the relative angle between the applied electric and magnetic fields when both are applied within the plane of the interface. An enhancement of effective mass has also been observed with an increasing applied magnetic field. These observations fundamentally advance our understanding of the SdH oscillation and shed new light on the intricate interplay between electronic and magnetic properties in conducting interfaces. The implications of our findings extend beyond the specific material systems investigated in this study, offering promising avenues for exploring nontrivial electronic and spin textures in momentum space across various materials.



Figure 5.1: RHEED oscillations for 4 ML LVO-KTO sample. The figure's inset shows the RHEED image of the surface of the sample before and after the deposition. b) The schematic of the measurement geometry of the sample.

The thin film of LVO was deposited on Ta terminated KTO (001) single crystal employing the pulsed laser deposition system. The thickness of the sample was monitored using the reflection high energy electron diffraction (RHEED) method. The oscillations of the specular spot are shown in **Figure 5.1 a**). From the oscillations we can say that there is successful deposition of LVO thin film of 4 monolayers over KTO single crystal. The inset of the figure shows the RHEED image of the sample before and after the deposition of LVO thin film. The RHEED image shows the crystalline thin film deposition. **Figure 5.1 b**) is showing the measurement geometry of the sample.

5.2 <u>Results and Discussion:</u> 5.2.1 <u>Out-of-plane measurements:</u>

Figure 5.2 represents the resistance vs temperature measurement for LVO/KTO interface. The resistance goes down with the temperature down to 2 K confirming the metallic nature of the interface. The inset represents the Hall measurement for the interface. The Hall data shows that the sample is n-type doped and the carrier density calculated from the Hall measurements is $5.12 \times 10^{13} \text{ cm}^{-2}$.



Figure 5.2: Resistivity as a function of temperature for LVO/KTO interface. The inset shows the Hall resistance as a function of the magnetic field at 2 K.

Figure 5.3 a) shows the magnetoresistance (MR) measurement for the LVO/KTO interface. The MR [defined mathematically as $((R_{xx}(B) - R_{xx}(0)/R_{xx}(0)) \times 100]$ measured at 2 K in $\theta = 90^{\circ}$, $\phi = 0^{\circ}$ configuration is overall positive with ~ 35% change in resistance at 14 T as shown in **Figure 5.3 a**). The MR shows oscillating behavior. After subtracting a suitable polynomial from MR, the oscillatory part is shown as a function of magnetic field (B) in **Figure 5.3 b**). We have also plotted the oscillatory part as a function of the inverse of the magnetic field (1/B) shown in **Figure 5.3 c**)

for the interface. A continuous increase in frequency has been observed with an increase in B. We have plotted the Landau index (n) plot as a function of 1/B, which was supposed to be a linear function of 1/B following the conventional Onsager quantization rule $[n = F(1/B) - \gamma]$. But to our surprise we find n to be a non-linear function of 1/B, it fits well with the modified Onsager equation written [25],

$$n = F\left(\frac{1}{B}\right) - \gamma + CB \tag{4}$$

Here, F is the frequency of the oscillations at a low magnetic field regime, γ is the phase of the SdH oscillations that correspond to the intercept of asymptote for $1/B \rightarrow \infty$ with the y-axis in the Landau plot, and C is the nonlinearity term associated with the susceptibility correction in the Onsager's relation[30]. In this case, C is arising from the chiral spin texture in the momentum space, which has a zero net magnetization but non-vanishing susceptibility. This is illustrated within the framework of a three-dimensional strong spin-orbit coupled system that has both a linear band crossing and a chiral spin texture in the momentum space. **Figure 5.3 d**) shows Landau fan diagram fitting, using Eq. (4). It shows an excellent fit.



Figure 5.3: a) The MR % as a function of the magnetic field for LVO/KTO at 2 K for $\theta = 90^{\circ}$ and, $\varphi = 0^{\circ}$. b) ΔR_{xx} as a function of a magnetic field. c) ΔR_{xx} as a function of the inverse of the magnetic field for LVO/KTO. d) The Landau plot for LVO/KTO interface corresponds to c).

