Investigation of Titanium Sesquioxide Ti$_2$O$_3$: Synthesis and Physical Properties

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ABSTRACT

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Titanium is one of the earth-abundant elements, and its oxides including titanium dioxide (TiO$_2$) and strontium titanium oxide (SrTiO$_3$) are widely used in technologies of electronics, energy conversion, catalysis, sensing, and so on. Generally, the Ti ions in these compounds have a valence of 4+ with the outer shell electron configuration of 3$d^0$. In this thesis, we explore interface and titanite containing Ti$^{3+}$ ions with $3d^1$ itinerate electrons, which we believe open new doors towards some new titanite-based technologies.

In the first part of this thesis (Chapter 3), we will discuss the nanoscale chemical and valence evolution at a metal/oxide interface: Ti/SrTiO$_3$. In many devices, metal-oxide interfaces are ubiquitous and play important roles in the performance of a wide range of electronic and optoelectronic devices. This motivated us to examine the microscopic structure of the interfaces between strontium titanium oxide and metals. In this work, one unit cell of cubic perovskite Ti$_2$O$_3$ was observed at the Ti/SrTiO$_3$ interface, and oxygen diffusion depth of ~3.2 nm was observed in the sample fabricated at room temperature. Meanwhile, oxygen vacancy domains in the SrTiO$_3$ substrates was observed and characterized by low angle annular dark field (LAADF) imaging and electron energy loss spectra (EELS).

In the main part of this thesis, we will focus on the structure and physical properties of Ti$_2$O$_3$, a titanite which has received less attention so far in the research community.
Different from TiO$_2$ and SrTiO$_3$, Ti$_2$O$_3$ has a much narrower band-gap (~0.1 eV), and we will discuss some preliminary results of its physical properties and potential applications.

In Chapter 4, we will discuss the photothermal application and mid-infrared photodetectors using Ti$_2$O$_3$ nanoparticles based on its ultra-narrow bandgap. Photothermal effect via a Ti$_2$O$_3$/membrane structure is further applied to seawater desalination. A high temperature of 70 °C was achieved when this Ti$_2$O$_3$/membrane double layer structure floating on top surface of water subjected to the white light illumination of 7 kW/cm$^2$. Furthermore, room temperature mid-infrared (10 μm) photodetectors based on Ti$_2$O$_3$/graphene hybrid structure was fabricated and studied. The photoresponsivity of this hybrid device, operated from 4.5 to 10 μm, is above ~ 100 A/W, which, to our knowledge, is the highest value for the mid-infrared photodetectors operating in the photocurrent (PC) mode.

In chapter 5, structure, optical, transport properties of Ti$_2$O$_3$ epitaxial thin films on sapphire fabricated by pulsed laser deposition (PLD) will be discussed. By tailoring growth conditions, two different: trigonal and orthorhombic, of Ti$_2$O$_3$ were stabilized on Al$_2$O$_3$ substrates. More interestingly, the orthorhombic Ti$_2$O$_3$ has never been reported, and, moreover, superconductivity (~8 K) and high temperature ferromagnetism (up to 700 K) was discovered in this new stabilized phase. More details of the physical properties of Ti$_2$O$_3$ will be discussed in the following chapters of this dissertation.

**Keywords:** Titanium sesquioxide; interface; nanoparticles; epitaxial thin films; superconductivity; ferromagnetism; carrier behavior
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DC – Direct Current
FFT – Fast Fourier Transform
FIB – Focused Ion Beam
ITO – Indium Tin Oxide
PLD – Pulsed Laser Deposition
SEM – Scanning Electron Microscope
STEM – Scanning Transmission Electron Microscopy
EELS – Electron Energy Loss Spectra
TEM – Transmission Electron Microscopy
HAADF – High Angle Annular Dark Field
ABF – Annular Bright field
TFT – Thin-Film Transistor
FET – Field Effect Transistor
XPS – X-ray Photoelectron Spectroscopy
XRD – X-ray Diffraction
AFM – Atomic Force Microscopy
TiO$_2$ – Titanium Dioxide
Ti$_2$O$_3$ – Titanium Sesquioxide
STO – Strontium Titanate
PPMS – Physical Property Measurement System
SQUID – Superconducting Quantum Interference Device
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Chapter 1 Introduction

1.1 Importance of Metal/oxide interfaces in modern technologies

Interactions between metals and oxides at their interfaces are key factors determining the performance of metal/oxide hetero-junctions, which are ubiquitous in modern technologies including electronics, photonics, catalysis, energy conversion, sensors, and so on (Fig. 1-1). It is well recognized that metal/semiconductor interfaces must be properly prepared and controlled in order to achieve the optimal performance in functional devices. For example, ohmic contacts play a key role in the fabrication of high-performance optoelectronics such as light emitting diodes and laser diodes.\textsuperscript{[1-3]} Such transparent contacts allow high charge injection and improve thermal stability, which is critical for reliable device operation. Electrodes with different metals and their combinations have been extensively explored,\textsuperscript{[4-8]} which motivated researchers to investigate the microscopic structures of the interfaces between semiconductors and metals.

Functional oxides have a broad range of technological applications due to their unique properties such as ferroelectricity, piezoelectricity, high-$T_C$ superconductivity, colossal magnetoresistance, and so on. Considering majority of metals form Schottky barriers when deposited on oxide surfaces,\textsuperscript{[9-11]} fabricating reliable, low-resistance ohmic contacts is of critical importance to the advance of oxide electronics. Among functional oxides, Ti-based oxides including titanium dioxide (TiO\textsubscript{2}) and strontium titanium oxide (SrTiO\textsubscript{3}) are widely investigated. STO is well-known as a popular substrate not only for film growth, but also for many interesting properties, such as superconductivity,\textsuperscript{[12]} blue-light emission,\textsuperscript{[13-15]} insulator-metal transition\textsuperscript{[16]} and photocatalysis.\textsuperscript{[17]} Recently, STO
has also been explored for resistive switching memory\cite{18} and optoelectronic applications.\cite{19-21} Ti is one of the earth-abundant elements, and it is frequently used to form contacts with oxides. Although the importance of metal/oxide interfaces has been well recognized,\cite{22-24} there have been few works devoted to understanding the microscopic phenomena at such buried interfaces.

Fig. 1-1 Schematic presentation for the importance of metal/oxide interfaces in modern technologies.

1.2 Narrow band-gap semiconductors

Narrow band-gap semiconductors have a smaller band gap than silicon ($E_g = 1.12$ eV). And they usually have excellent transport properties and strong light absorption, extending to mid-infrared range. Therefore, these semiconductors are used in infrared
detectors and thermoelectric devices. Following is a list of narrow band-gap semiconductors with $E_g < 0.4$ eV (300 K).

**Tab. 1-1** List of narrow band-gap ($E_g < 0.4$ eV (300 K)) semiconductors.

<table>
<thead>
<tr>
<th>Group</th>
<th>Material</th>
<th>Formula</th>
<th>Band gap (eV)</th>
<th>Gap type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV</td>
<td>Silicon</td>
<td>Si</td>
<td>1.12</td>
<td>indirect</td>
<td>Used in conventional crystalline silicon (c-Si) solar cells, and in its amorphous form as amorphous silicon (a-Si) in thin film solar cells. Most common semiconductor material in photovoltaics; dominates worldwide PV market; easy to fabricate; good electrical and mechanical properties. Forms high quality thermal oxide for insulation purposes.</td>
</tr>
<tr>
<td>IV</td>
<td>Gray tin</td>
<td>Sn</td>
<td>0.08</td>
<td>indirect</td>
<td>Low temperature allotrope (diamond cubic lattice).</td>
</tr>
<tr>
<td>VI</td>
<td>Tellurium</td>
<td>Te</td>
<td>0.33</td>
<td>direct</td>
<td></td>
</tr>
<tr>
<td>III-V</td>
<td>Indium arsenide</td>
<td>InAs</td>
<td>0.36</td>
<td>direct</td>
<td>Used for infrared detectors for 1–3.8 μm, cooled or uncooled. High electron mobility. InAs dots in InGaAs matrix can serve as quantum dots. Quantum dots may be formed from a monolayer of InAs on InP or GaAs. Strong photo-Dember emitter, used as a terahertz radiation source.</td>
</tr>
<tr>
<td>III-V</td>
<td>Indium</td>
<td>InSb</td>
<td>0.17</td>
<td>direct</td>
<td>Used in infrared detectors and</td>
</tr>
<tr>
<td>IV-VI</td>
<td>Lead selenide</td>
<td>PbSe</td>
<td>0.27</td>
<td>direct</td>
<td>Used in infrared detectors for thermal imaging. Nanocrystals usable as quantum dots.</td>
</tr>
<tr>
<td>--------</td>
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<td>------</td>
<td>------</td>
<td>--------</td>
<td>------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>IV-VI</td>
<td>Lead (II) sulfide</td>
<td>PbS</td>
<td>0.37</td>
<td></td>
<td>Mineral galena, first semiconductor in practical use, used in cat's whisker detectors; the detectors are slow due to high dielectric constant of PbS. Oldest material used in infrared detectors. At room temperature can detect SWIR, longer wavelengths require cooling.</td>
</tr>
<tr>
<td>IV-VI</td>
<td>Lead telluride</td>
<td>PbTe</td>
<td>0.32</td>
<td></td>
<td>Low thermal conductivity, good thermoelectric material.</td>
</tr>
<tr>
<td>V-VI, layered</td>
<td>Bismuth telluride</td>
<td>Bi$_2$Te$_3$</td>
<td>0.16</td>
<td>indirect</td>
<td>Efficient thermoelectric material when alloyed with selenium or antimony. Narrow-gap layered semiconductor. High electrical conductivity, low thermal conductivity. Topological insulator.</td>
</tr>
<tr>
<td>II-V</td>
<td>Cadmium arsenide</td>
<td>Cd$_3$As$_2$</td>
<td>0.14</td>
<td>N-type intrinsic semiconductor. Very high electron mobility. Used in infrared detectors, photodetectors, dynamic thin-film pressure sensors, and magnetoresistors. Recent measurements suggest that 3D Cd$_3$As$_2$ is actually a zero band-gap Dirac semimetal in which electrons behave relativistically as in graphene.</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>III-V</td>
<td>Indium gallium arsenide</td>
<td>In$<em>x$Ga$</em>{1-x}$As</td>
<td>0.36-1.43</td>
<td>direct</td>
<td>Well-developed material. Can be lattice matched to InP substrates. Use in infrared technology and thermophotovoltaics. Indium content determines charge carrier density. For $x=0.015$, InGaAs perfectly lattice-matches germanium; can be used in multijunction photovoltaic cells. Used in infrared sensors, avalanche photodiodes, laser diodes, optical fiber communication detectors, and short-wavelength infrared cameras.</td>
</tr>
<tr>
<td>III-V</td>
<td>Aluminium indium arsenide</td>
<td>Al$<em>x$In$</em>{1-x}$As</td>
<td>0.36-2.16</td>
<td>direct/indirect</td>
<td>Buffer layer in metamorphic HEMT transistors, adjusting lattice constant between GaAs substrate and GaInAs channel. Can form layered heterostructures acting as quantum wells, in e.g. quantum cascade lasers.</td>
</tr>
<tr>
<td>II-VI</td>
<td>Mercury cadmium</td>
<td>HgCdTe</td>
<td>0-1.5</td>
<td>Known as &quot;MerCad&quot;. Extensive use in sensitive</td>
<td></td>
</tr>
</tbody>
</table>
Mercury cadmium telluride (HgCdTe) is a common material capable of operating in both 3–5 μm and 12–15 μm atmospheric windows. It can be grown on CdZnTe.

Commercial Ti$_2$O$_3$ is prepared by reacting titanium dioxide with titanium metal at 1600 °C. It has the corundum (Al$_2$O$_3$) structure, trigonal space group R$ar{3}$c, Z=2 (rhombohedral system); Z=6 (hexagonal system). At around 200 °C, there is a metal-insulator transition. Its band gap is between 0.1 eV and 0.2 eV at room temperature.

Infrared photodetection is one of the most important applications of the narrow bandgap semiconductors. As shown in **Fig. 1-2**, the earth’s atmospheric transmittance around 10 μm is very high, which can be used for telecommunications. However, in this
range, the most effective material by now is HgCdTe, as shown in Fig. 1-3. The application of Ti$_2$O$_3$ in this range has not been studied or reported yet.

![Fig. 1-2 Rough plot of Earth’s atmospheric transmittance (or opacity) to various wavelengths of electromagnetic radiation.][25]

![Fig. 1-3 Enlarged plot of Earth’s atmospheric transmittance (or opacity) at the mid-infrared range.](image)

By now, HgCdTe is the only common material that can detect infrared radiation in both of the accessible atmospheric windows. These are from 3 to 5 µm (the mid-wave infrared window, abbreviated MWIR) and from 8 to 12 µm (the long-wave window, LWIR). HgCdTe is the common materials in the photodetectors of Fourier transform infrared spectrometers. It is also found in military field, remote sensing and infrared
astronomy research. Military technology has depended on HgCdTe for night vision. In particular, the US air force makes extensive use of HgCdTe on all aircraft, and to equip airborne smart bombs. A variety of heat-seeking missiles are also equipped with HgCdTe detectors. HgCdTe detector arrays can also be found at most of the world’s major research telescopes including several satellites.

Fig. 1-4 Photo of a cooled thermal core based on MCT detectors.[26]

The main limitation of HgCdTe-based LWIR detectors is that they need cooling to near liquid nitrogen temperatures (77K) to reduce the thermally excited noise, as shown in Fig. 1-4. MWIR HgCdTe cameras can be operated at temperatures accessible to thermoelectric coolers with a small performance penalty. Hence, HgCdTe detectors are relatively heavy compared to bolometers and require maintenance. Thus, room temperature mid-infrared photodetectors are significantly crucial for portable applications in telecommunication and LWIR infrared cameras.

Furthermore, most of the narrow band-gap semiconductors contain Hg, As, Pb, and Te elements, which makes them poisonous or hazardous, while Ti$_2$O$_3$ is a narrow band-gap oxide semiconductor with no harm to the environment. Thus, it could be a wonderful
material for infrared applications. Therefore, it is crucial to investigate its physical properties and applications. Moreover, room temperature mid-infrared photodetectors based on Graphene/Ti$_2$O$_3$ nanoparticles will be discussed in chapter 4.

1.3 Structures of Sesquioxides

As the last part of the introduction, we would like to comment on the structures of Ti$_2$O$_3$. Extensive efforts have been undertaken to figure out a general structural forming sequence of sesquioxides, which usually have a corundum-type lattice (R$\overline{3}$c space group, #167) at ambient conditions. A main transition path or sequence under gradual compression has been reported $^{[27]}$, that is corundum $\rightarrow$ post corundum (presumably of Rh$_2$O$_3$ (II) (Pbna space group, #60) or perovskite-type (Pnma space group, #62)) $\rightarrow$ post perovskite (Cmcm space group, #63, the CaIrO$_3$ structural type). And some other reports verified the same forming sequence for Al$_2$O$_3$ $^{[28]}$, Fe$_2$O$_3$ $^{[29, 30]}$ and Cr$_2$O$_3$ $^{[31]}$. Six different lattices of Ti$_2$O$_3$ were predicted, which are corundum, Rh$_2$O$_3$ (II)-type, perovskite, post-perovskite, $\alpha$-Gd$_2$S$_3$-type, and Th$_2$S$_3$-type, as shown in Fig. 1-1. However, only corundum and Th$_2$S$_3$-type were experimentally found $^{[27]}$. 


Fig. 1-5 Potential structures for sesquioxides. All these lattice structures had been found in other sesquioxides like In$_2$O$_3$, Fe$_2$O$_3$, and Cr$_2$O$_3$. 
Chapter 2 Experimental techniques

2.1 Pulsed laser deposition

Pulsed laser deposition (PLD)\textsuperscript{[32]} is a physical vapor deposition (PVD) technique where a high-power pulsed laser beam is focused inside a vacuum chamber to strike a target of the material that is to be deposited (\textbf{Fig. 2-1} and \textbf{Fig. 2-2}). This material is vaporized from the target (in a plasma plume) which deposits it as a thin film on a substrate (such as a silicon wafer facing the target). This process can occur in ultra-high vacuum or in the presence of a background gas, such as oxygen which is commonly used when depositing oxides to fully oxygenate the deposited films.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{pulsed_laser_deposition_system.png}
\caption{Photo of the pulsed laser deposition system.}
\end{figure}
While the basic setup is simple relative to many other deposition techniques, the physical phenomena of laser-target interaction and film growth are quite complex. When the laser pulse is absorbed by the target, energy is first converted to electronic excitation and then into thermal, chemical and mechanical energy, which result in evaporation, ablation, plasma formation and even exfoliation. The ejected species expand into the surrounding vacuum in the form of a plume containing many energetic species including atoms, molecules, electrons, ions, clusters, particulates and molten globules, before depositing on the typically hot substrate.
The detailed mechanisms of PLD are very complex including the ablation process of the target material by the laser irradiation, the development of a plasma plume with high energetic ions, electrons as well as neutrals and the crystalline growth of the film itself on the heated substrate. The process of PLD can generally be divided into five stages: 1) Laser absorption on the target surface; 2) Laser ablation of the target material and creation of a plasma; 3) Dynamic of the plasma; 4) Deposition of the ablation material on the substrate; 5) Nucleation and growth of the film on the substrate surface. Each of these steps is crucial for the crystallinity, uniformity and stoichiometry of the resulting film.