5.2.2 In-plane measurements:

The in-plane longitudinal magnetoresistances (LMR) are measured for two different configurations. Let us now describe the measurement geometry in detail. We assume that the interface of LVO/KTO is confined in the x-y plane. Let us define the direction of current Vis a Vis



Figure 5.4: (a-b) Percentage magnetoresistance of LVO/KTO in $\theta = 0^0$, $\varphi = 0^0$, and $\theta = 0^0$, $\varphi = 90^0$, respectively. The inset of Figure (a-b) is showing the corresponding schematic of the measurement geometry, c-d) ΔR_{xx} as a function of magnetic field for $\theta = 0^0$, $\varphi = 0^0$, and $\theta = 0^0$, $\varphi = 90^0$, respectively for LVO/KTO interface, e-f) ΔR_{xx} as a function of the inverse of magnetic field for $\theta = 0^0$, $\varphi = 0^0$, $\varphi = 0^0$, and $\theta = 0^0$, $\varphi = 90^0$, respectively, and the corresponding Landau fan diagram is shown in (g-h) for LVO/KTO.

the applied electric field (E) as the x-axis, we will keep this convention of the direction constant throughout our all measurements. In addition, the direction of the x-axis coincides with the crystallographic < 100 > direction, unless otherwise it is mentioned. The z-axis is taken as perpendicular to the interface in the direction of grown thin films (LVO), as shown in the inset of **Figure 5.4 a-b**).

The resistance as a function of the applied magnetic field was measured along the x-direction. We have used two different orientations of the applied magnetic field: i) $\theta = 0^{\circ}$, $\phi = 0^{\circ}$ the magnetic field is along the direction of E or x-axis, and ii) $\theta = 0^{\circ}$, $\phi = 90^{\circ}$ the magnetic field is along the y-axis. The negative LMR is observed for both $\theta = 0^{\circ}$, $\phi = 0^{\circ}$ (B//E//x-axis) and $\theta = 0^{\circ}$, $\phi = 90^{\circ}$ (B// y-axis) as shown in **Figure 5.4 a-b**). All the data presented in **Figure 5.4 a-b**) are measured at 2 K. The signature of oscillation had been observed in the raw data of LMR for both B//x and B//y configurations, for both the samples. The oscillatory parts extracted after subtraction of the polynomial as a function of B are shown in **Figure 5.4 c-d**) for B//x and B//y configuration for LVO/KTO, respectively, as mentioned in the figures. The observation of oscillations in all three configurations (B//z, B//x, and B//y) suggests the presence of the three-dimensional nature of SdH oscillations for both samples. To further look at these oscillations, we plotted them as a function of 1/B in **Figure 5.4 e-f**). For both configurations, a continuous increase in frequency in all directions has been observed with increasing B. In **Figure 5.4 g-h**), we have plotted the Landau index (n) as a function of 1/B, which was supposed to be a linear function of 1/B following the Onsager quantization rule. But to our surprise, we find n to be a non-



Figure 5.5: The band dispersion of the 2D Rashba model without any magnetic field. The electronlike branches (positive band velocity) are marked in blue, whereas the hole-like branches (negative band velocity) are in red. The solid (dashed) line represents the conduction (valence) band.

linear function of 1/B, but in all cases, they fit well with the modified Onsager equation as shown in Eq. (4).

Now, we explicitly calculate the quantum oscillations for a three-dimensional (3D) spin-orbit coupling (SOC) system described by the Hamiltonian,

$$\mathcal{H} = \frac{\hbar^2 k^2}{2m} \sigma_0 + \alpha \sigma. k \tag{5}$$

The band structure and spin texture for this model Hamiltonian are shown in Figure 5.5.

In the presence of the magnetic field, the above Hamiltonian becomes,

$$\mathcal{H} = \frac{\Pi^2}{2m} \sigma_0 + \frac{\alpha}{\hbar} \Pi . \sigma + \Delta_z \sigma_z \tag{5}$$

Here the Pauli matrices denote the actual spin of the system, $\Pi = \hbar k$ -eA, and $\Delta_z \propto B$ ($\Delta_z = \frac{g\mu_B B}{2}$) captures the Zeeman coupling, keeping the lowest order magnetic field terms, we find that the LL index can be expressed as,

$$n + \frac{1}{2} = \frac{h}{eB} N_0(\epsilon) + \frac{hB}{2e} \chi'_0(\epsilon)$$
(6)

For simplicity of theoretical calculation, we apply \vec{B} in z-direction. However, as the Hamiltonian (\mathcal{H}) is isotropic, it does not affect the conclusions drawn from the calculations.

It is evident from equation 6 that n is no more a linear function of 1/B, but contains an additional B linear term. This equation can be restated to the modified Onsager equation with $F = \frac{h}{e}N_0(\epsilon)$ and $C = \frac{h}{2e}\chi'_0(\epsilon)$. It is obvious that the non-linearity in the Landau fan diagram solely arising from the susceptibility term originated due to the non-trivial spin texture in the momentum space as a result of strong SOC in the system.

Figure 5.6 a) and b) present the SdH oscillations as a function of 1/B for the B//y-axis and B//xaxis, respectively at selected temperatures as mentioned in the figure. To calculate the effective mass for both configurations, we have plotted the temperature-dependent ΔR_{xx} amplitude as shown in **Figure 5.6 c-d**). Following Lifshitz-Kosevich theory, we have fitted the amplitude of ΔR_{xx} as a function of temperature data with the following equation,



Figure 5.6: (a-b) Temperature-dependent ΔR_{xx} as a function of the inverse of the magnetic field for LVO/KTO is shown for $\theta = 0^0$, $\varphi = 90^0$, and $\theta = 0^0$, $\varphi = 0^0$, respectively. (c-d) is showing temperature-dependent ΔR_{xx} amplitude for $\theta = 0^0$, $\varphi = 90^0$ and $\theta = 0^0$, $\varphi = 0^0$, respectively followed by L-K fitting. The figure's inset shows the ratio of effective mass vs mass of electron as a function of the magnetic field.

$$R(T) = \frac{\lambda T}{\sinh(\lambda T)} \tag{7}$$

Here, $\lambda = 2\pi^2 k_B m^*/\hbar eB$, m* is effective mass, k_B is Boltzmann's constant, e is electric charge, \hbar is reduced Plank's constant, and T is temperature.

By employing the Lifshitz-Kosevich theory to analyze our data, we were able to determine that the effective mass (m*) that increases with the applied magnetic field for both configurations (θ , ϕ) = (0°, 90°) and (θ , ϕ) = (0°, 0°) at the LVO/KTO interface [refer to the inset in **Figure 5.6 c-d**)]. It is important to recall that the effective mass is proportional to the energy derivative of the

cyclotron orbit area, given by $m^* = (\hbar^2/2\pi) \partial Se/\partial E$. Consequently, our findings align with the corrections to Onsager's relation. Onsager's relation relies on the total carrier density, which is proportional to the cyclotron orbit area and incorporates a correction arising from magnetic susceptibility. This correction can be interpreted as either a magnetic field-induced modification in the density of states itself or a magnetic susceptibility-induced alteration in the effective mass. The magnetic field dependence of the effective mass serves as a clear indication of the spinor structure of the wave functions within the underlying energy bands or, in our case, the momentum space spin texture.

We will now focus only on the in-plane LMR geometry, where $\theta = 0^{\circ}$ and LMR will be measured for selected values of ϕ for $90^{\circ} \ge \phi \ge 0^{\circ}$. This implies that the applied magnetic field is kept always in the plane of the interface. **Figure 5.7 a**) represent SdH oscillations as a function of 1/B measured at 2 K for selected values of ϕ .



Figure 5.7: (a) ΔR_{xx} a function of the inverse of the magnetic field in the pane of the sample ($\theta = 0^0$ and varying φ). The inset shows the geometry of measurement. (b) Shows the Landau fan diagram for $\varphi = 0^0$ and $\varphi = 90^0$. (c) The ln ΔR_{xx} vs inverse of magnetic field for different φ values.. (d) Showing the mobility of the LVO-KTO interface as a function of in-plane angle(φ). The solid line represents the fitting curve using $\cos^2 \varphi$.



Figure 5.8: (a) and e) The ΔR_{xx} a function of the inverse of the magnetic field in the pane of the sample ($\theta = 0^{0}$ and varying φ) for LVO/KTO in <010> and <110>, respectively. The inset is showing the geometry of measurement. (b) And (f) is showing the Landau fan diagram for $\varphi = 0^{0}$ and $\varphi = 90^{0}$ for LVO/KTO in <010> and <110>, respectively. (c) And (g) ln ΔR_{xx} vs inverse of magnetic field for different φ values for LVO/KTO in <010> and <110>, respectively. (d) And (h) is showing the mobility of the LVO-KTO in <010> and <110>, respectively as a function of in-plane angle (φ). The solid line represents the fitting curve using cos² φ .