2.1.1 Laser ablation of the target material and creation of a plasma

The ablation of the target material upon laser irradiation and the creation of plasma are very complex processes. The removal of atoms from the bulk material is done by vaporization of the bulk at the surface region in a state of non-equilibrium. In this the incident laser pulse penetrates into the surface of the material within the penetration depth. This dimension is dependent on the laser wavelength and the index of refraction of the target material at the applied laser wavelength and is typically in the region of 10 nm for most materials. The strong electrical field generated by the laser light is sufficiently strong to remove the electrons from the bulk material of the penetrated volume. This process occurs within 10 ps of an ns laser pulse and is caused by non-linear processes such as multiphoton ionization which are enhanced by microscopic cracks at the surface, voids, and nodules, which increase the electric field. The free electrons oscillate within the electromagnetic field of the laser light and can collide with the atoms of the bulk material thus transferring some of their energy to the lattice of the target material within
the surface region. The surface of the target is then heated up and the material is vaporized.

2.1.2 Dynamic of the plasma

In the second stage the material expands in the plasma parallel to the normal vector of the target surface towards the substrate due to Coulomb repulsion and recoil from the target surface. The spatial distribution of the plume is dependent on the background pressure inside the PLD chamber. The density of the plume can be described by a \( \cos^n(x) \) law with a shape similar to a Gaussian curve. The dependency of the plume shape on the pressure can be described in three stages: 1) Vacuum stage, where the plume is very narrow and forward directed; almost no scattering occurs with the background gases. 2) The intermediate region where a splitting of the high energetic ions from the less energetic species can be observed. The time-of-flight (TOF) data can be fitted to a shock wave model; however, other models could also be possible. 3) High pressure region where we find a more diffusion-like expansion of the ablated material. Naturally this scattering is also dependent on the mass of the background gas and can influence the stoichiometry of the deposited film.

The most important consequence of increasing the background pressure is the slowing down of high energetic species in the expanding plasma plume. It has been shown that particles with kinetic energies around 50 eV can resputter the film already deposited on the substrate. This results in a lower deposition rate and can furthermore result in a change in the stoichiometry of the film.
2.1.3 Deposition of the ablation material on the substrate

The third stage is important to determine the quality of the deposited films. The high energetic species ablated from the target are bombarding the substrate surface and may cause damage to the surface by sputtering off atoms from the surface but also by causing defect formation in the deposited film. The sputtered species from the substrate and the particles emitted from the target form a collision region, which serves as a source for condensation of particles. When the condensation rate is high enough, a thermal equilibrium can be reached and the film grows on the substrate surface at the expense of the direct flow of ablation particles and the thermal equilibrium obtained.

2.1.4 Nucleation and growth of the film on the substrate surface

The nucleation process and growth kinetics of the film depend on several growth parameters including:

- **Laser parameters** – several factors such as the laser density [J/cm²], laser energy, and ionization degree of the ablated material will affect the film quality, the stoichiometry, and the deposition flux. Generally, the nucleation density increases when the deposition flux is increased.

- **Surface temperature** – The surface temperature has a large effect on the nucleation density. Generally, the nucleation density decreases as the temperature is increased.

- **Substrate surface** – The nucleation and growth can be affected by the surface preparation (such as chemical etching), the miscut of the substrate, as well as the roughness of the substrate.
**Background pressure** – Common in oxide deposition, an oxygen background is needed to ensure stoichiometric transfer from the target to the film. If, for example, the oxygen background is too low, the film will grow off stoichiometry which will affect the nucleation density and film quality.

In the PLD, a large supersaturation occurs on the substrate during the pulse duration. The pulse lasts around $10^{-40}$ microseconds depending on the laser parameters. This high supersaturation causes a very large nucleation density on the surface as compared to molecular beam epitaxy or sputtering deposition. This nucleation density increases the smoothness of the deposited film. Depending on the deposition parameters, three growth modes are possible:

**Step-flow growth** – All substrates have a miscut associated with the crystal. These miscuts give rise to atomic steps on the surface. In step-flow growth, atoms land on the surface and diffuse to a step edge before they have a chance to nucleate a surface island. The growing surface is viewed as steps traveling across the surface. This growth mode is obtained by deposition on a high miscut substrate, or depositing at elevated temperatures.

**Layer-by-layer growth** – In this growth mode, islands nucleate on the surface until a critical island density is reached. As more material is added, the islands continue to grow until the islands begin to run into each other. This is known as coalescence. Once coalescence is reached, the surface has a large density of pits. When additional material is added to the surface the atoms diffuse into these pits to complete the layer. This process is repeated for each subsequent layer.

**3D growth** – This mode is similar to the layer-by-layer growth, except that once an island is formed an additional island will nucleate on top of the 1st island. Therefore the
growth does not persist in a layer by layer fashion, and the surface roughens each time material is added.

2.2 X-ray diffraction

X-ray Diffraction (XRD) is one of the primary techniques used by mineralogists and solid state chemists to examine the physico-chemical make-up of solids (Fig. 2-3). It is a versatile, non-destructive analytical technique that reveals detailed information about the chemical composition and type of molecular bond of crystalline phase. It is an efficient technique to expose the crystallographic structure of natural and manufactured materials and a technique in which analytical results are correlated with references and standards of the International Centre for Diffraction Data (ICDD).
There are many advantages of XRD, such as precise phase determination of the solid material; the X-ray spectra generated provide a structural fingerprint of the unknown; determination of material characteristic; and highest quality and reproducibility.

Diffraction is a scattering phenomenon. When X-rays are incident on crystalline solids, they are scattered in all directions. In some of these directions, the scattered beams are completely in phase and reinforce one another to form the diffracted beams. The Bragg’s law describes the conditions under which this would occur. It is assumed that a perfectly parallel and monochromatic X-ray beam, of wavelength $\lambda$, is incident on a crystalline sample at an angle $\theta$ (Fig. 2-4).
Fig. 2-4 Diagram for the principle of XRD (Bragg’s Law).

The concept of X-ray diffraction can be described by the Bragg's Law that is diffraction will occur if:

\[ 2d \sin \theta = n\lambda \quad \text{or} \quad d = \frac{n\lambda}{2\sin \theta} \]  

Where d is the distance between atomic planes, n is integer (1, 2, …, n), \( \lambda \) is the wavelength of the x-ray, and \( \theta \) is the angle of incidence of the x-ray beam and the atomic planes. \( 2d \sin \theta \) is the path length difference between two incident x-ray beams where one x-ray beam takes a longer, but parallel, path because it "reflects" off an adjacent atomic plane. This path length difference must equal an integer value of the \( \lambda \) of the incident X-ray beams for constructive interference to occur such that a reinforced diffracted beam is produced.

By varying the angle \( \theta \), the Bragg's Law conditions are satisfied by different d-spacing in polycrystalline materials. Plotting the angular positions and intensities of the resultant diffracted peaks of radiation produces a pattern, which is characteristic of the sample. Where a mixture of different phases is present, the resulting diffractogram is formed by addition of the individual patterns. Based on the principle of X-ray diffraction, a wealth
of structural, physical and chemical information about the material investigated can be obtained.

For a given $\lambda$ of incident x-rays and interplanar spacing, $d$, in a mineral, only specific $\theta$ angles will satisfy the Bragg equation. No "reflections" will occur until the incident beam makes an angle $\theta$ that satisfies the Bragg equation with $n = 1$. Continued rotation leads to other "reflections" at higher values of $\theta$ and correspond to when $n = 2, 3, \ldots$ etc.; these known as 1st, 2nd, 3rd order, etc., "reflections".

### 2.3 Raman spectroscopy

Raman spectroscopy is a spectroscopic technique used to observe vibrational, rotational, and other low-frequency modes in a system (Fig. 2-5). It relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the vibrational modes in the system. Infrared spectroscopy yields similar, but complementary, information.
Typically, a sample is illuminated with a laser beam. Light from the illuminated spot is collected with a lens and sent through a monochromator. Wavelengths close to the laser line due to elastic Rayleigh scattering are filtered out while the rest of the collected light is dispersed onto a detector. Spontaneous Raman scattering is typically very weak, and as a result the main difficulty of Raman spectroscopy is separating the weak inelastically scattered light from the intense Rayleigh scattered laser light. Historically, Raman spectrometers used holographic gratings and multiple dispersion stages to achieve a high degree of laser rejection. In the past, photomultipliers were the detectors of choice for dispersive Raman setups, which resulted in long acquisition times. However, modern instrumentation almost universally employs notch or edge filters for laser rejection and spectrographs (either axial transmissive (AT), Czerny-Turner (CT) monochromator, or FT (Fourier transform spectroscopy based), and CCD detectors.
The Raman Effect occurs when light impinges upon a molecule and interacts with the electron cloud and the bonds of that molecule. Fig. 2-6 shows the Energy level diagram showing the states involved in Raman signal. For the spontaneous Raman Effect, which is a form of light scattering, a photon excites the molecule from the ground state to a virtual energy state. When the molecule relaxes it emits a photon and it returns to a different rotational or vibrational state. The difference in energy between the original state and this new state leads to a shift in the emitted photon's frequency away from the excitation wavelength. The Raman effects, which is a light scattering phenomenon, should not be confused with absorption (as with fluorescence) where the molecule is excited to a discrete (not virtual) energy level.

If the final vibrational state of the molecule is more energetic than the initial state, then the emitted photon will be shifted to a lower frequency in order for the total energy of the
system to remain balanced. This shift in frequency is designated as a Stokes shift. If the final vibrational state is less energetic than the initial state, then the emitted photon will be shifted to a higher frequency, and this is designated as an anti-Stokes shift. Raman scattering is an example of inelastic scattering because of the energy transfer between the photons and the molecules during their interaction.

A change in the molecular polarization potential or amount of deformation of the electron cloud with respect to the vibrational coordinate is required for a molecule to exhibit a Raman Effect. The amount of the polarizability change will determine the Raman scattering intensity. The pattern of shifted frequencies is determined by the rotational and vibrational states of the sample. This dependence on the polarizability differs from Infrared spectroscopy where the interaction between the molecule and light is determined by the dipole moment; this contrasting feature allows to analyze transitions that might not be IR active via Raman spectroscopy, as exemplified by the rule of mutual exclusion in centrosymmetric molecules.

In colloquial usage, Raman shifts are typically in wavenumbers, which have units of inverse length. In order to convert between spectral wavelength and wavenumbers of shift in the Raman spectrum, the following formula can be used

\[ \Delta \omega = \left( \frac{1}{\lambda_0} - \frac{1}{\lambda_1} \right) \]

Where \( \Delta \omega \) is the Raman shift expressed in wavenumber; \( \lambda_0 \) is the excitation wavelength; and \( \lambda_1 \) is the Raman spectrum wavelength. Most commonly, the units chosen for expressing wavenumber in Raman spectra is inverse centimeters (cm\(^{-1}\)). Since wavelength is often expressed in units of nanometers (nm), the formula above can scale
for this units conversion explicitly, giving \( \Delta \omega (\text{cm}^{-1}) = \left( \frac{1}{\lambda_0 (\text{nm})} - \frac{1}{\lambda_1 (\text{nm})} \right) \times 10^7 \), effectively multiplying by \( \frac{\text{nm}}{\text{cm}} \).

Raman spectroscopy offers several advantages for microscopic analysis. Since it is a scattering technique, specimens do not need to be fixed or sectioned. Raman spectra can be collected from a very small volume (< 1 \( \mu \text{m} \) in diameter); these spectra allow the identification of species present in that volume. Water does not generally interfere with Raman spectral analysis. Thus, Raman spectroscopy is suitable for the microscopic examination of minerals, materials such as polymers and ceramics, cells, proteins and forensic trace evidence. A Raman microscope begins with a standard optical microscope, and adds an excitation laser, a monochromator, and a sensitive detector (such as a charge-coupled device (CCD), or photomultiplier tube (PMT)). FT-Raman has also been used with microscopes. Ultraviolet microscopes and UV enhanced optics must be used when a UV laser source is used for Raman microspectroscopy.

### 2.4 Transmission electron microscopy

Transmission electron microscopy (TEM) is well used in the scientific research, and has become a fundamental tool to assist our research, which is very useful and powerful (Fig. 2-7). TEM operates on the same basic principles as the light microscope but uses electrons instead of light. Actually, what you can see with a light microscope is limited by the wavelength of light. TEMs use electron guns as the "light source" to eject electrons and their much lower wavelength makes it possible to get a resolution a thousand times better than that with a light microscope.
With TEM, people could see objects to the order of a few Angstrom ($10^{-10}$ m), which makes it possible to study small details in the cell or different materials down to atomic levels. The possibility for high magnifications has made the TEM a valuable tool in both medical, biological and materials research.

### 2.4.1 Basic principles of transmission electron microscopy

A "light source" at the top of the microscope emits the electrons that travel through vacuum in the column of the microscope. Instead of glass lenses focusing the light in the light microscope, the TEM uses electromagnetic lenses to focus the electrons into a very...
thin beam. The electron beam then travels through the specimen you want to study. Depending on the density of the material present, some of the electrons are scattered and disappear from the beam. At the bottom of the microscope the un-scattered electrons hit a fluorescent screen, which gives rise to a "shadow image" of the specimen with its different parts displayed in varied darkness according to their density. The image can be studied directly by the operator or photographed with a camera.

Electrons, which come from the condenser system of the TEM, are scattered by the sample, situated in the object plane of the objective lens. The interaction between electrons and the sample can generate many kinds of signals (Fig. 2-8). Electrons scattered in the same direction are focused in the back focal plane, and, as a result, a diffraction pattern is formed there. Electrons coming from the same point of the object are focused in the image plane. In the TEM, the first intermediate image is magnified by further lenses (projective system).

Fig. 2-8 Interaction of electrons with matter. Signals generated when a high-energy beam of electrons interacts with a thin specimen. Most of these signals can be detected in different types of TEM. The directions shown for each signal do not always represent the physical direction of
the signal, but indicate, in a relative manner, where the signal is strongest or where it is detected.[36]

Basically, a transmission electron microscope is a kind of instrument used for recording diffraction patterns similar to an XRD machine as well as for magnifying rather small structures. It is the combination of both possibilities which make such an instrument a universal tool for the investigation of lattice mismatched hetero-structures. The diffraction patterns will contain information on the symmetry of the atomic arrangement of the crystals investigated and the interatomic spacing of individual parts of the lattice mismatched hetero-structures when operating in Selected Area Diffraction (SAD) mode. The micrographs may be used for the determination of the layer morphology and the defect structure when experiments are carried out under well-defined conditions, e.g. by high resolution transmission electron microscopy (HRTEM) or by bright field imaging under two beam conditions in conventional TEM.

2.4.2 Imaging mode in transmission electron microscopy

A transmission electron microscope is constituted of: (1) two or three condenser lenses to focus the electron beam on the sample, (2) an objective lens to form the diffraction in the back focal plane and the image of the sample in the image plane, (3) some intermediate lenses to magnify the image or the diffraction pattern on the screen. If the sample is thin (< 200 nm) and constituted of light chemical elements, the image presents a very low contrast when it is focused.
To obtain an amplitude-contrasted image, an objective diaphragm is inserted in the back focal plane to select the transmitted beam (and possibly few diffracted beam): the crystalline parts in Bragg orientation appear dark and the amorphous or not Bragg oriented parts appear bright. This imaging mode is called bright field (BF) mode (Fig. 2-9). If the diffraction is constituted by many diffracting phases, each of them can be
differentiated by selecting one of its diffracted beams with the objective diaphragm. To do that, the incident beam must be tilted so that the diffracted beam is put on the objective lens axis to avoid off axis aberrations (Fig. 2-10). This mode is called dark field (DF) mode. The BF and DF modes are used for imaging materials to nanometer scale. The signal collected for the dark field image is from the diffracted beam, and the signal collected for the bright field image is from the direct beam.

![Diagram of bright and dark field modes for imaging.](image)

**Fig. 2-10** Bright and dark field modes for imaging.[38]

### 2.4.3 Diffraction mode in transmission electron microscopy

The selected area diaphragm is used to select only one part of the imaged sample for example a particle or a precipitate. This mode is called selected area diffraction SAED. The spherical aberrations of the objective lens limit the area of the selected object to few
hundred nanometers. Nevertheless, it is possible to obtain diffraction patterns of a smaller object by focusing the electron beam with the projector lenses to obtain a small spot size on the object surface (2-10nm). The spots of SAED become disks whose radii depend on the condenser diaphragm. This is called micro-diffraction (Fig. 2-11).

**Fig. 2-11** Micro-diffraction mode.\(^{[37]}\)

SAED and micro-diffraction patterns of a crystal permit to obtain the symmetry of its lattice and calculate its inter-planar distances (with the Bragg law). This is useful to confirm the identification of a phase, after assumptions generally based on the literature of the studied system and on chemical analyses.
It is very clear that how to switch the mode from imaging mode to diffraction mode from Fig. 2-12. In diffraction mode, another intermediate lens (SAD aperture) is inserted to image on the screen the diffraction pattern of the back focal plane, and the objective aperture is removed. Thus, the diffraction mode was achieved from the imaging mode.

The diffraction conditions for a periodic object can be formulated in terms of direct space, i.e. of the real lattice, or in terms of diffraction space, i.e. of the reciprocal lattice. The two formulations have the same physical content but the latter is often more convenient and more directly related to the diffraction pattern. If the attention is focused on the lattice, the diffraction condition is Bragg's law which states that the path difference between waves “reflected” by successive lattice planes is an integer number of wavelength (Fig. 2-13)
\[ 2a_{hkl}\sin\theta_{hkl} = n\lambda \] (2.3)

where \(a_{hkl}\) denotes the interplanar spacing between lattice planes characterized by the set of Miller indices \((hkl)\), \(\theta_{hkl}\) is the corresponding Bragg angle and \(n\) is an integer. This statement might create the wrong impression that “reflection” takes place. However, the difference to specular reflection is important: only for the discrete angles \(\theta_{hkl}\) does “reflection” take place, whereas in specular reflection all angles are permitted. This clearly shows that we have, in fact, interference rather than reflection. Since the notation “reflection” is nevertheless been extremely useful, especially in structure determination, it continues to be used by microscopists. Due to the small wavelength of electron (\(\approx 2 \times 10^{-3}\) nm) Bragg angles are quite small (\(\approx 10^{-3}\) mrad) in transmission electron microscopy and Bragg’s law can often be approximated by

\[ 2a_{hkl}\theta_{hkl} = n\lambda \] (2.4)

In reciprocal space the diffraction condition can be formulated in terms of Ewald’s sphere, i.e.

\[ \mathbf{k}_g = \mathbf{k}_0 + \mathbf{g}_{hkl} \] (2.5)

where \(\mathbf{k}_0\) is the wave vector of the incident plane wave \((\mathbf{k}_0 = (1/\lambda)\mathbf{e}_n\), where \(\mathbf{e}_n\) is the normal to the plane wave front) and \(\mathbf{k}_g\) is the wave vector of the scattered wave. The term \(\mathbf{g}_{hkl}\) is a reciprocal lattice vector, called the diffraction vector. It is an element of the reciprocal space and is thus specified by a set of three integers \((hkl)\), referred to as the Miller indices. This vector is perpendicular to the set of lattice planes \((hkl)\) in real space and the amount of the vector \(\mathbf{g}_{hkl}\) is related to the real space lattice plane distances \(a_{hkl}\) by

\[ \mathbf{g}_{hkl} = 1/a_{hkl} \] (2.6)
where

\[ a_{hkl} = a / \sqrt{h^2 + k^2 + l^2} \]  

(2.7)

with \( a \) denoting the lattice parameter of the solid.

Fig. 2-13 Geometry of Bragg scattering.\textsuperscript{[36]}

Fig. 2-14 Ewald construction. The Ewald sphere with a radius \( |k_0| = |k_g| = 1/\lambda \) passes through the node G with \( k_0, k_g \) and \( g_{hkl} \) denoting the incident beam wave vector, the diffracted beam wave vector and the diffraction vector, respectively.\textsuperscript{[36]}

The Ewald condition gives rise to an elegant construction shown in Fig.2-14. Let \( k_0 \) represent the incident wave and its endpoint coincide with the origin O of the reciprocal
space. Its starting point C is then the center of a sphere, called Ewald's sphere, with a radius \( r(r = 1/\lambda) \). If this sphere passes through another reciprocal lattice node G a diffracted beam \( CG = k_g \) is produced. Tilting the specimen is equivalent to tilting the reciprocal lattice over the same sample angle about a parallel axis. Tilting thus permits the “excitation” of specific nodes of the reciprocal lattice. It is worth mentioning that since the electron wavelength is in the order of 0.001 nm, i.e. \( |k_0| = 10 \text{ nm}^{-1} \), whereas the mesh size of the reciprocal lattice is in the order of 0.1 nm\(^{-1} \), the sphere radius is quite large and it can be approximated for most practical purposes by a plane normal to the incident wave vector \( k_0 \). The diffraction pattern is thus obtained as a central projection of a planar section of the reciprocal space on to the viewing screen of an electron microscope.

Fig. 2-15 Schematic view on geometrical parameters used for the analysis of diffraction patterns obtained with a transmission electron microscopy. \( \theta_{hkl}, a_{hkl}, D \) and \( g_{hkl} \) denote the Bragg angle, the real lattice plane spacing, the effective camera length of the microscope as well as the distance between the transmitted beam and a refection \( g_{hkl} \) recorded on the viewing screen, respectively.\(^{[36]} \)
When recording diffraction patterns with a transmission electron microscopy, we do not directly measure the Bragg angle $\theta_{hkl}$ belonging to a certain set of lattice planes but spacing $g_{hkl}$ of diffracted beams with regard to the transmitted beam as illustrated in Fig. 2-15. However, contrasting to light microscopy where the camera length of the microscope is given by the distance of the object investigated and the imaging plane, the variable set up possibilities of electromagnetic lenses in a TEM allow to use a wide range of camera length values dependent on the excitation of the lenses. Thus it is convenient to refer to an effective camera length $D$ when analysing diffraction patterns obtained by TEM. However, Fig. 2-15 demonstrates that

$$2\theta_{hkl} \approx \tan(2\theta_{hkl}) \approx \sin(2\theta_{hkl}) = g_{hkl}/D$$

and by combination of eqns. (2.4 and 2.6) we obtain

$$a_{hkl} = \frac{D\lambda}{g_{hkl}}$$

which allows us to calculate lattice spacing $a_{hkl}$ associated with a set of planes $(hkl)$ based upon the measurement of reflection positions $g_{hkl}$ from recorded micrographs when we know about the effective camera length $D$ chosen and the wavelength $\lambda$ of the electrons of the incident wave.

2.4.4 X-rays energy dispersive spectrometry mode in transmission electron microscopy

The first step in phase identification before the analysis of the diffraction patterns is a chemical analysis that can be done in a TEM microscope by X-rays energy dispersive spectrometry (EDS), or electron energy loss spectrometry (EELS). In addition to many other advantages such as the possibility of obtaining information on the chemical bonding
and its good spatial resolution, EELS is particularly appropriated for light elements \((Z < Z_{Al})\), but the identification of the chemical elements and the interpretation of the spectra are not as straight forward as in EDS which remains a quick method for identifying and quantifying the elements thanks to user-friendly software (Fig. 2-16). EDS has been widely used for the identification and, to a lesser degree, for quantification. Basic knowledge of EDS theory is required to be aware about the limitation and the resolution of this technique.

Fig. 2-16 Electron path in the TEM imaging mode and EDS mode.\[38\]

The X-ray microanalyses date from 1950’s with the thesis of R. Castaing who built a microprobe on a wave dispersive spectrometry (WDS). This was followed in 1956 by the work of Cosslet and Duncumb who developed it on a scanning electron microscope (SEM). EDS is now quasi-systematically associated with TEM to constitute a powerful set called analytical electron microscopy (AEM).
Inelastic interactions between electrons and matter give different kinds of signals: secondary electrons, Auger electrons, X-rays, light and lattice vibrations. The X-ray energy corresponds to a difference between two energy levels of the electron cloud of an atom ($K, L$). Since these levels are quantified, the X-ray energy spectrum represents the signature of the atom (Fig. 2-17a). The X-rays are detected by a semi-conductor and processed by a detector protected by an ultrathin window (Fig. 2-17b) and cooled at liquid nitrogen temperature to avoid the thermal noise and the diffusion of the dopant in the semi-conductor. The EDS spectrum is constituted by a background produced by the Bremsstrahlung X-rays and by peaks characteristic to the chemical elements of the material.

The identification is quite straightforward for elements beyond C when the peaks do not overlap. For lighter elements, the energy of relaxation of excited atoms is in great part carried off as the kinetics energy of Auger electrons (94% of the relaxation process).
Moreover, the potential emitted X-rays are in great part absorbed by the window. If there is an overlapping of the peaks, a deconvolution is required, and gives poor results for close elements, such as Mg in an Al matrix. That is the reason why no quantitative results were reported on the Mg content inside the Al matrix of the studied composites. The quantification is more difficult. It takes into account the link between the weight fraction and the generated intensities (ionization cross section) and between the generated intensity and the measured intensity (absorption and fluorescence effects). The measured intensity of an element depends on the other elements present in the sample.

For thin samples, where fluorescence and electron absorption are negligible, the weight fraction of the elements are linked by

\[
\frac{W_j}{W_A} = k_{JA} \left( \frac{I_j}{I_A} \right)_m
\]

where \(W\) is the weight fraction, \(I_m\) the measured intensity and the subscripts represent the element. \(k_{JA}\) is the Cliff-Lorimer ratio. They can be measured with thin standard specimens of known composition (Cliff-Lorimer method) or calculated for each pair of elements if their ionic cross-sections, fluorescence yields and the detector efficiencies are known (standard-less method). Then, the ratios are used for other samples containing the corresponding elements. The Cliff-Lorimer method is the most precise one but it imposes a heavy task before obtaining the first results. In this work all the quantifications were done with the standard-less method. The thickness of the sample was not taken into account in most of our quantifications on the elements Al, Mg, Si, Cu, Ag because Al, Mg, and Si are very close elements and because the Cu or Ag contents are very low (which reduces the eventual absorption by these elements of X-rays produced by the light atoms). In other cases, for example for the quantification of O, absorption is evaluated
after estimating the sample thickness with the thickness fringes observed by TEM in two beam conditions. A precision of 10% can be expected in the quantification (1% with the Cliff-Lorimer method), and of 0.1% for detection threshold in the absence of overlaps. The spatial resolution directly corresponds to the probe size (10 nm for the CM20 microscope and 1 nm for the HF2000 microscope) thanks to the thinness of the TEM samples.

2.5 Physical property measurement system

The Quantum Design physical property measurement system (PPMS) represents a unique concept in laboratory equipment: an open architecture, variable temperature-field system, designed to perform a variety of automated measurements (Fig. 2-18). It is an open architecture variable temperature-field system that is optimized to perform a variety of automated measurements, including the electro-transport, thermal transport, magnetometry and heat capacity properties. Use the PPMS with specially-designed measurement options, or easily adapt it to your own experiments. Sample environment controls include fields up to ± 9 tesla, and temperature range of 1.8 - 400 K. Its advanced expandable design combines many features in one instrument to make the PPMS the most versatile system of its kind.
The PPMS consists of a 9 Tesla superconducting magnet in a helium dewar with sample temperature range of 1.9-400K. The numerous combinations of electrical measurements, magnetic fields and temperatures allow for a multitude of measurements: 1) Resistivity, determination of superconductivity critical temperatures; 2) AC Transport, Hall Effect measurements; 3) Rotating sample holder for 360 degree sample rotation in field; 4) Magnetic susceptibility and M-H hysteresis loop measurements; 5) Open software architecture allows for additional types of electrical measurements.

For magnetic measurements, samples are placed on a sample rod and magnetic response is measured via two pickup coils. The ACMS option can measure with $2.5 \times 10^{-5}$ emu sensitivity in DC mode, and $10^{-8}$ emu sensitivity in AC mode. The VSM option is
capable of high-speed DC measurements with $1 \times 10^{-6}$ emu sensitivity at a collection rate of 1 point/second and a sensitivity approaching $1 \times 10^{-7}$ emu at ~20 seconds per point.

For electrical measurements, each sample is attached to a puck (Fig. 2-19) which has up to 12 electrical leads for performing DC resistivity, AC resistivity, I-V curves, Hall Effect, and critical current measurements. A horizontal sample rotator allows any of these electrical measurements with 360-degree sample rotation in the magnetic field.

Fig. 2-19 Photo of the puck used in PPMS.

Fig. 2-20 Two different types of configuration, (a) Van der pauw; (b) Hall bar geometry, used in the resistivity measurements.
In this dissertation, the resistivity function was used as the most common technique, with the four wire connection (Fig. 2-19). As shown in Fig. 2-20, two different types of configuration were used in the resistivity measurements. Low temperature glue was used to attach the samples on the puck, while gold wires were used as the connections. Metal Indium (or Tin) or wire bonder was performed to connect the wires to the sample or puck. Moreover, Ti/Pt double layer electrodes were deposited to the sample using Sputtering before the connection.

2.6 Superconducting quantum interference device

A superconducting quantum interference device (SQUID) is a very sensitive magnetometer used to measure extremely subtle magnetic fields, based on superconducting loops containing Josephson junctions (Fig. 2-21). SQUIDs are sensitive enough to measure fields as low as 5 aT (5×10⁻¹⁸ T) within a few days of averaged measurements. Their noise levels are as low as 3 fT·Hz⁻¹. For comparison, a typical refrigerator magnet produces 0.01 tesla (10⁻² T), and some processes in animals produce very small magnetic fields between 10⁻⁹ T and 10⁻⁶ T. The traditional superconducting materials for SQUIDs are pure niobium or a lead alloy with 10% gold or indium, as pure lead is unstable when its temperature is repeatedly changed. To maintain superconductivity, the entire device needs to operate within a few degrees of absolute zero, cooled with liquid helium.[39]

In 2006, proof of concept has be shown for CNT-SQUID sensors built with an Aluminum loop and a single walled carbon nanotube Josephson junctions. The sensors is few 100 nm size and operates at 1K or below. Such sensors allow to counting spins. High-temperature SQUID sensors are more recent; they are made of high-temperature
superconductors, particularly YBCO, and are cooled by liquid nitrogen which is cheaper and more easily handled than liquid helium. They are less sensitive than conventional low temperature SQUIDs but good enough for many applications.

![Photo of the Quantum Design SQUID.](image)

**Fig. 2-21** Photo of the Quantum Design SQUID.

Probably the most common commercial use of SQUIDs is in magnetic property measurement systems (MPMS). These are turn-key systems, made by several manufacturers, which measure the magnetic properties of a material sample: ferromagnetic, diamagnetic and paramagnetic. This is typically done over a temperature range from that of 2 K to roughly 300 K. With the oven functionality, the temperature range can be spread to 1000 K. With the decreasing size of SQUID sensors since the last
decade, such sensor can equip the tip of an AFM probe. Such device allows simultaneous measurement of roughness of the surface of a sample and the local magnetic flux.

In this dissertation, the magnetic measurements were performed in the Quantum Design SQUID system. All samples, used for the SQUID measurements, were handled with a ceramic tweezers to avoid any magnetic contamination. All substrates used are double-side-polished $\alpha$-Al$_2$O$_3$ (001) substrates. Silver paste used during the PLD deposition was carefully removed from the substrates. A quartz holder was used to support the Ti$_2$O$_3$ thin film samples during the SQUID measurements, and the magnetic field is parallel to the film surface. Straw holders were used to when the magnetic field was perpendicular to the surface of sample. When the oven mode is on, from 300 K to 1000 K, an oven stick was used to support the samples. Moreover, the SQUID chamber was purged using Helium for five times, and then pumped to high vacuum (<0.1 mTorr) before the measurements.
Chapter 3 Nanoscale valence and chemical evolution at Ti/SrTiO$_3$ Interface

Metal/oxide interfaces are ubiquitous in a wide range of applications such as electronics, photovoltaics, memories, catalysis and sensors. However, there have been few investigations dedicated to the nanoscale structural and chemical characteristics of these buried interfaces. In this work, the metal/oxide interface between Ti and SrTiO$_3$ (STO) is examined as a prototypical system using high-resolution scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS). We discover an atomic-thin Ti$_2$O$_3$-like layer at the Ti/STO interface prepared at room temperature, and first-principles calculations predict a metallic band structure of this two-dimensional electron system. As a universal feature of such interfaces prepared at different temperatures, we find near the interface nanoscale oxygen-deficient domains and continuous modulation of Ti valence. Overall, our results directly reveal complex chemical and valence evolutions at the metal/oxide interfaces, providing microscopic insights on such heterostructures.