We plot the Landau fan diagram—the Landau level index as a function of 1/B, in **Figure 5.7 b**) for $\phi = 0^{\circ}$ and $\phi = 90^{\circ}$. Both of them show nonlinear dependence in 1/B and can be fitted with the modified Onsager's relation. In both cases, Berry's phase (γ) calculated from the fitting turned out to be approximately π . This suggests the possible existence of a Dirac point near the Fermi surface or non-trivial band structure consistent with the effective mass analysis.

Figure 5.7 c) presents the Dingle plots for four selected values of ϕ as marked in the figure. The Dingle plot is fitted with the Dingle factor, $R_D = \exp(-\lambda T_D)$, derived from Lifshitz-Kosevich theory. Here, $T_D = \hbar/2\pi k_B \tau$, and τ is the carrier lifetime that defines the average time of an electron in a given quantum state. The quantum mobility is calculated using the relation $\mu = e\tau/m^*$. The quantum mobility of the carriers at different values of ϕ was estimated from the Dingle plot and plotted as a function of ϕ in **Figure 5.7 d**). It is surprising to note that quantum mobility is a function of the relative orientation of E and B. It follows a $\cos^2(\phi)$ behavior. To eliminate the possibility of any relationship with crystallographic orientations, we have changed the direction of E. So far, all measurements were done for E parallel to < 100 > direction.



Figure 5.9: (a-b) the ΔR_{xx} as a function of the inverse of magnetic field for $\theta = 0^{\circ}$ and $\phi = 0^{\circ}$ and $\phi = 0^{\circ}$ and $\phi = 0^{\circ}$. The solid lines represent the fitting curve using the conventional Lifshitz-Kosevich equation and the modified Lifshitz-Kosevich equation.

A similar analysis but with E applied parallel to < 010 > and < 001 >, respectively, has been shown in **Figure 5.8**. It is evident that the dependence and values of quantum mobility are independent of the crystallographic orientation and solely depend on the relative orientation of B and E.

Moving further we now analyze the SdH oscillations as a function of 1/B in detail for both B//x and B//y-axis, **Figure 5.9 a**) and **b**), respectively. First, we show the fitting of (yellow curve) these raw data (red circles for LVO/KTO and blue circles for EO/KTO) with the conventional Lifshitz-Kosevich equation:

$$\Delta R_{xx} = -R_T R_D \cos\left[2\pi \left\{\frac{F}{B} - \left(\frac{1}{2} - \phi\right)\right\}\right] \tag{8}$$

Here the phase $\phi = \frac{\phi_B}{2\pi} - \delta$, ϕ_B is defined as the Berry phase and δ is arises from the dimensionality of the charge carrier. For a 3-dimensional Fermi surface, δ takes the value $\pm 1/8$ (+ for hole-like and - for electron-like) whereas $\delta = 0$ for a two-dimensional Fermi surface.

It is evident from **Figure 5.9 a**) and **b**) that the experimental data could not be fitted with this conventional equation. Then recalling the non-linear dependence of n with 1/B, we have used a modified Lifshitz-Kosevich equation:

$$\Delta R_{xx} = -R_T R_D \cos\left[2\pi \left\{ \left(\frac{F}{B} - \gamma - CB\right) - \left(\frac{1}{2} - \phi\right) \right\} \right]$$
(9)

To our surprise, we find an excellent fitting of this modified Lifshitz-Kosevich equation with our experimental data for both B//x and B//y-axis. This further strengthens the fact that the observed SdH oscillations capture the signature of the non-trivial spin texture in the momentum space.

5.3 <u>Conclusion:</u>

In conclusion, we have made several exciting observations of a three-dimensional Shubnikov de Haas (SdH) oscillation originating from the conducting interface of LVO/KTO. These oscillations exhibit a distinct characteristic, deviating from the conventional SdH oscillations, as they demonstrate a non-linear relationship between the carrier density (n) and the magnetic field strength (1/B). This unconventional dependence of n on 1/B can be accurately described by a revised Onsager relation, which effectively captures the unique features arising from the non-trivial electronic structure and non-trivial spin texture present in momentum space.

We were particularly fascinated by the angular dependence of quantum mobility, which displayed a reliance on the relative orientation between the electric field (E) and the magnetic field (B). Notably, this dependence was independent of the absolute orientation of E. Our comprehensive analysis strongly suggests that these observations have opened up a promising avenue for investigating SdH oscillations from a renewed perspective. This approach not only allows us to capture the distinctive signature of nodal points in the electronic structure but also conveys valuable information about the non-trivial spin texture in momentum space through the susceptibility term.