In this project, we investigated the Ti/STO interfaces as a prototypical system using a series of complimentary imaging tools including high-resolution high-angle annular dark field (HAADF) and low-angle annular dark field (LAADF) scanning transmission electron microscopy (STEM), electron energy loss spectrum (EELS) and secondary ion mass spectrometry (SIMS). We observed substantial oxygen inter-diffusion at the metal/oxide interface, which is accompanied by the gradual evolution of the Ti valence from $4^+$, $3^+$ to 0. Importantly, we discovered atomic-thin layer of cubic perovskite Ti$_2$O$_3$
(Ti$^{3+}$) and anatase TiO$_2$ (Ti$^{4+}$) at the interfaces prepared at room temperature and 200 °C, respectively. Overall, our in-depth atomic-scale characterizations of the Ti/STO interfaces providing valuable structural and chemical information for such heterostructures, which could be generalized to the investigation of other interface systems.

3.1 Sample Growth and TEM Characterizations

Fig. 3-1a is the schematic representation of the Pt/Ti/STO structure. The purpose of the top Pt layer is to protect the sample surfaces from mechanical damages during processing. The samples were prepared using direct current magnetron sputtering, and the thicknesses of the Pt and the Ti layers are 50 nm and 65 nm, respectively. Focused ion beam (FIB) and Ar ion beam milling were used to prepare the TEM lamella. The cross-section of the Pt/Ti/STO structure was characterized using an FEI aberration-corrected Titan Cubed transmission electron microscope operated at 300 kV. The valence evolution across the interface was obtained from the line scans of the electron energy loss spectra (EELS). The cross-section STEM image of the Pt/Ti/STO structure is shown in Fig. 3-1b. The top Pt layer appears to be continuous, providing full coverage and surface protection.

![Fig. 3-1 (a) Schematic representation of the Pt/Ti/STO heterostructure. Thin films of 65 nm Ti and 50 nm Pt (protecting layer) were deposited on a (001) STO substrate using magnetron sputtering. (b) Cross-section STEM image of the Ti/STO interface. (c) SIMS depth profiles of the Pt/Ti/STO samples deposited at room temperature.](image-url)
To investigate the chemical evolution at the Ti/STO interface, SIMS measurements were performed under the ultra-high vacuum condition. The raw depth profiling data, displayed in Fig. 3-1c, show the variation of O, Pt, Ti and Sr signals as a function of the sputtering time for the sample deposited at room temperature. The most striking observation is the variation of the oxygen intensity at the Ti/STO interface as a result of oxygen diffusion. Interestingly, a clear oxygen signal was observed in the Ti layer, which is accompanied by a notable drop of the oxygen level in the STO substrate near the interface. Furthermore, a notable increase of the Ti signal was observed in STO in the same interface region, which could be associated with the high-concentration oxygen vacancies due to the matrix effect. [40, 41]
Fig. 3-2 (a) HAADF-STEM image of the Ti/STO interface prepared by sputtering Ti at room temperature. (b) The images, from left to right, are lattice structure, high resolution HADDF-STEM image (in Grayscale) overlaid with supposed structure and high resolution HADDF-STEM image (in Temperature scale) for the area marked with a yellow rectangle in (a), respectively. O: red. Sr: blue. Ti: cyan. (c) High-resolution HAADF-STEM image (upper) for the cross-section of Ti/STO interface, at a smaller scale than (a). And the HAADF signal profile, obtained from the whole above image, was shown at the bottom. HAADF signal profile for the yellow dashed line squared area was inserted. (d) High resolution HAADF-STEM image (upper) for the cross-section of Pt/STO interface, deposited at room temperature, and the HAADF signal profile, obtained from the blue rectangle area, was shown at the bottom.

High-resolution HAADF-STEM images of the metal/oxide interface prepared at room temperature are shown in Fig. 3-2. Surprisingly, in the overview [100] HAADF-STEM image (Fig. 3-2a) collected at the Ti/STO interface, we observed an ultrathin well-defined crystalline layer of TiOₓ, which is formed as a result of interfacial oxygen diffusion. In such STEM observations, Sr atoms exhibit much brighter contrast than Ti.
atoms due to their much higher Z number. The lattice structure of this interfacial layer, as shown in Fig. 3-2b, appeared to be similar to the STO substrate. However, different from the STO substrate, no Sr atom was observed in this ultrathin layer. Fig. 3-2 shows the HAADF signal profile along with the image. The TiO$_2$ termination layer on the STO single crystal substrate surface was clearly observed, and the crystalline structure above the TiO$_2$ layer seems to exist mostly within one atomic layer. Most likely, Ti atoms react with the oxygen from the STO substrate, and the crystalline structure of the formed TiO$_x$ monolayer strictly follows that of the STO substrate underneath. Discontinuous Ti-containing crystalline structures also appear to exist in a couple of atomic layers above this TiO$_x$ layer, but the contrast in the HAADF images is much weaker.

As a reference, a high-resolution HAADF-STEM image and a HAADF signal profile were also collected at a Pt/STO interface sample prepared under identical experimental conditions. As shown in the Fig. 3-2d, no extra oxidized layer was observed. Apparently, the structural differences between the Ti/STO and the Pt/STO interfaces are a result of the metal property: the noble metal Pt does not react with the oxygen ions from the STO substrate, while Ti is much more active and react with the oxygen ions diffused from the STO substrates. It is important to note that this atomic-scale oxidation reaction at the Ti/STO interface occurs even at room temperature, which thermodynamically requires no external activation.
3.2 EELS Characterizations of the Ti/STO Interface

Fig. 3-3 EELS spectra for Ti-L₂,3 and EELS fitting. (a) Electron energy loss spectra (EELS) of Ti-L₂,3 edge taken from Ti layer (far from interface), Ti/STO interface and STO substrate (far from interface), respectively. (b) EELS fitting: I=Ix<Ti>+Y<STO>; X+Y=1. The EELS spectra of Ti-L₂,3 edge, taken from Ti layer (blue line) and STO substrate (black line), are used.

To shed light on the Ti valence evolution at the Ti/STO interface, we used EELS to investigate the samples. EELS is a powerful technique to study the element distribution and valence states at the atomic level. [42, 43] In the EELS experiments, we analyzed the energy of the transmitted electron beam and performed the core level spectroscopy at the atom level. This technique allowed us to directly probe the internal structures at the Ti/STO interface, unlike surface-sensitive methods. As shown in Fig. 3-3, EELS spectra were collected from three locations: inside the Ti layer (far from the interface), at the Ti/STO interface and inside the STO substrate (far from the interface). As expected, the EELS spectra of the Ti layer and the STO substrate are in line with the reports on Ti⁰ and Ti³⁺ valence, respectively. As shown in Fig. 3-3a, four peaks, i.e., t₂g (L₃) at 459.64 eV, e₉ (L₃) at 462.92 eV, t₂g (L₂) at 465.18 eV, and e₉ (L₂) at 467.26 eV were observed in the Ti³⁺ spectra. In contrast, there are only peaks of e₉ (L₃) at 458.91 eV and e₉ (L₂) at 464.61 eV observed in the Ti⁰ spectra. More importantly, as shown in Supporting Information
Fig. 3-3b, the Ti-L$_{2,3}$ edge spectrum collected from the interface appears to be much more complex, and it cannot be taken as a simple superposition of the spectra from the Ti layer (Ti$^0$) and the STO substrate (Ti$^{4+}$).

![Image of HAADF-STEM and EELS spectra](image)

Fig. 3-4 (a) High resolution HAADF-STEM image of the Ti/STO interface prepared at room temperature. (b) EELS spectra of Ti-L$_{2,3}$ and O-K edges obtained from line scans across the interface shown in (a). The spacing along the line scan between consecutive EELS spectra is 4 Å. The spectra at the interface and valence evolution points are highlighted by thicker lines. For the spectra of Ti-L$_2$ and Ti-L$_3$, peak broadening and less pronounced peak splitting at the interface were clearly observed, indicating the valence evolution of Ti (from Ti$^{4+}$ to Ti$^{3+}$, and then to Ti$^0$). (c) Peak positions of Ti-L$_{2,3}$ edges. (d) Evolution of the integrated intensity of O EELS edges. The gradual fading intensity indicates the oxygen diffusion from the STO substrate to the Ti layer. (e) Schematic presentation for the Ti valence evolution across the Ti/STO interface.

In order to investigate in detail the Ti valence evolution across the Ti/STO interface, EELS line scans were collected at the atomic level. Fig. 3-4 shows the data taken on the sample deposited at room temperature. Specifically, the titanium L$_{2,3}$ (Ti-L$_{2,3}$) and
oxygen K (O-K) edges can be simultaneously recorded, with an energy resolution of ~0.1 eV and a spatial resolution of ~0.4 nm. We performed a line scan from the Ti layer to the STO substrate, crossing the Ti/STO interface. **Fig. 3-4a** presents the scan direction and position, which overlays with the high-resolution HAADF-STEM image of the Ti/STO interface. The region of EELS line scans has a length of 9.6 nm. The background-subtracted EELS spectra for both Ti-L$_{2,3}$ and O-K edges are shown in **Fig. 3-4b**, and the valence evolutions of Ti and O appear to occur gradually. The spectra, at the interface and the points where Ti valence change, are highlighted. As references, as-received STO substrate and commercial Ti$_2$O$_3$ powder were also measured, and their EELS data are shown in **Fig. 3-5**. In the spectra of Ti-L$_{2,3}$ edge shown in **Fig. 3-4b**, peak broadening and less pronounced peak splitting were clearly observed at the Ti/STO interface, which could be attributed to the presence of Ti$^{3+}$ valence.$^{[44]}$ Here, it should be noted that we cannot exclude the existence of Ti$^{2+}$ between the Ti$^{3+}$ and Ti$^0$ layer. As shown in **Fig. 3-6**, the EELS spectra for Ti$^{2+}$ and Ti$^{3+}$ are quite similar, especially at the Ti-L$_{2,3}$ edge (two peaks).$^{[45]}$ Moreover, the intensity of the O K edge is weak and noisy, which cannot be used to distinguish Ti$^{2+}$ from Ti$^{3+}$.

**Fig. 3-4c** shows the peak positions of Ti-L$_{2,3}$ edge along the line scan direction. Clearly, the Ti-L$_{2,3}$ valence changes from Ti$^{4+}$ in the STO substrate to Ti$^{3+}$ at the interface, then to Ti$^0$ in the Ti metal layer. The interfacial region with the dominant Ti$^{3+}$ valence spans approximately 3.2 nm. **Fig. 3-4d** shows the integrated intensity of O-K edge as a function of the distance from the interface. The decrease of oxygen intensity from the STO substrate to the Ti layer illustrates the chemical evolution of the content as a result of the oxygen diffusion from the oxygen-rich STO to the oxygen-less Ti. Comparison of
Fig. 3-4c and Fig. 3-4d indicates the strong correlation of the Ti valence evolution and the oxygen diffusion. Overall, in this Ti/STO sample prepared at room temperature, the oxidation of the Ti layer and the reduction of the STO substrate occur within an interfacial region with a thickness of 6.8 nm.

![EELS spectra for Ti-L2,3 and O K edges](image)

**Fig. 3-5** EELS spectra for Ti-L$_{2,3}$ and O K edges, collected from commercial Ti$_2$O$_3$ (Ti$^{3+}$) powder and STO (Ti$^{4+}$) substrate.
Based on the EELS spectra of Ti-L\textsubscript{2,3} and O-K edges, we distinguished the nanoscale valence evolution at the Ti/STO interface as six regions, as shown in Fig. 3-4e. The region I is featured by four clear and sharp peaks at the Ti-L\textsubscript{2,3} edge, indicating the characteristic Ti\textsuperscript{4+} ions in STO. The integrated intensity of oxygen remains constant in this region (Fig. 3-4d). In the region II, the integrated oxygen intensity starts to decrease from the STO substrate to the Ti layer, as a result of the oxygen diffusion. Concurrently,
Ti\(^{4+}\) partially changed into Ti\(^{3+}\), in order to maintain the charge neutrality in the region. As shown in Fig. 3-4b and Fig. 3-4c, the four peaks at the Ti-L\(_{2,3}\) edge became broader, with peak separations less pronounced, and even part of the t\(_{2g}\) peaks at the Ti-L\(_{2,3}\) edge could not be unambiguously identified, demonstrating the existence of Ti\(^{3+}\).\(^{[44]}\) In the region III, the integrated intensity of oxygen-related EELS peaks keeps decreasing, and the EEL spectra of Ti-L\(_{2,3}\) edge shows the characteristic two-peak feature of Ti\(^{3+}\) shown in Fig. 3-4b. In the region IV, oxygen signal was detected in the Ti layer, indicating the oxygen diffusion into the metal Ti layer. In this region, the EEL spectra of Ti-L\(_{2,3}\) edge still shows the feature of Ti\(^{3+}\) (Fig. 3-4b), indicating the formation of a TiO\(_x\) (Ti\(_2\)O\(_3\)-like) interfacial layer. In the region V, the two peaks of Ti-L\(_{2,3}\) edge slightly shift to lower energies, indicating the emergence of the Ti\(^0\) component. Finally, in the region VI, the integrated intensity of oxygen decreased to the minimum, and the EELS data at the Ti-L\(_{2,3}\) edge indicate the pure Ti\(^0\) valence in the Ti metal layer. Interestingly, each region with Ti valence change has a thickness of approximately 1.6 nm, and the overall chemical and valence evolutions occur within a thickness of approximately 6.8 nm (regions II, III, IV and V) at the interface, and the TiO\(_x\) (Ti\(_2\)O\(_3\)-like) alloy layer in regions IV and V has a thickness of 3.2 nm.

### 3.3 Observation of Oxygen-Deficient Domains

It is well recognized that oxygen vacancies are ubiquitous in oxides, and their characteristics are important to understand the physical properties of oxides and to harness their functionalities. There are few reports on how oxygen vacancies are distributed at metal/oxide interfaces because interfaces are buried underneath the top layers and difficult to directly probe. Atomic-scale study of oxygen vacancy profiles in
STO was carried out in 2004 using low-angle annular dark field (LAADF) imaging and EELS. LAADF imaging records dechannelling from the strain field surrounding the oxygen vacancies, while HAADF imaging is sensitive mostly to atomic number. In order to imaging the oxygen vacancies, we decreased the ADF inner angle from 70 mrad to 25 mrad to switch from the HAADF imaging mode to the LAADF mode.

Fig. 3-7 (a) LAADF-STEM image of the room-temperature Ti/STO interface sample. Scale bar: 5 nm. Two marked areas were chosen for EELS measurements. (b) EELS spectra of Ti-L\(_{2,3}\) and O-K edges obtained from those two domains shown in (a), compared with the stoichiometric STO. (c) EELS fitting according to \(I = X \times <Ti^{3+}> + Y \times <Ti^{4+}>\), with the constraint that X+Y=1. The EELS spectra for Ti\(^{3+}\) and Ti\(^{4+}\) were taken from the commercial Ti\(_2\)O\(_3\) powder and the stoichiometric STO substrate, respectively. (d) Parameter \(R = \frac{I(e_g(L_{3})) - I_0}{I(t_{2g}(L_{3})) - I_0}\) plotted as a function of X. We set the intensity for the valley point between \(e_g(L_{3})\) and \(t_{2g}(L_{3})\) as \(I_0\). The values of R and X for the areas A and B are highlighted.
**Fig. 3-7** shows the LAADF image and EELS analysis of oxygen-vacancy domains near the Ti/STO interface prepared at room temperature. Some small oxygen-vacancy domains with sizes of smaller than 5 nm and bright contrast to the surrounding areas were observed in the STO substrate, as shown in **Fig. 3-7a**. The oxygen deficiency caused some tiny structural changes in the STO lattice, and the white contrast in the LAADF images evidences the strain field surrounding the oxygen-vacancy domains. In fact, the brightness of the oxygen-deficient domains is directly correlated with the quantity of oxygen vacancies.\(^{[42]}\) To illustrate the effectiveness of this approach, two areas (marked with A and B with different contrast in the LAADF imaging) were selected for EELS analysis. **Fig. 3-7b** shows the EEL spectra of Ti-L\(_{2,3}\) and O-K edges from the areas A, B and the stoichiometric STO substrate. These data indicate that the Ti valence shifts from 4\(^+\)-like in STO to 3\(^+\)-like in oxygen-deficient domains, which is expected since oxygen vacancies are electron donors.

In addition, the O-K edge fine structure is sensitive to the O-O ordering and damps out as the vacancy concentration increases. According to the EELS fittings in **Fig. 3-7c**, we could obtain the value of \(\delta\) in SrTiO\(_{3,\delta}\) with a precision of 1\% for the oxygen-deficient SrTiO\(_{3,\delta}\) areas. The reference spectra for Ti\(^{4+}\) and Ti\(^{3+}\), used in the fittings in **Fig. 3-7c**, were taken from a bare STO substrate and commercial Ti\(_2\)O\(_3\) powders, respectively. Assuming that the actual EELS spectra at the Ti-L\(_{2,3}\) edge is the superposition of Ti\(^{4+}\) and Ti\(^{3+}\) with different weights, fitting the data to \(I = X \times <\text{Ti}^{3+}> + Y \times <\text{Ti}^{4+}>\), with the constraint of \(X + Y = 1\) can be used to reveal the fractional contributions of Ti\(^{4+}\) and Ti\(^{3+}\).\(^{[46]}\) In order to conveniently link the experimental data with the fitting result, we
defined a parameter $R = \frac{I(e_g(L_3)) - I_0}{I(t_{2g}(L_3)) - I_0}$ with $I_0$ being the intensity of the valley point between $e_g(L_3)$ and $t_{2g}(L_3)$ peaks for each Ti-L$_{2,3}$ spectrum. Then, we obtained the value of $R$ for each spectrum of Ti-L$_{2,3}$ edge, which has a one-to-one correspondence with the value of $X$ (Fig. 3-7d). As examples, $R$ (X) values calculated from the experimental spectra, taken from the oxygen-deficient areas A and B, are 10.2381 (0.42) and 5.0645 (0.24), respectively. Since one oxygen vacancy in SrTiO$_{3-\delta}$ will result in two Ti$^{3+}$ ions, the value of $\delta$ should be half of X. Thus, the values of $\delta$ for area A and B are $\sim$0.21 and $\sim$0.12, respectively, which falls in the range of $\delta$ reported for similar oxygen-deficient SrTiO$_{3-\delta}$ films.$^{[42]}$

**3.4 Properties of Ti/STO Interfaces Prepared at Higher Temperatures**

Temperature of the STO substrate during the Ti layer growth is clearly an important parameter because more substantial oxygen diffusion is expected at the Ti/STO interface at higher temperatures. In order to investigate the temperature dependence, we prepared another Ti/STO interface sample by depositing the Ti metal layer at 200 °C. As shown in Fig. 3-8, the HAADF-STEM image of the 200 °C sample significantly differs from the room temperature one. An inhomogeneous interfacial layer with nm-scale crystalline domains was observed in the Ti side near the interface. Interestingly, the high-resolution HAADF image and its fast Fourier transform (FFT) (Fig. 3-9) indicate that the lattice of this interfacial layer is consistent with that of anatase TiO$_2$. In fact, the in-plane lattice parameters of TiO$_2$ match well with those of STO, as shown in Fig. 3-8c. The anatase TiO$_2$ has a tetragonal structure (a=b=3.785 Å; c=9.514 Å), while STO has a cubic structure (a=3.905 Å). According to Fig. 3-8a and Fig. 3-9, the “epitaxial” relationship is
[100]TiO$_2$/[100]STO with in-plane mismatch of ~3.1%. This small lattice mismatch resulted in the formation of nanoscale TiO$_2$ domains on the STO when the sample was prepared at 200 °C. In fact, the higher oxygen content in this interfacial layer, compared to the TiOx layer observed in the room temperature sample, is in line with the more substantial oxygen diffusion from the STO substrate to the Ti metal layer at the higher growth temperature.

Fig. 3-8 (a) High resolution HAADF-STEM image of the Ti/STO interface prepared by depositing Ti at 200 °C. (b) From left to right: lattice structure, high-resolution HAADF-STEM image (in gray scale) with supposed structure and high-resolution HAADF-STEM image (in temperature scale). (c) c-plane views of STO (left) and anatase-structured TiO$_2$ (right). Red: O; Blue: Sr; Cyan: Ti.
As expected, larger oxygen-vacancy domains were observed at higher temperature (200 °C and 600 °C) samples, which are shown in Fig. 3-10. Much larger and brighter areas are observed in the LAADF images obtained on these higher temperature samples, which is consistent with the more oxygen diffused from STO to Ti expected at higher temperatures. Moreover, for the sample prepared at 600 °C, the EELS data shown in Fig. 3-10 indicate that the whole Ti layer was oxidized by the oxygen diffused from the STO substrate.
3.5 First-Principles Calculations of the Ti/STO Interface

As one of the most important findings in this work, an ultra-thin (one unit cell) Ti$_2$O$_3$-like layer was discovered at the Ti/STO interface fabricated at room temperature. In a general perspective, our experiments provide a viable approach towards the synthesis of atomic thin oxide layers. It could be expected that the property of this TiOx layer at the Ti/STO interface is different from those of both Ti and STO. However, it is difficult to probe the transport properties of this atomic thin layer because the top metallic Ti layer is highly conductive. Instead, we turned to calculations using density functional theory.
(DFT) to predict the possible physical properties of this interfacial layer containing Ti$^{3+}$ ions.

**Fig. 3-11** (a) Total DOS and atomic pDOS of the Ti$_2$O$_3$/STO interface calculated using the HSE method. The crystal structure of the interface is shown as inset. (b) Layer-resolved pDOS of TiO$_2$ and TiO planes shown in the inset of (a). The Fermi level is positioned at zero, around which the states mostly come from the Ti ions in Layer 2.

In our calculations, the model Ti$_2$O$_3$/STO heterostructure is consisted of two SrO layers, three TiO$_2$ layers and one TiO layer, and the relaxed lattice structure is shown as inset in **Fig. 3-11a**. Based on the generalized gradient approximation (GGA) optimized structure, the hybrid functional calculations based on Heyd-Scuseria-Ernzerhof (HSE) exchange are performed to give a more accurate description of the band structure of this interface. The density of states (DOS) and atomic projected DOS (pDOS) of the interface are shown in **Fig. 3-11a**. Layer-resolved pDOS results, shown in **Fig. 3-11b**, indicate that the electronic states around the Fermi energy mainly comes from the contribution of Ti 3$d$ orbitals, especially from the sandwiched TiO layer, where the 2D electron gas could
be generated. Interestingly, the pseudo-gap tendency is observed, implying a probably localization of carriers.

![Graph showing DOS comparison between Ti$_2$O$_3$/STO interface and bulk Ti$_2$O$_3$.](image)

**Fig. 3-12** Total DOS comparison between Ti$_2$O$_3$/STO interface and bulk Ti$_2$O$_3$, using the HSE method.

As a comparison to the Ti$^{3+}$-contained interface, we also calculated the band structure of bulk Ti$_2$O$_3$ using the same HSE method. Bulk Ti$_2$O$_3$ usually features a corundum (trigonal) lattice (R 3 c space group, # 167), and it is a narrow band gap (~0.1 eV) semiconductor.\(^{[47]}\) The total DOS of the cubic Ti$_2$O$_3$/STO interface and bulk Ti$_2$O$_3$ is shown in **Fig. 3-12**. As expected, a band gap of 0.09 eV was obtained for bulk corundum Ti$_2$O$_3$, which is in contrast to the metallic cubic-structured Ti$_2$O$_3$/STO interface. It would be interesting to etch off the top Ti layers from the Ti/STO interface samples and to directly probing the physical properties of the Ti$_2$O$_3$/STO interface, which is however out of the scope of this work.
3.6 Conclusion

In summary, we characterized the chemical and valence evolution at the Ti/STO interface using complementary microscopic techniques. Interestingly, an atomic-thin Ti$_2$O$_3$-like interfacial layer was observed at the Ti/STO interface in the sample deposited at room temperature. Furthermore, oxygen vacancies were generated in the STO substrates in all samples, and the density and size of oxygen-deficient domains increases with the Ti deposition temperature. When the Ti deposition temperature increased to 200 °C, we observed an ultra-thin continuous TiO$_2$ interfacial layer between the STO substrate and nanoscale island-like domains of crystalline anatase TiO$_2$. Clearly, such metal/oxide interfaces are far from atomically sharp as people usually conceive, and interfacial phases with varied Ti valences must be carefully considered. From a future perspective, our calculation results suggested that the ultra-thin Ti$_2$O$_3$ (Ti$^{3+}$/STO interface may possess metallic transport properties. Overall, our work demonstrated the nanoscale chemical and valence evolution at the Ti/STO (metal/oxide) interface, providing insights on the operation of interface-based devices.
Chapter 4 Properties and applications for Ti$_2$O$_3$ nanoparticles

4.1 Synthesis, physical and optical properties for Ti$_2$O$_3$ nanoparticles

Ti$_2$O$_3$ nanoparticles were obtained by ball milling using the commercial Ti$_2$O$_3$ powders (Sigma-Aldrich, 99.9 %, 100 mesh). Agate balls (Diameter: 10 mm and 5 mm) and agate containers were used in the ball milling process. Ethanol was used as the solvent. The milling speed was fixed at 300 rpm.

Fig. 4-1 Crystal structure characterization of Ti$_2$O$_3$. a) and b) are XRD pattern and Raman spectrum, collected from commercial Ti$_2$O$_3$ powder, respectively.

Ti$_2$O$_3$ exists in the corundum (trigonal) structure, the same as α-Al$_2$O$_3$. Structural characterizations of the commercial Ti$_2$O$_3$ powders are summarized in Fig. 4-1. Fig. 4-1a shows the X-ray diffraction (XRD) θ-2θ scan of the commercial Ti$_2$O$_3$ powders from 20° to 80°. The strong XRD diffraction peaks also indicate the Ti$_2$O$_3$ powders are highly crystalline, and the crystalline phase is consistent with the corundum structure of Ti$_2$O$_3$. The stability of the commercial Ti$_2$O$_3$ powders was studied by annealing the powder in air and Ar up to 900 °C and 1000 °C, respectively. The XRD patterns of the annealed powders are shown in Fig. 4-2. Below 400 °C, the corundum Ti$_2$O$_3$ powders show no
structural change, when 2 gram powders were annealed in air for 2 hour. However, the black corundum Ti$_2$O$_3$ powders were fully transformed to white rutile TiO$_2$, when powders (2 gram) were annealed in air at 900 °C for 2 hour, as shown in Fig. 4-2a and Fig. 4-3. Fig. 4-2b shows the XRD results of annealing Ti$_2$O$_3$ powders (2 gram) in Ar for 3 hour. No phase transition was observed during annealing in Ar below 1000 °C, which is consistent with the previous report. A small amount of Ti$_2$O$_3$ was converted to TiO$_2$ above 900 °C, which can be attributed to the impurity in Ar gas.

**Fig. 4-2** XRD pattern of commercial Ti$_2$O$_3$ powders (2 gram) annealed in a) Air and b) Ar at different temperatures for 2 hour and 3 hour, respectively.
Fig. 4-3 (a) XRD pattern collected from commercial corundum Ti$_2$O$_3$ powder at ambient condition. The inset shows the optical image of Ti$_2$O$_3$ powder at room temperature. (b) XRD patterns of Ti$_2$O$_3$ powders annealed in air at different temperatures. (c) The corresponding optical images for Ti$_2$O$_3$ powders after annealing at different temperatures.

Raman spectroscopy was also used to examine the structure of the commercial powders of Ti$_2$O$_3$, as shown in Fig. 4-1b, respectively. Same corundum structure is confirmed, corroborating the previous findings of the XRD studies. The corundum Ti$_2$O$_3$ (Space group: R-3c) is expected to show seven Raman active modes with the irreducible representations of $2A_{1g}+5E_g$. Fig. 4-1b shows seven distinct peaks at 221.9, 267.4, 299.7, 341.8, 450.2, 501.3, and 558.0 cm$^{-1}$. The frequencies of the peaks agree with the seven Raman modes in corundum Ti$_2$O$_3$.

Fig. 4-4 Optical properties of Ti$_2$O$_3$ nanoparticles. a) Transient absorption spectra of Ti$_2$O$_3$ nanoparticles (after ball milling), dispersed in ethanol. b) Optical photograph of the nanoparticles in ethanol.
The optical properties of Ti$_2$O$_3$ were investigated using the Ti$_2$O$_3$ nanoparticles, as shown in Fig. 4-4. Ti$_2$O$_3$ nanoparticles were obtained after a ball milling process using the commercial Ti$_2$O$_3$ powders. Since the size of the commercial Ti$_2$O$_3$ powder is quite large (~100 mesh: 149 μm), ball milling process were performed to reduce it. There samples (B-12, B-24, and B-48) of Ti$_2$O$_3$ nanoparticles were obtain after ball milling for 12 h, 24 h, and 48 h, respectively. Ethanol and agate (SiO$_2$) balls were used during the ball milling process. TEM images and EDS spectrum for commercial Ti$_2$O$_3$ powder (before ball milling) and Ti$_2$O$_3$ nanoparticles (after ball milling) (B-24) are shown in Fig. 4-5. According to the EDS spectrum, negligible Si was observed in the Ti$_2$O$_3$ nanoparticles after ball milling for 24 hour, attributed to the agate (SiO$_2$) balls and agate container (inside). Size distribution of Ti$_2$O$_3$ nanoparticles were measured by Zetasizer. As shown in the Fig. 4-6, the size of the nanoparticles is decreased with increase the time of ball milling. The structure of the nanoparticles was investigated by Raman spectroscopy. As shown in the Fig. 4-7a, Ti$_2$O$_3$ nanoparticles remain the corundum structure with distinct seven active Raman modes. As shown in Fig. 4-7b, the Raman peaks were shifted to lower frequency (cm$^{-1}$) when the particle size is smaller, except the E$_g$ mode at around 559 cm$^{-1}$.
Fig. 4-5 TEM results of the Ti$_2$O$_3$ powder samples. a) and c) TEM images for commercial Ti$_2$O$_3$ powder and Ti$_2$O$_3$ nanoparticles (B-24), respectively. b) and d) EDS spectrum taken from commercial Ti$_2$O$_3$ powders and Ti$_2$O$_3$ nanoparticles (B-24), respectively.

Fig. 4-6 Size distribution of the Ti$_2$O$_3$ nanoparticles, measured by the Zetasizer.
After the confirmation of the composition and structure of Ti$_2$O$_3$ nanoparticles, the absorption spectra of these Ti$_2$O$_3$ nanoparticles samples were studied and summarized in Fig. 4-4a, along with the solar spectrum as background. The optical image of the Ti$_2$O$_3$ nanoparticles dispersed in ethanol is shown in Fig. 4-4b. Due to the strong absorption of ethanol in the infrared range, the absorption data of Ti$_2$O$_3$ nanoparticles (~200 μg/mL), after background subtraction, is represented up to 1400 nm. As expected, the Ti$_2$O$_3$ nanoparticles exhibit strong absorption from UV to NIR. Depending on Fig. 4-4, highly strong absorption at the full range of solar spectrum is obtained for Ti$_2$O$_3$, which provide the fundamental property for efficient solar vapor generation. (Reflection and transmission should be added)

The strong photo-thermal effect of the Ti$_2$O$_3$ nanoparticles (B-24) were investigated using 808 nm and 1064 nm lasers, as shown in Fig. 4-8.
4.2 Seawater desalination based on Ti$_2$O$_3$ nanoparticles

Conversion of solar energy to heat is one of the most important aspects in solar energy harvesting. It enables a broad range of applications including solar power generation, chemical separation/purification, as well as seawater desalination. In conventional solar-to-heat systems, photothermal materials were mainly used as light absorbers to increase the absorption and conversion efficiency of solar energy. For instance, metallic nanoparticles such as gold nanoparticles have been applied as the light absorbers benefiting from their surface plasmonic effect. Under light irradiation at a resonance wavelength, these nanoparticles give rise to dramatic increasing in surrounding temperatures. This effect has been utilized in various applications such as solar vapor generation, liquid-liquid phase separation, and localized water heating. Besides, black materials such as polypyrrole organic polymers and carbon-based composite materials have also presented good photothermal capability thanks to their strong light absorption. Despite their usefulness, the metallic nanomaterials, however, only
respond to a limited range of solar spectrum,[65] and most of light-absorbing organic materials suffer from ageing instability.[66] Therefore, it remains as a challenge to develop high-performance photothermal convertors which have outstanding solar energy conversion ability and can be easily scaled-up for practical uses.

Generally, ideal photothermal materials must meet the following criteria: i) they must have a wide absorption capability covering the full solar spectrum range (from 250 nm to 2500 nm); ii) they must be less emissive which ensures the largest photo-to-heat conversion efficiency; and iii) they must be made from world abundant elements and can be cost-effectively scaled-up for industrial productions. In this work, we propose that narrow bandgap titanium oxide semiconductors may meet the above requirements. Titanium is the ninth earth abundant element and its metal oxide composites such as titanium dioxide have been intensively investigated due to the good photoresponse capability, low cost, and high thermal stability.[67-74] However, owing to the intrinsic large bandgap (~3 eV), typical titanium dioxide only responds to UV irradiation with wavelength <400 nm. During the past decades, considerable efforts have been made to narrow the bandgap of titanium dioxide to absorb the solar energy in visible spectrum range.[75,76] The state-of-the-art studies on reduced titanium dioxides have narrowed the bandgap to 1.5 eV, extending the photoresponse of titanium dioxide to wavelength of 800 nm and around 40% of the total solar energy.[77-84] However, it is desirable to narrow the bandgap of titanium oxides further to less than 0.5 eV in order to develop efficient full spectrum solar energy convertor with high solar energy utilization.

Herein we report the first example of using nanosized titanium sesquioxide (Ti$_2$O$_3$) as a novel light absorber for solar-thermal conversion. The fairly small bandgap (~0.1
eV) endows Ti$_2$O$_3$ the ability to absorb solar energy in the full spectrum range. By combining the ultrasmall bandgap and the nanosize features of the Ti$_2$O$_3$, we successfully achieve a nearly 100% internal and ~92% external solar-thermal conversion efficiency outperforming most of the conventional photothermal materials.