To summarize, the presence of a topologically non-trivial spin texture in real space is accurately reflected in the transverse magnetoresistance (Hall measurements) as the topological Hall Effect. Conversely, the existence of a topologically non-trivial spin texture in momentum space is captured in the longitudinal magnetoresistance (LMR) as a non-linear 1/B dependence of the Landau index. These observations and the associated physics are not confined to a specific system but can be extended to materials hosting relativistic quantum charge carriers with linear band crossings and non-trivial spin textures in momentum space.

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Chapter 6: Summary and Future Scope

6.1 <u>Summary:</u>

Crystalline superlattices, thin films, and heterostructures have garnered significant attention and interest within the condensed matter physics community. The fabrication of these materials offers the opportunity to venture beyond equilibrium and delve into the intriguing properties, functionalities, and fundamental aspects of physics. Transition metal oxides (TMOs) serve as compelling starting points for such explorations due to their diverse range of emergent properties. The interfaces of these TMOs exhibit a multitude of intriguing characteristics, including tunable superconductivity, spin-orbit interaction, and the quantum Hall effect. As a result, they have been proposed as a promising platform for nanoelectronics fabrication. This growing interest in TMO-based systems stems from their ability to provide unique opportunities for studying and harnessing novel phenomena at the interface, paving the way for advancements in both fundamental science and technological applications.

Precise control of atomic arrangements during fabrication is essential for the study of artificial materials. Currently, pulsed laser deposition systems are the preferred tools for growing interfaces and thin films in this context. In this thesis, our primary focus is on fabricating interfaces of transition metal oxides (TMOs) and investigating the carrier dynamics of the resulting two-dimensional electron gas (2DEG) formed at these interfaces. Strontium titanate (STO) is commonly used as a substrate for interface fabrication due to its cubic crystal structure and lattice constant, which closely matches that of a range of perovskite oxides. In our initial work, we developed a protocol to obtain a single-terminated step-terrace-like structure on <001>, <110>, and <111> oriented STO single crystals. These prepared substrates were subsequently utilized for interface fabrication. To achieve improved results, we employed chemical etchants, specifically buffered hydrofluoric acid (BHF) and acid mixtures. Various parameters can impact the surface of the substrate during the etching process, such as temperature, concentration (pH), and time. In this study, we focused on two crucial parameters: etching time and concentrations when using BHF

etching. However, in the case of ACID etching, the etching time was independent of the crystallographic orientation. To confirm the single termination of the prepared surfaces, we conducted measurements using a lateral force microscope (LFM). The average frictional force observed across the substrate surface provided evidence of the single atomic termination.

Overall, this research effort emphasizes the importance of precise control over atomic arrangements during fabrication processes and provides insights into the formation of 2DEGs at TMO interface.

The discovery of 2DEG at the interface of LAO/STO was extensively studied because of its emergent properties like superconductivity, ferromagnetism, ferroelectricity, and many more as discussed in Chapter 1. The genesis of the 2DEG at the interface of two band insulators is the intriguing question highlighted by this discovery. Many models have been suggested to explain the same are electronic reconstruction, cation intermixing, oxygen vacancy, and structural distortion, among all of them the most accepted model is electronic reconstruction. We have taken LVO/STO as a case to study electronic reconstruction. Employing photoluminescence and transport measurement, we calculated the spatial carrier distribution, carrier density, energy subbands, wave function, and quantum well depth at the interface. The calculated carrier density is $(2.1 \times 10^{14} \text{ cm}^{-2})$ very close to what was predicted from the electronic reconstruction/polar catastrophe model which is $3 \times 10^{14} \ cm^{-2}$. The carrier density was exponentially decaying but not reaching the zero value indicates that during the fabrication some oxygen vacancies or defects were created. But most of the carriers are confined within the 10 nm region only. We have also shown from the energy subband diagram that the system is confined to 2 dimensions, resulting in discrete energy levels. At low temperatures (3 K), we found that the Hall is non-linear. The nonlinearity of Hall is described by two band model/multiple conducting channels. Finally, the energy subbands and the carrier density calculated from the Hall data were overlapping with the optical data.

Furthermore, in search of some novel features, we have switched from STO to KTO substrate. Since KTO shows high spin-orbit coupling strength than STO (almost 25 times higher). We have taken LVO/KTO to study the carrier dynamics of the 2DEG forming with KTO substrate. The results were very similar to LVO/KTO results. For both interfaces, the full-width half maxima of
the depth of the conducting channel at the interface are estimated to be around 10 nm by using spectroscopy techniques of photoluminescence and time-correlated single-photon counting: suggesting a quasi-2-dimensional nature of the conducting electrons.