The outstanding light absorption property of the Ti$_2$O$_3$ nanoparticles offers unique opportunities for the development of highly efficient solar-thermal conversion systems. As a proof-of-concept, we demonstrate the use of Ti$_2$O$_3$ nanoparticles for solar enabled water evaporation. In our design, a thin layer of Ti$_2$O$_3$ nanoparticles was supported by a cellulose membrane to form a double-layer-structured device. The device is then floated on water surface and acted as a localized photothermal convertor. Under solar radiation, the Ti$_2$O$_3$ can efficiently heat up the surface portion of water, generating steam from the water surface (Fig. 4-9a). By collecting the condensed water from the steam, it is possible to use this design for desalination and water purification using sunlight as the only power source.$^{[58,63]}$

In a typical experiment, Ti$_2$O$_3$ nanoparticles were firstly dispersed in water, followed by deposition on a cellulose membrane under vacuum condition (Fig. 4-9b). Cellulose membrane was chosen as a bottom supporting layer because of its unique inner microporous structure and hydrophilicity (Fig. 4-9c). The microporous structure of the cellulose membrane enables efficient absorption of water through capillary effect. This effect enables more rapid replenishment of surface water after evaporation while the hydrophilicity would benefit the water adhesion and speed up the water transfer upwards. As an added benefit, cellulose membrane can minimize deleterious heat loss from Ti$_2$O$_3$ layers to bulk water due to its relatively low thermal conductivity (0.02 W m$^{-1}$ K$^{-1}$).$^{[85]}$
Under illumination of a solar simulator at power density of 7 kW m\(^{-2}\), the solar-thermal system can be quickly heated up in 2 min and generates visible steam flow on top of the water surface (Fig. 4-9d and Fig. 4-10). Notably, when the temperature of the film surface reached 70 °C, the temperature at most of the other parts remains almost unchanged (Fig. 4-9e). This is due to a strong localized solar light heating effect induced by the Ti\(_2\)O\(_3\) nanoparticles.

**Fig. 4-9** Solar vapor generation using the Ti\(_2\)O\(_3\)/CM bilayer structure. a) Scheme showing the experimental design of solar vapor generation using Ti\(_2\)O\(_3\) coated porous membrane. b) A photograph for the bilayer membrane sample and c) the corresponding SEM image of the membrane sample showing the layered structure of porous filter paper and Ti\(_2\)O\(_3\). d) Side-view photograph and e) infrared image of the black Ti\(_2\)O\(_3\) membrane under light illumination of 7 kW m\(^{-2}\) when floating on the top surface of water.
Fig. 4-10 a) The water evaporation weight against the amount of Ti$_2$O$_3$ nanoparticles on the cellulose film. The solar simulator intensity is 5 kW m$^{-2}$. b) The temperature relationship against time with or without solar light illumination. The solar simulator intensity is 7 kW m$^{-2}$. All experiments are conducted at ambient temperature of 20 °C and the humidity of 55%.

It should be mentioned that the localized heat effect can significantly improve the solar-vapour generation by preventing energy loss during heating the bulk water.$^{[58,63]}$

Without a Ti$_2$O$_3$ nanoparticle based film, we found that the temperature increment of bulk water was almost negligible after 15 min continuous solar light irradiation at 5 kW m$^{-2}$ (Fig. 4-11a). In contrast, under the identical illumination condition, the surface temperature of seawater sample with Ti$_2$O$_3$ film was heated to about 50 °C. Quantitative measurements on the temperature variations further prove that the localized heating is originated from the concentration of solar energy by the Ti$_2$O$_3$ layer rather than the block of direct radiation by a cellulose layer. We further investigated the performance of solar-vapour generation of Ti$_2$O$_3$ by monitoring the weight loss of seawater while evaporation.
As expected, Ti$_2$O$_3$ induced enhanced evaporation efficiency under various irradiation powers. We observed evaporation rates of 1.32 kg m$^{-2}$ h$^{-1}$ and 5.03 kg m$^{-2}$ h$^{-1}$ for Ti$_2$O$_3$ samples at 1 and 5 kW m$^{-2}$ solar irradiances, which is 2.65 and 4.18 times higher than pure water evaporation. The Ti$_2$O$_3$ nanoparticle based thin film also presents 11-23% higher solar-vapour generation rate than graphite under the same structure design and light illumination condition (Fig. 4-11b-e). The durability of the Ti$_2$O$_3$ thin film was also investigated under different light illumination intensities. The film presented stable performances during 25 experiment cycles, indicating good recycle stability. Taken together, these results unambitiously indicate the feasibility of using the Ti$_2$O$_3$ nanoparticles for efficient solar vapour generation.
Fig. 4-11 Performance of the bilayer structure. a) Infrared images of pure water (left), graphite membrane (middle), and Ti$_2$O$_3$ membrane (right) under the same light illumination of 5 kW m$^{-2}$. The evaporation mass loss of water with different heat absorption materials under 1kW/m$^2$ (b), c)) and 5 kW/m$^2$ (d), e)) irradiation of a solar simulator. b) and d) are under the full range solar irradiation while c) and e) are under IR range (wavelength longer than 750nm). All experiments are conducted in ambient temperature of 24°C and the humidity of 55%.

4.3 Mid-infrared graphene/Ti$_2$O$_3$ hybrid photodetectors

Various applications ranging from imaging sensors, chemical variation spectrum to optical communications require high-performance infrared photodetectors that can convert infrared light into electrical signals.$^{[86,87]}$ Practically these detectors are screaming for high light absorption, low noise level at room temperature and high response speed
with wavelength dependence, which still remains a challenge with conventional narrow band gap semiconductors such as HgCdTe thin films and InP quantum wells. \[88\] Significant efforts have been devoted to colloidal quantum dots (CQD) due to its high absorption efficiency and easy manufacturing processes. \[89\] However, CQD based photodetectors suffer from the operation spectrum originated from its band gap. Alternatively, graphene appears to be a promising candidate and provides unique properties superior to those of the conventional counterparts such as ultrahigh carrier mobility and broadband absorption. Up to date, graphene has been successfully demonstrated as a broadband photodetector from visible to the terahertz wavelength regimes, \[90, 91\] however, its low absorption \[92\] and fast carrier recombination rate \[93\] restrict its application in photodetection due to the low photoresponsivity.

Nowadays ultrahigh optical gain has been achieved in hybrid graphene-CQD structures, where graphene serves as a ultrahigh carrier transporter and CQD serves as the light absorber. \[94-96\] In this architecture, one type of carrier is trapped in the CQD film while the other type of carrier circulates in the graphene channel. Similar designs are also employed in the visible and near infrared photodetectors with hybrid graphene-TiO\(_2\), \[97\] graphene-ZnO, \[98\] graphene-dye \[99\] and graphene-perovskite structures. \[100\] However, the light absorption bandwidth in these hybrid structures is limited by the band gap of light absorbers, for instance, the most commonly used CQD (PbS and PbSe with band gaps ~0.6 eV-1.0 eV) have a absorption cut-off in the short infrared regime (\(\lambda < 3 \mu m\)). \[101\] As a result, it is essential to explore novel, narrow band gap light absorbers to enhance the performance of hybrid graphene photodetectors in the mid-infrared. We demonstrate here that mid-infrared hybrid graphene photodetector can be realized by hybridizing graphene
with a narrow band gap semiconductor, Ti$_2$O$_3$ nanoparticles, which are synthesized by ball milling method. The light is absorbed by the Ti$_2$O$_3$ nanoparticles where electron-hole pairs are generated, and then the photo-excited electrons can be trapped by the Ti$_2$O$_3$ nanoparticles. The proper band gap corresponding to the mid-infrared photon energy and optimized charge transfer efficiency make the hybrid graphene/Ti$_2$O$_3$ nanoparticles structure, a promising candidate in mid-infrared photodetection and opens up a new pathway towards mid-infrared optoelectronics and photonics.

**Fig. 4-12** Schematic illustration of the hybrid graphene/Ti$_2$O$_3$ nanomaterial structure.

The schematic top view and operation of the hybrid graphene/ Ti$_2$O$_3$ nanoparticle device architecture is illustrated in **Fig. 4-12**. In our design, the incident light is absorbed by the Ti$_2$O$_3$ nanoparticles and the photoexcited electron-hole pairs are separated at the graphene/Ti$_2$O$_3$ nanoparticles interface, the detailed mechanism will be discussed later in the next section. The unique narrow band gap of Ti$_2$O$_3$ nanoparticles makes it proper light absorber for hybrid graphene photodetector operating in the mid-infrared.
Fig. 4-13 Optoelectronic properties of the hybrid graphene/ Ti$_2$O$_3$ photodetector. (a) $I_d$-$V_d$ of the hybrid graphene/ Ti$_2$O$_3$ photodetector in dark and under laser illumination, the gate voltage is 0 V. (b) $I_d$-$V_d$ of the hybrid graphene/ Ti$_2$O$_3$ photodetector in dark and under laser illumination, the gate voltage is 80 V. (c) $I_d$-$V_g$ curve of the hybrid graphene/ Ti$_2$O$_3$ photodetector in dark and under laser illumination. The source-drain voltage in this measurement is $V_d=2$ mV. (d) Temporal response traces of the device under illumination with 10 µm laser. (e) The time-dependent photocurrent measurement of 20 periods under mid-infrared laser illumination. (f) The photoresponsivity of the hybrid graphene/ Ti$_2$O$_3$ photodetector at different illumination wavelengths in the mid-infrared regime from 4.5 µm to 7.0 µm.

In this experiment, we investigate the photodetection performance of field effect transistors (FET) of hybrid graphene/Ti$_2$O$_3$ structure. (Hereafter, if not especially declared, graphene refers to monolayer graphene in case of any misconception with the discussion of multilayer graphene later.) The photodetection measurement is performed under 10 µm laser illumination by a quantum cascade laser (QCL). As shown in Fig. 4-13a, the net photocurrent is negligible without any gating voltage ($V_g=0$). This is consistent with the previous results that the charge transfer process is limited due to the band misalignment between graphene and Ti$_2$O$_3$ in the hybrid structure. On the contrary,
the photocurrent dynamically increases when the device is positively biased at $V_g = 80$ V as indicated in Fig. 4-13b as the hole injection efficiency to graphene is greatly enhanced. In Fig. 4-13c, the electrical characterization of the hybrid graphene/Ti$_2$O$_3$ FET shows the classical $I_d$-$V_g$ curve of graphene with the Dirac point at $\sim -1$ V ($V_D \sim -1$ V). The charge transfer to graphene channel is not energy favourable until the graphene is n-type doped, that is, when the gate voltage exceeds the Dirac point. Furthermore, the net photocurrent is negative because the injection of holes from Ti$_2$O$_3$ neutralizes the electron concentration and thus increases the resistance of the n-doped graphene channel. To achieve the highest photocurrent in the photodetector, we choose to operate the photodetector under $V_g = 80$ V in the following measurements.

Fig. 4-13d exhibits the photoresponse measured in one on/off period with the elimination of the dark current. The hybrid graphene/ Ti$_2$O$_3$ photodetector shows a net photocurrent $\sim 50$ nA corresponding to a photoresponsivity of $\sim 100$ A/W under a source–drain bias of 2 mV. On the other hand, the response times are determined by the rising (or falling) time from 10% to 90% (or 90% to 10%) of the total photocurrent and by fitting the rise and decay curve by the following equation: $I_{rise} = I_0 - A exp(-(t - t_1)/\tau_1)$ and $I_{decay} = I_0 + B exp(-(t - t_2)/\tau_2)$, where $\tau$ is the time constant and $t$ is the time when laser is switched on or off, $I_{dark}$ is the dark current, and $A$ is the scaling constant. As shown in Fig. 4-13d, both estimation methods unanimously give the rise and fall time to be $\sim 1.2$ ms $\sim 2.6$ ms respectively. The response speed is 3 orders of magnitude faster than that of mid-infrared hybrid graphene nanoribbon/C$_{60}$ photodetector we demonstrated recently, where C$_{60}$ acts as the electron trapping center while graphene nanoribbon serves as both light absorber and charge transporter.$^{[102]}$ However, the
response speed in our proposed photodetector is limited by the scattering/trapping centers in graphene/Ti$_2$O$_3$ interface induced by the device fabrication process.\cite{103} The device also exhibits good stability with multi-period measurements as indicated in Fig. 4-13e, and the device retains its performance even after one month of storage in Ar filled container. Intriguingly, the hybrid graphene/Ti$_2$O$_3$ photodetector shows remarkable photoresponse in a broad spectrum range, as demonstrated in our experiment, from 4.5 µm to 7.0 µm. The photoresponsivity is about 120 A/W with a relatively low source-drain voltage, $V_d = 2$ mV for all the wavelengths, which is consistent with the uniform absorption spectrum. The high photoresponse under low extraction source-drain voltage further confirms the efficient transfer process of holes generated by the laser excitation to the graphene channel.

**Fig. 4- 14** Graphene layer dependent photodetection performance and mechanism analysis. (a) Photocurrent measurement of hybrid graphene/Ti$_2$O$_3$ photodetector under 10 µm QCL laser illumination with the monolayer, bilayer and trilayer graphene. (b) Laser power dependence of the photocurrent of hybrid graphene/Ti$_2$O$_3$ photodetector traced at 10 µm laser illumination with various layers of graphene.
From the theoretical point of view, the charge transfer from the semiconducting absorber to adjacent two dimensional material is thickness (layer) dependent.\textsuperscript{105} It is clearly shown in Fig. 4-14a that the photoresponse for the hybrid graphene/Ti$_2$O$_3$ photodetector represents a noteworthy enhancement when the graphene layer increases from monolayer to trilayer, which is opposite to the trend in PbS QD sensitized MoS$_2$ photodetector. The layer-dependent photoresponse is further verified by the power dependence of the photocurrent as shown in Fig. 4-14b. The photocurrent increases as a function of the incident laser intensity, which satisfies the relation: $I_{pc} = CP^\gamma$, where $C$ is a constant and $P$ is the illumination laser intensity, respectively. We obtain the fitting $\gamma_1=0.78$ for the hybrid monolayer graphene/Ti$_2$O$_3$ photodetector, while $\gamma_2=0.94$ and $\gamma_3=1.12$ for the bilayer case and trilayer case, respectively. Commonly, the $\gamma$ value indicates the recombination kinetics of photocarriers by the traps states in both the carrier injection interface and the transport channels. As a result, the increase of the $\gamma$ value with the increase of graphene layers can be attributed to the enhancement of the transfer rate of the photoexcited holes from Ti$_2$O$_3$ to the underneath graphene. The layer-dependent charge transfer efficiency accounts for the competition between careening and absorption of the electric field of the dipoles of semiconducting nanoparticles and the graphene layer.\textsuperscript{106, 107} To the best of our knowledge, this is the first time we reveal the effect of the number of graphene layers (thickness) on the photodetection performances in the hybrid graphene photodetectors systems. Even though the transfer process needs to be directly investigated by time-resolved mid-infrared photoluminescence measurements to extract the lifetime of carriers and transfer rates, the results here provide critical insights toward related 0D-2D hybrid optoelectronic devices.
The unique properties of the hybrid graphene/Ti$_2$O$_3$ make it a promising candidate for mid-infrared photodetection. As a demonstrative example, we achieve an optimized photoresponsivity of ~ 200 A/W for hybrid trilayer graphene/Ti$_2$O$_3$ photodetector under 10 µm laser illuminations. However, the photoresponse is quite low compared to the hybrid graphene/QD structures because of the high absorption coefficient of QD in particular wavelength ranges. Possible strategies to optimize the performance of hybrid graphene/Ti$_2$O$_3$ photodetector are to further enhance the charge transfer rate and efficiency by engineering the surface states of Ti$_2$O$_3$ nanoparticles with chemical treatment or introduce suitable ligands on the surface of Ti$_2$O$_3$ nanoparticles.

To summarize, a novel photodetector with high photoresponse in the mid-infrared regime is proposed and demonstrated in hybrid graphene/Ti$_2$O$_3$ structure thanks to the high absorption of Ti$_2$O$_3$ nanoparticles, together with efficient charge transfer between the light absorber and charge acceptor under optimized band alignment condition. We have also elucidated that the charge transfer efficiency increases with the increasing number of graphene layers and achieved the optimized photoresponsivity of ~ 200 A/W for Ti$_2$O$_3$ nanoparticles hybrid with trilayer graphene. This work highlights the importance of exploring mid-infrared absorbers and controlling charge transfer process for hybrid graphene photodetectors and opens new venues for exploring graphene based optoelectronic devices.
Chapter 5 Synthesis and Physical properties of Ti$_2$O$_3$ thin films

5.1 Synthesis of Ti$_2$O$_3$ thin films

Ti$_2$O$_3$ thin films with a thickness range of ~40 - 280 nm were deposited on (0001) sapphire substrates with a size of 5×5×0.5 mm$^3$ using pulsed laser deposition (PLD). A Ti$_2$O$_3$ (corundum phase) target (Sigma-Aldrich 99.99%) was used. Before deposition, the pressure of the PLD chamber was lower than 3.0 × 10$^{-9}$ Torr. The deposition was performed at high temperatures from 500 °C to 900 °C with a 248 nm Laser (KrF, Coherent). The energy density of the laser on the target was varied from 2 J/cm$^2$ to 3 J/cm$^2$. The distance between target and substrates were fixed at 5.6 cm. More synthesis details are given in Table 5-1.

Titanium sesquioxide Ti$_2$O$_3$ powder was first investigated by studying its stability in air (Also shown in Fig. 4-3). Bulk Ti$_2$O$_3$ is a narrow band gap semiconductor, with a corundum structure. X-ray diffraction (XRD) pattern was collected from the commercial Ti$_2$O$_3$ powder at room temperature, as shown in Fig. 5-1a. Interestingly, we found that annealing in air at temperatures higher than 500 °C (2 hour) converted the corundum Ti$_2$O$_3$ (2 gram) into rutile TiO$_2$, as shown in Fig. 5-1b and Fig. 5-1c. However, that is, Ti$_2$O$_3$ could survive at ambient conditions.

Depending on this, epitaxial Ti$_2$O$_3$ thin films were deposited on α-Al$_2$O$_3$ (0001) substrates in high vacuum (< 3.0 × 10$^{-9}$ Torr) using pulsed laser deposition (PLD). X-ray diffraction (XRD) was used to examine the crystal structure and phase of the as-deposited films. Diffraction patterns of Ti$_2$O$_3$ thin films grown at 600 °C (C-2) and 900 °C (R-1) on α-Al$_2$O$_3$ substrates are shown in Fig. 5-1d. (Cross-sectional TEM images of C-2 and R-1 are shown in Fig. 5-2).
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<th>Deposition Time (hour)</th>
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<th>Laser Frequency (10Hz)</th>
<th>Ti₂O₃ Phase</th>
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Tab. 5-1 Deposition conditions of PLD for C-Ti₂O₃ and R-Ti₂O₃ thin films.
Fig. 5-1 Structural characterizations of Ti$_2$O$_3$ using XRD, Raman and XPS. (a) XRD pattern collected from commercial corundum Ti$_2$O$_3$ powder at ambient condition. The inset shows the optical image of Ti$_2$O$_3$ powder at room temperature. (b) XRD patterns of Ti$_2$O$_3$ powders annealed in air at different temperatures. (c) The corresponding optical images for Ti$_2$O$_3$ powders after annealing at different temperatures. (d) X-ray θ-2θ scans of C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$ thin films show single diffraction peaks, indicating their single-phase nature. The inset zooms in the range from 35° to 45°. (e) Raman spectra of C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$ thin films. Raman modes obtained from α-Al$_2$O$_3$ are also marked. (f) O 1s XPS spectra and Ti 2p XPS spectra collected from C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$ thin films.

Fig. 5-2 Scanning transmission electron microscope (STEM) images of C-Ti$_2$O$_3$/Al$_2$O$_3$ (C-2) and R-Ti$_2$O$_3$/Al$_2$O$_3$ (R-1) heterostructures. a and b Low resolution HAADF-STEM images for C-Ti$_2$O$_3$/Al$_2$O$_3$ and R-Ti$_2$O$_3$/Al$_2$O$_3$ heterostructures, respectively.
Apart from the substrate peak, the peak at 39.06° in the 600 °C grown sample (C-Ti$_2$O$_3$) agrees well with the (0006) planes of the known corundum (trigonal) structure of Ti$_2$O$_3$ (R$\bar{3}$c space group, # 167, a = b =5.15 Å, c = 13.61 Å), indicating a fully relaxed bulk-like phase. Surprisingly, the XRD peak of the 900 °C sample (denoted as R-Ti$_2$O$_3$) is located at a different location of 37.77°, presumably indicating a phase distinct from C-Ti$_2$O$_3$. Furthermore, we carefully explored the PLD synthesis parameters and determined the conditions for growing C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$ phases (Fig. 5-3). We should note here that both R-Ti$_2$O$_3$ and C-Ti$_2$O$_3$ thin films are stable. No change was observed on their appearance and structure after being stored in ambient conditions for over half a year (Fig. 5-4).

As shown in Fig. 5-1e, the seven Raman modes observed in the C-Ti$_2$O$_3$ (C-2) film are consistent with the $D_{34}$ point-group symmetry of the corundum structure.$^{[108]}$ On the other hand, for the as-deposited R-Ti$_2$O$_3$ (R-1) film, only four peaks were observed, indicating...
a different lattice structure. Moreover, the less Raman modes observed in R-Ti$_2$O$_3$ indicating a higher lattice symmetry than C-Ti$_2$O$_3$. Additional Raman data collected from C-Ti$_2$O$_3$ powder, and R-Ti$_2$O$_3$ films are shown in Fig. 5-4. Fig. 5-1f presents the O 1s and Ti 2p X-ray photoelectron spectroscopy (XPS) spectra of these Ti$_2$O$_3$ thin films. C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$ films show almost identical XPS spectra, indicating that their Ti ions share the same valence. Furthermore, the positions of the XPS peaks (464.1 eV and 458.5 eV for Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$, respectively) are consistent with those of corundum Ti$_2$O$_3$ single crystals$^{[109,110]}$, indicating a dominant Ti valence of 3+.

Fig. 5-4 Raman spectra characterization. a, Raman spectra of commercial Ti$_2$O$_3$ powder (corundum, 99.9 %; ALDRICH). b, Raman spectra of the R-Ti$_2$O$_3$/Al$_2$O$_3$ heterostructures. c, and d, Raman spectra of the C-Ti$_2$O$_3$/Al$_2$O$_3$ and R-Ti$_2$O$_3$/Al$_2$O$_3$ heterostructures, respectively, collected six month after growth, representing the same structure as the sample was deposited. As expected, the color of the samples kept black, observed from the inserted photograph. A double side polished Al$_2$O$_3$ substrate acted as the reference.
5.2 Microstructural characterizations and determinations of C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$ thin films

Fig. 5-5 Structural characterizations of C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$ thin films using STEM. (a)(c)(e)(g) High resolution HAADF-STEM images taken on C-Ti$_2$O$_3$/Al$_2$O$_3$ and R-Ti$_2$O$_3$/Al$_2$O$_3$ samples. Fast Fourier transform images from the films are shown as insets. (b)(d)(f)(h) Inversed Fast Fourier transform images for films (upper) and sapphire (lower) are taken from (a)(c)(e)(g), respectively. The unit cells of C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$ are illustrated as insets in Figure 2e and 2g, respectively. Small red spheres are oxygen, and large blue and cyan spheres are titanium and aluminum, respectively. Scale bar in (a)(c)(e)(g) is 2 nm.

The discovery of this new Ti$_2$O$_3$ R-phase motivated us to carry out in-depth TEM experiments. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images were collected at the interfaces of C-Ti$_2$O$_3$/Al$_2$O$_3$ and R-Ti$_2$O$_3$/Al$_2$O$_3$. The HAADF-STEM images taken from two different zone axes (Fig. 5-5a and Fig. 5-5e) on the C-Ti$_2$O$_3$ sample (C-2) show identical lattice structure from the film and the substrate, and the epitaxial relationship between C-Ti$_2$O$_3$ and α-Al$_2$O$_3$ is confirmed to be [11$ar{2}$0] C-Ti$_2$O$_3$‖[11$ar{2}$0] α-Al$_2$O$_3$ and [10$ar{1}$0] C-Ti$_2$O$_3$‖[10$ar{1}$0] α-Al$_2$O$_3$. 

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Fast Fourier transform (FFT) patterns, obtained from the C-Ti$_2$O$_3$ film, are shown as the insets of Fig. 5-5a and Fig. 5-5e, which are consistent with the simulated electron diffraction data (Fig. 5-6). Inversed FFT (IFFT) images in Fig. 5-5b and Fig. 5-5f again confirm the structure of C-Ti$_2$O$_3$.

![Fig. 5-6](image)

**Fig. 5-6** a, FFT taken from Fig. 5-5 (C-Ti$_2$O$_3$). b, Simulated electron diffraction pattern obtained from the C-Ti$_2$O$_3$ crystal structure (Fig. 5-8) along $<11 \overline{2} 0>$. c, FFT taken from Fig. 5-5 (C-Ti$_2$O$_3$). d, Simulated electron diffraction pattern obtained from the C-Ti$_2$O$_3$ crystal structure (Fig. 5-8) along $<10 \overline{1} 0>$. 
**Fig. 5-7** Atomic comparison between R-Ti₂O₃ and C-Ti₂O₃. a and b Differences observed from [11\(\bar{2}\)0] view and [10\(\bar{1}\)0] view in IFFT images, respectively. c, Reconstruction of R-Ti₂O₃ from C-Ti₂O₃, by layer displacements and pairing Ti atoms rotation. d and e Views of [0001] (top view of C-Ti₂O₃/Al₂O₃) in C-Ti₂O₃ and [0\(\bar{1}\)1] (top view of R-Ti₂O₃/Al₂O₃) in R-Ti₂O₃, respectively. f and g Views from [11\(\bar{2}\)0] Al₂O₃ and [0\(\bar{1}\)1] R-Ti₂O₃, using one unit cell, respectively.

HAADF-STEM images from the R-Ti₂O₃/Al₂O₃ sample (R-1), shown in **Fig. 5-5c** and **Fig. 5-5g**, suggest a crystalline structure different from corundum C-Ti₂O₃. Close-up views of the film and substrate lattices are shown in the IFFT images in **Fig. 5-5d** and **Fig. 5-5h**. In fact, the structure of R-Ti₂O₃ can be reconstructed from that of C-Ti₂O₃ with the assistant of first-principles calculation (**Fig. 5-7**). The unit cells of C-Ti₂O₃ (R\(\bar{3}\)c
space group, # 167) and R-Ti$_2$O$_3$ (Immm space group, # 71) are shown as insets in Fig. 5-5e and Fig. 5-5g, respectively. Unit cell parameters of R-Ti$_2$O$_3$ are $a = 9.3850$ Å, $b = 4.4225$ Å, $c = 2.8095$ Å, and the structural comparison with $\alpha$-Al$_2$O$_3$ and C-Ti$_2$O$_3$ is given in Fig. 5-8. Excellent agreements were obtained between the experimental HAADF-STEM images and the projections of the reconstructed structure with the same zone axis, as shown in Fig. 5-5d and Fig. 5-5h (as well as the reciprocal space in Fig. 5-9). Furthermore, as shown in Fig. 5-10, the selected area electron diffractions (SAED) patterns collected from R-Ti$_2$O$_3$/Al$_2$O$_3$ are consistent with the simulated results using the reconstructed structure. Finally, the epitaxial relationship between R-Ti$_2$O$_3$ and $\alpha$-Al$_2$O$_3$ is confirmed to be [110] R-Ti$_2$O$_3$||[1010] $\alpha$-Al$_2$O$_3$ or [011] R-Ti$_2$O$_3$||[1120] $\alpha$-Al$_2$O$_3$, as shown in Fig. 4-5c and Fig. 4-5g, respectively.

**Fig. 5-8** Crystal structures of $\alpha$-Al$_2$O$_3$, C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$. Small red spheres are oxygen. Large spheres in a, b, and c are aluminum, titanium, and titanium, respectively. Colorful polyhedra represents bicapped-trigonal prism.
Fig. 5-9  a, FFT image taken from Fig. 5-5 (R-Ti$_2$O$_3$). b, Simulated electron diffraction pattern obtained from the R-Ti$_2$O$_3$ crystal structure (Fig. 5-8) along <011>. c, FFT taken from Fig. 5-5 (R-Ti$_2$O$_3$). d, Simulated electron diffraction pattern obtained from the R-Ti$_2$O$_3$ crystal structure (Fig. 5-8) along <133>.
Fig. 5-10 Structural examination of R-Ti$_2$O$_3$ using electron diffraction in TEM. a, Electron diffraction pattern taken from R-Ti$_2$O$_3$ along [010]. b, Simulated electron diffraction pattern obtained from the R-Ti$_2$O$_3$ crystal structure (Fig. 5-8) along [010]. c, Electron diffraction pattern taken from R-Ti$_2$O$_3$ along [001]. d, Simulated electron diffraction pattern obtained from the R-Ti$_2$O$_3$ crystal structure (Fig. 5-8) along [001].

Fig. 5-11 Epitaxial depositions of C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$. a and b Schematic presentations of the structure of C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$ on α-Al$_2$O$_3$, respectively. (C: C-Ti$_2$O$_3$. R: R-Ti$_2$O$_3$. S: Sapphire α-Al$_2$O$_3$.)
Determination of the crystal structure of C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$ in turn sheds light on the stabilization of these distinct phases in epitaxial thin film growth. Fig. 5-11 schematically illustrates the in-plane epitaxial relationship between the film and the α-Al$_2$O$_3$ substrate. The in-plane lattice mismatch between C-Ti$_2$O$_3$ and α-Al$_2$O$_3$ is approximately 8.4 %, while that between R-Ti$_2$O$_3$ and α-Al$_2$O$_3$ is about 2.2 % and 5.4% along [011] R-Ti$_2$O$_3$ and [100] R-Ti$_2$O$_3$, respectively. As a consequence, when the PLD growth temperature is higher (900 °C), the Ti and O atoms have higher kinetic energies to rearrange themselves into the R-Ti$_2$O$_3$ phase to achieve a smaller mismatch with the substrate.

5.3 Emergent superconductivity in R-Ti$_2$O$_3$

Searching for new superconductors capable to carry loss-free current has been a long-lasting theme of research in condensed matter physics for the past decades. Among superconducting compounds, titanates have not been as much pursued as Cu$^{2+}$ (3$d^9$) cuprates and Fe$^{2+}$ (3$d^6$) compounds. Particularly, Ti$^{3+}$-containing compounds or electron systems with a special filling of 3$d^1$ are deemed to be promising candidates as high-$T_C$ superconductors, but there has been no report on such superconducting titanates. With the advent of thin film growth technology, new epitaxially stabilized phases in single-crystalline thin films, which may be different from the bulk counterparts, are promising to realize usual physical properties. Here we report the discovery of emergent superconductivity in orthorhombic-structured thin films of Ti$_2$O$_3$, a 3$d^1$ electron system, in strong contrast to the conventional corundum-structured Ti$_2$O$_3$ which exhibits no superconductivity. Superconductivity at 8 K is observed in the orthorhombic Ti$_2$O$_3$ films, indicated by zero-resistance and Meissner effect. Our discovery introduces a hitherto
unrecognized route towards searching for superconductors via stabilizing new crystalline structures in epitaxial thin films.

Most milestones in superconductivity research were set by the discoveries of new materials such as cuprates\(^{[111,112]}\) and Fe-based superconductors\(^{[113-116]}\). Within the 3d-transition-metal series, Ti\(^{3+}\)-containing compounds were predicted as the third promising candidate as high-\(T_C\) superconductors as a result of their special filling (3\(d\)\(^3\) and \(S=1/2\))\(^{[117]}\), but superconducting titanates have been limited to materials like electron-doped SrTiO\(_3\)\(^{[118]}\), non-stoichiometric titanium monoxide TiO\(_x\)\(^{[119,120]}\) and ternary oxide Li-Ti-O\(^{[121]}\). In a broader perspective, there has been little progress made in the past decades on searching for binary-oxide superconductors. Among the few superconducting binary oxides reported to date, monoxide NbO exhibits \(T_C\) of 1.38 K\(^{[122]}\). Among sesquioxides, Zn-doped and Sn-doped In\(_2\)O\(_3\) were reported to be superconducting at 3.3 K\(^{[123]}\) and 4 K\(^{[124]}\), respectively. With the recent advent of thin film synthesis techniques, there have been pioneering works on ultra-thin superconducting films and heterostructures. For example, superconductivity above 100 K in single-layer FeSe films has been reported\(^{[125]}\), while bulk FeSe shows superconductivity below 8 K\(^{[126]}\). Inspired by these discoveries, we postulate that investigating titanites in the thin film form might open a new door towards searching for new oxide superconductors.