We have taken the critical thickness sample to study the shape of the Fermi surface and unravel the dynamics of carriers at the LVO/KTO interface. Where the thickness of the LVO film is 4 ML, which is the critical thickness required for the interface to be conducted. We have done the angledependent magnetotransport measurement at different temperature values. In our measurement, we observed oscillations in both cases when B//E and when $B\perp E$. We have also done the angledependent measurement in the plane of the sample and observed oscillations for each angle. This indicates that the Fermi surface is 3 dimensional. The oscillations are more prominent in the plane of the sample suggesting the non-spherical nature of the Fermi surface. The Landau fan diagram plotted from the oscillations is non-linear (usually Landau fan diagram is a linear function between n and 1/B). This nonlinearity is explained by the modified Onsager quantization rule. The nonlinearity is coming from the zero magnetic field susceptibility term. This zero magnetic field susceptibility is suggesting that we have some non-trivial spin texture in the k-space. In addition, we have observed a surprising dependence on quantum mobility when the electric field (E) and magnetic field (B) are applied in the plane of the interface. Quantum mobility depends on the relative orientation of E and B. The quantum mobility in the B//E configuration was four times larger compared to the mobility in the B_LE configuration. These observations may open up new directions in the field of quantum oscillation observed in systems with non-trivial electronic and magnetic textures in the momentum space.

6.2 **Future Aspects:**

In the realm of material science, the study of carrier dynamics plays a pivotal role in harnessing the potential of materials for practical applications. In the context of this thesis, we aimed to unravel the intricacies of carrier dynamics within the two-dimensional electron gas (2DEG) at the interface of two transition metal oxides. To delve into this phenomenon, we chose the LVO/STO interface as a captivating case study. Remarkably, we discovered that the optical method proved to be just as effective as transport measurements in unraveling the mysteries of carrier dynamics. Looking ahead, our curiosity is piqued by the prospect of inducing the 2DEG in more exotic parent materials, such as KTO. KTO holds tremendous interest due to the presence of the 5d transition

metal Ta, which exhibits remarkable emergent properties including high spin-orbit coupling, low effective mass, and the intriguing realm of correlated electron physics, among others. Our investigation focused on the LVO/KTO interface, where we encountered fascinating phenomena that defied convention. Notably, we observed aperiodic Shubnikov de-Haas oscillations and non-linear Landau fan diagrams, signifying the nontrivial nature of the material's band structure. In the future, we intend to explore the depths of the band structure by conducting Angle-resolved photoelectron spectroscopy measurements at the interface. Furthermore, the LVO/KTO interface exhibited exceptionally high spin-orbit coupling and a substantial Rashba order parameter. This has instilled in us a strong motivation to investigate the inverse Edelstein effect, also known as a spin-to-charge conversion, within the LVO/KTO system. Additionally, KTO, being a quantum paraelectric material, holds the potential for achieving ferroelectricity through doping or by applying strain and stress. The emergence of ferroelectricity would serve as a valuable tool in manipulating the superconducting temperature.

The combination of high spin-orbit coupling and induced ferroelectricity has inspired us to explore the magnetoelectric effects within KTO or KTO-based interfaces in the future. Furthermore, KTO exhibits a high Seebeck coefficient, making it an advantageous material for thermoelectric devices. These remarkable characteristics and features are poised to revolutionize the landscape of future electronics and technology

List of Publications

(A) Included in the thesis

(a). Published

- <u>Anamika Kumari</u>, Joydip De, Sushanta Dattagupta, Hirendra N Ghosh, Santanu Kumar Pal, S Chakraverty, <u>Probing conducting interfaces by combined photoluminescence and transport</u> <u>measurements: LaVO₃ and SrTiO₃ interface as a case study</u>, *Phys. Rev. B* (Letters) 104(8), L081111(2021).
- Harsha Silotia, <u>Anamika Kumari</u>, Anshu Gupta, Joydip De, Santanu Kumar Pal, Ruchi Tomar, Suvankar Chakraverty, <u>Possible Signatures of Chiral Anomaly in the</u> <u>Magnetoresistance of a Quasi-2-Dimensional Electron Gas at the Interface of LaVO₃ and KTaO₃, Adv. Elec. Mater. 8(9), 2200195(2022).
 </u>
- <u>Anamika Kumari</u>, Anshu Gupta, Saveena Goyal, Ripudaman Kaur, Suvankar Chakraverty Realization of the atomically flat single terminated surface of SrTiO₃ (001), (110), and (111) substrate by chemical etching. *Indian J. Phys.* (1-7), (2023).

(b). Not published

1. <u>Anamika Kumari</u>, Harsha Silotia, Sunit Das, Shama, Vivek K Malik, Amit Aggarwal, Suvankar Chakraverty, A new perspective in the Shubnikov de Haas oscillation at the conducting interface of LaVO₃ and KTaO₃: Signature of the non-trivial spin texture in momentum space and angular dependence of mobility in the quantum mobility.

(B) Not included in the thesis

(a). Published

- Anshu Gupta, Harsha Silotia, Anamika Kumari, Manish Dumen, Saveena Goyal, Ruchi Tomar, Neha Wadehra, Pushan Ayyub, and Suvankar Chakraverty. *Advanced Materials*, 34, 2106481 (2022).
- Ripudaman Kaur, <u>Anamika Kumari</u>, Bibek Ranjan Satapathy, Anshu Gupta, Suvankar Chakraverty, Effect of Light and Electrostatic Gate at oxide interface LaFeO₃-SrTiO₃ at Room Temperature. Adv. Phys. Res., https://doi.org/10.1002/apxr.202200087 (2023).
- Anshu Gupta, Deepak S Kathyat, Arnob Mukherjee, <u>Anamika Kumari</u>, Ruchi Tomar, Yogesh Singh, Sanjeev Kumar, Suvankar Chakraverty, Unique Signatures of Rashba Effect in Angle Resolved Magnetoresistance, *Adv. Quan. Tech.* 5(1), 2100105(2022).
- Soumyadip Halder, Mona Garg, Nikhlesh Singh Mehta, <u>Anamika Kumari</u>, Rajesh Sharma, Tanmoy Das, Suvankar Chakraverty, Goutam Sheet, <u>Unconventional</u> <u>Superconductivity at LaVO₃/SrTiO₃ Interfaces</u>, ACS Appl. Elect. Mater. https://doi.org/10.1021/acsaelm.2c01027 (2022).

(b). Not published

 Ripudaman Kaur, Anamika Kumari, Mohd Anas, Bibek Ranjan Satapathy, Sanjeev Kumar, V. K. Malik, D.D. Sarma, Suvankar Chakraverty, Room-temperature transparent oxide spin electronics, Under revision in Physical Review Letter.
 Manuscript ID: LA17985

Workshops and Conferences

- Oral Presentation at "The 4th International Conference on Materials: ADVANCED AND EMERGING MATERIALS, Spain (19th October 2022 to 21st October 2022)" Organized by MDPI.
- Oral Presentation at "Conference on Emergent Phenomena in Quantum Materials (E-QMAT 2022)" organized by IIT-Roorkee, India (12th to 14th October 2022).
- Poster Presentation in "Annual Conference on Quantum Condensed Matter (QMAT-2022)" Organized by IIT-Kanpur, India (18th to 22nd September 2022).
- Poster presentation in "Institute of Nano Science and Technology-Indian Institute of Science Education and Research 1st bilateral Meeting" organized by Institute of Nano Science and Technology, Mohali, Punjab India (14th -15th March 2022).
- Poster Presentation in "Indo-Japan Workshop on Interface Phenomena for Spintronics (IJW-IPS 2022)" organized by National Institute of Science Education and Research, Bhubaneswar, India (8th March 2022 to 10th March 2022).
- Oral Presentation at "2nd PNM22 (2022) (Physics of nano-Materials)" by Quantum Material and Devices Unit in the Institute of Nano Science and Technology, Mohali, Punjab, India.
- Oral Presentation at "1st PNM21 (2021) (Physics of nano-Materials)" by Quantum Material and Devices Unit in the Institute of Nano Science and Technology, Mohali, Punjab, India.
- Contributed Talk to "Asia-Pacific Conference on Condensed Matter Physics 2021 (Dec 1st to 3rd Online)" Organized by Institut de Chimie des Milieux et Matériaux de Poitiers, France.
- Participated in "1st Online RIEC International Workshop on Spintronics" organized by Research Institute of Electrical Communication (RIEC), Tohoku University, Japan (18th November 2021).