In this work, we report the discovery of emergent superconductivity in epitaxial new stabilized orthorhombic-structured Ti\(_2\)O\(_3\) thin films grown on \(\alpha\)-Al\(_2\)O\(_3\) substrates. Although six different lattices of Ti\(_2\)O\(_3\) were predicted, i.e. corundum, Rh\(_2\)O\(_3\) (II)-type, perovskite, post-perovskite, \(\alpha\)-Gd\(_2\)S\(_3\)-type and Th\(_2\)S\(_3\)-type, only corundum and Th\(_2\)S\(_3\)-type had been reported experimentally\(^{[127]}\). Surprisingly, we found that Ti\(_2\)O\(_3\) thin films can
adapt an orthorhombic Rh$_2$O$_3$-like structure if grown under tailored deposition conditions. Furthermore, although the conventional corundum-type Ti$_2$O$_3$ is a regular narrow-bandgap semiconductor, the orthorhombic thin films turned out to be a new oxide superconductor with $T_C$ of 8 K. In fact, this is, to our knowledge, the first report demonstrating superconductivity in thin films that is absent in the bulk counterpart. Our result opens a new door toward searching for new superconductors in phase-stabilized epitaxial thin films.

![Fig. 5-12](image_url) Metal-insulator transitions observed in R-Ti$_2$O$_3$/Al$_2$O$_3$ heterostructures. a, b, c, Temperature dependence of the sheet resistance at the range of 350 K – 400 K for R-1, R-2, and R-3, respectively. All R-Ti$_2$O$_3$ samples have a metal-insulator transition between 372 K and 385 K.

As a notable feature of transport characteristics, a metal-insulator transition (Fig. 5-12) was found for R-Ti$_2$O$_3$ samples around 370 K, which is much lower than the transition temperature reported for the corundum-structured bulk Ti$_2$O$_3$ (500 K) $^{[128]}$. Hall Effect measurements on the C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$ thin films are shown in Fig. 5-13. C-Ti$_2$O$_3$ is a p-type semiconductor, which is consistent with the previous work $^{[129]}$, whereas R-Ti$_2$O$_3$ is an n-type semiconductor. The carrier concentration of R-Ti$_2$O$_3$ is on the scale of $10^{22}$/cm$^3$, about one order of magnitude higher than that of C-Ti$_2$O$_3$. 

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Fig. 5-13 Hall effect measurements for C-Ti$_2$O$_3$/Al$_2$O$_3$ heterostructure (C-2) and R-Ti$_2$O$_3$/Al$_2$O$_3$ heterostructures (R-1, R-2, and R-3). a, Schematic presentation of the Hall bar symmetry. The inset is an optical image of the sample. b, Temperature dependence of the hall coefficient at the range of 125 K – 400 K. c, Temperature dependence of the carrier mobility in C-Ti$_2$O$_3$/Al$_2$O$_3$ and R-Ti$_2$O$_3$/Al$_2$O$_3$ samples. d, Temperature dependence of carrier concentration for C-2, R-1, R-2, and R-3 samples.

Fig. 5-14 Transport property measurements of the Ti$_2$O$_3$/Al$_2$O$_3$ thin film samples. a, and b, Temperature dependence of sheet resistance obtained from the C-Ti$_2$O$_3$/Al$_2$O$_3$ and R-Ti$_2$O$_3$/Al$_2$O$_3$ heterostructures, respectively. No zero-$R_S$ state was found in C-Ti$_2$O$_3$, while all the R-Ti$_2$O$_3$ shows superconductivity at low temperatures.
As the most important discovery, we found that all R-Ti$_2$O$_3$ samples were superconducting at low temperatures, while C-Ti$_2$O$_3$ samples remained semiconducting (Fig. 5-14). As shown in Fig. 5-15a, a critical transition temperature ($T_C$) of 8 K was obtained in R-Ti$_2$O$_3$ (sample R-3), which to our knowledge is the highest $T_C$ ever observed in binary-oxide superconductors. Fig. 5-15b shows that an external magnetic field can suppress the superconducting transition temperature of R-Ti$_2$O$_3$, an expected behavior of superconductors. The contour plot shown in Fig. 5-15c summarizes the variation of sample resistance as a function of magnetic field and temperature, illustrating
a phase diagram with sharp phase boundary between the superconducting and semiconducting regimes.

Moreover, magnetic-field dependence of the sample resistance was measured, and as shown in Fig. 5-15d, the critical field $H_C$ increased with decreasing temperature. Below 4 K, the critical field was found to be larger than 9 T, which is much higher than those found in other superconducting binary oxides such as Zn-doped In$_2$O$_3$ (3 T)\textsuperscript{123}. In Fig. 5-15e, the critical transition fields at different temperatures is fitted to the empirical equation\textsuperscript{125}: $H/H_C = 1 - (T/T_C)^2$. From the fitting, the critical field is derived as 15.4 ± 0.5 T at zero-temperature and the critical temperature at zero-field as 8.16 ± 0.04 K. The superconductivity was further confirmed by the Meissner effect measurement carried out on sample R-2, and as shown in Fig. 5-15f, the $T_C$ obtained from the onset temperature of the Meissner effect (7.2 K) matches well with that obtained from the electrical measurement (7.3 K).

The structural properties of both Ti$_2$O$_3$ phases have been further elucidated using calculations based on density functional theory (DFT). More details of DFT calculations can be found in Supplementary Materials. The electronic structures of C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$ are shown in Fig. 5-16a and Fig. 5-16b, respectively. To simulate the experimental condition, we adopt the experimental lattice constants and relax the inner atomic positions based on the generalized gradient approximation with Hubbard $U$ (GGA+$U$). However, as shown in Fig. 5-16c, the GGA+$U$ calculations led to metallic states with zero bandgap for both C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$ (except in the large $U$ limit for C-Ti$_2$O$_3$), different from the experimental semiconducting result. Therefore, newly developed hybrid functional calculations were employed to recalculate the electronic structures,
based on the GGA+U relaxed structures. As shown in Fig. 5-16a and Fig. 5-16b, both C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$ are semiconductors with very narrow band gaps close to the experimental values (0.105 eV and 0.115 eV, respectively, as estimated from the optical absorption data in Fig. 5-19). As expected, the bands around Fermi level are contributed by Ti 3d orbitals.

![Diagram](image)

**Fig. 5-16** Theoretical calculations. (a) and (b) Density of states (DOS) calculated using HSE for C-Ti$_2$O$_3$ ($U$=0 eV) and R-Ti$_2$O$_3$ ($U$=3 eV), respectively. (c) Summary of band gaps calculated using both GGA+U and HSE methods. In the reference of experimental data, the HSE method clearly gives a better description of band gaps. (d) Phonon dispersion spectrum, (e) Total phonon DOS, and (f) Eliashberg function $\alpha^2F(\omega)$ (solid line) and frequency-dependent electron-phonon coupling $\lambda(\omega)$ (dashed line) calculated for relaxed R-Ti$_2$O$_3$. (g) $T_c$ of the two Ti$_2$O$_3$ phases calculated using different $\mu^*$ values.

The fact that superconductivity was only observed in orthorhombic-structured Ti$_2$O$_3$ film, but not in the corundum bulk phase, suggests that the underlying mechanism is
probably different from the Cu$^{2+}$ ($3d^9$) and Fe$^{2+}$ ($3d^6$) systems. In the framework of Bardeen-Cooper-Schrieffer (BCS) theory, high electron concentration is favorable for the occurrence of superconductivity, which is consistent with our observation. To further shed light on the origin of superconductivity in R-Ti$_2$O$_3$, we calculated\textsuperscript{[130-134]} the electron-phonon (e-ph) coupling of R-Ti$_2$O$_3$. To reflect the intrinsic properties of R-Ti$_2$O$_3$, fully relaxed lattice structure is adopted in the calculations. Phonon dispersion, total phonon density of states, and frequency-dependent e-ph coupling $\lambda(\omega)$, are shown in \textbf{Fig. 5-16d}, \textbf{Fig. 5-16e} and \textbf{Fig. 5-16f}, respectively. Remarkably, the total e-ph coupling constant $\lambda$ is 1.114, which is a quite large value (in reference, for MgB$_2$ with $T_C = 40$ K, $\lambda = 0.73$) and capable to cause electrons to form Cooper pairs and to lead to a high superconducting transition temperature\textsuperscript{[135]}. In contrast, much weaker e-ph coupling was obtained for C-Ti$_2$O$_3$ (\textbf{Fig. 5-17}). The BCS superconducting transition temperature can be estimated using the standard Allen-Dynes McMillan equation. As shown in \textbf{Fig. 5-16g}, a typical Coulomb pseudopotential $\mu^* = 0.1$ can lead to a quite high $T_C$ above 24 K in R-Ti$_2$O$_3$. The deviation between the experimental $T_C$ and the calculation result might be a result of extrinsic factors such as structural defects and electronic inhomogeneity, which indicate possible room to further improve $T_C$ in R-Ti$_2$O$_3$. Here, we should note that because of the spin degree of freedom in Ti$_2$O$_3$, i.e., Ti ions have spin 1/2, superconducting mechanisms beyond the conventional BCS one involving strong quantum fluctuations, as in the cases of cuprates and iron-pnictides/selenides, are also possible. It will be interesting and important to perform further study to elucidate the superconductivity mechanism in R-Ti$_2$O$_3$, which in turn might help boost $T_C$ in this class of materials.
As a whole, our results suggest that stabilizing new crystalline phases in epitaxial thin films could be a viable route toward searching for new superconductors. In this work, we discovered that the orthorhombic phase of Ti$_2$O$_3$ (R-Ti$_2$O$_3$) stabilized in the epitaxial thin films surprisingly became superconducting at 8 K, the highest transition temperature in binary oxides known to date. Our calculations revealed particularly strong $e$-$ph$ coupling in orthorhombic-structured Ti$_2$O$_3$ compared to the bulk corundum phase. We envision that further increase of the superconducting temperature could be accomplished by
doping and applying pressure. Importantly, Ti$_2$O$_3$ is earth abundant, nontoxic and chemically stable, which are essential merits for potential power and communication applications. From the perspective of fundamental science, the discovery of superconductivity in this $3d^1$ electron system may provide a new platform to investigate superconductors, complimentary to the cuprates ($3d^9$) and iron-based ($3d^6$) systems.

5.5 Electrical Measurements and Phase-Dependent Carrier behavior

The discovery of this new Ti$_2$O$_3$ R-phase motivated us to carry out the physical and optical property measurements. The temperature dependence of electrical conductivity of the C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$ films is shown in Fig. 5-18a. All films show a semiconducting behavior with high conductivity (>3×10$^3$ Ω$^{-1}$ cm$^{-1}$ at 300 K). For C-Ti$_2$O$_3$ films, no metal-to-semiconductor transition was observed since it occurs at ~430 K in bulk, higher than the measured temperature range. Interestingly, the conductivity of epitaxial C-Ti$_2$O$_3$ films is much higher than that reported for bulk single crystals.$^{[136]}$ This difference in conductivity could be related to the defects (vacancies) in the films, which we will discuss later. For R-Ti$_2$O$_3$ films, an unexpected metal-insulator transition was observed around 370 K (Fig. 5-12).

To examine how the structural and symmetric variation affects the electronic properties, we carried out Hall Effect measurements on C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$ films. As shown in Fig. 5-18b, the Hall coefficient is positive for C-Ti$_2$O$_3$, indicating a p-type nature, which is consistent with previous report.$^{[137]}$ In contrast, the Hall coefficient is negative for R-Ti$_2$O$_3$, indicating an n-type nature. Furthermore, electrons appear to be responsible for charge transport even around the metal-insulator transition. The mobility and carrier concentration of C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$ films are exacted from the Hall effect
data and shown in Fig. 5-13. The mobility of C-Ti$_2$O$_3$ is found to be \( \sim 9 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1} \) at room temperature, which is consistent with that reported for single crystals.$^{136}$ The carrier mobility of R-Ti$_2$O$_3$ is around \( \sim 1 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1} \), which is lower than that of C-Ti$_2$O$_3$. However, carrier concentration of R-Ti$_2$O$_3$ is on the scale of 10$^{22}$/cm$^3$, which is about one order of magnitude higher than that of C-Ti$_2$O$_3$. Overall, the high carrier concentration and mobility make Ti$_2$O$_3$ one of the most conductive oxides (a table of comparing the transport properties of Ti$_2$O$_3$ with some common oxides is given in Table 5-2). Furthermore, to our knowledge, the observation that two Ti$_2$O$_3$ polymorphs exhibits opposite carrier types is unique for semiconductors.

Fig. 5-18 Electrical properties of the Ti$_2$O$_3$/Al$_2$O$_3$ thin films. a) Electrical conductivity of C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$ films measured as a function of temperature. b) Hall coefficient data collected on the films. Two R-Ti$_2$O$_3$ films have different thicknesses: R-1: 56 nm; R-2: 112 nm. c) Seebeck coefficient, d) Electrical conductivity and power factor data of C-Ti$_2$O$_3$ (120 nm) and R-Ti$_2$O$_3$ (112 nm) films.
Tab. 5-2 Comparison between different oxide films on the transport properties at 300 K.

In order to further confirm the contrast of carrier types in C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$, Seebeck coefficient measurements were performed on those films. Fig. 5-18c shows the Seebeck coefficient, as a function of temperature ($T$), of C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$. As expected, C-Ti$_2$O$_3$ shows a positive Seebeck coefficient, while R-Ti$_2$O$_3$ shows a negative one. For C-Ti$_2$O$_3$, the Seebeck coefficient is ~38 μV/K at 300 K and decreases with increasing $T$, which is lower than that of the C-Ti$_2$O$_3$ single crystals.[136] Similarly, the Seebeck coefficient of R-Ti$_2$O$_3$ is also low. During the Seebeck measurements, the conductivity was collected simultaneously from 300 K to 500 K for both C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$ films (Fig. 5-18d), and the measured temperature range complements that of the
transport data shown in Fig. 5-18a. The metal-insulator transition around 390 K was observed in R-Ti$_2$O$_3$, which is consistent with the electrical transport results (Fig. 5-18a and Fig. 5-12). For C-Ti$_2$O$_3$, the metal-insulator transition was observed at a higher temperature of ~430 K, which is consistent with that reported for C-Ti$_2$O$_3$ single crystals. Based on the conductivity and Seebeck coefficient, thermoelectric power factors ($\sigma S^2$) for C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$ films were calculated. As shown in the Fig. 5-18d, the power factors of Ti$_2$O$_3$ films is about 0.1 W m$^{-1}$K$^{-1}$ at 500 K.

5.6 Optical Measurements and Ultra-Narrow Bandgap

In the well-investigated TiO$_2$ (3$d^0$), the bandgap is between the Ti 3$d$ and O 2$p$ orbitals which are separated by a large energy gap of 3.3 eV. However, in Ti$_2$O$_3$ (3$d^1$), its electronic structure is more complicated as a result of a partially filled 3$d$-electron band. As pointed out by N. F. Mott, Coulomb repulsion between electrons leads to the emergence of an insulating phase.$^{[145-147]}$ In such Mott insulators, the original 3$d$ band is split into two bands under the influence of strong on-site electron correlation $U$. Mott insulators such as V$_2$O$_3$, Fe$_3$O$_4$, VO$_2$, and Ti$_2$O$_3$ exhibit metal-insulator transitions due to drastic electronic state changes.$^{[148,149]}$

In order to achieve an accurate description of the band structures of Ti$_2$O$_3$, newly developed hybrid functional calculations based on Heyd-Scuseria-Ernzerhof (HSE) exchange$^{[150]}$ were employed to calculate the electronic structures. In the calculations, generalized gradient approximation with Hubbard $U$ (GGA+$U$) relaxed structures was used. As shown in Fig. 5-19a, bandgaps for TiO$_2$, C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$ are 3.3 eV, 0.09 eV and 0.11 eV, respectively. As expected, the electronic states around Fermi levels in both Ti$_2$O$_3$ phases are contributed by Ti 3$d$ orbitals. Moreover, the upper valence band is
filled by the $3d^1$ electron, and the lower valence band is filled by O $2p$ electrons in Ti$_2$O$_3$, which is equivalent to the valence band of TiO$_2$.

![Band structures and absorption spectra](image)

**Fig. 5-19** Narrow bandgap and optical properties of Ti$_2$O$_3$. a) Band structures calculated for TiO$_2$ (Anatase), C-Ti$_2$O$_3$, and R-Ti$_2$O$_3$. b) and c) Experimental absorption spectra measured for C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$ films, as well as deconvoluted Gaussian peaks. The insets shows the $(αE)^2$ versus $E$ plots for analyzing the band gap of C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$. d) Schematic band diagram of R-Ti$_2$O$_3$ showing the proposed optical transitions that may contribute to the absorption.

In order to further study the band structures of two Ti$_2$O$_3$ phases, light absorption measurements were performed. It is important to note that the optical properties of Ti$_2$O$_3$ thin films have not been reported so far. **Fig. 5-19b** and **Fig. 5-19c** show the room temperature absorption spectra of C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$ epitaxial films (after substrate
subtraction), respectively, measured in the ranges of UV to Near-Infrared. Surprisingly, the absorption coefficient ($\alpha$), in both Ti$_2$O$_3$ phases, is above $0.5 \times 10^5$ from 200 nm to 3 $\mu$m, demonstrating strong wide-band light absorption. Furthermore, Fourier transform infrared spectroscopy (FTIR) was applied to measure their absorption properties in the Mid-infrared range (Fig. 5-20). Tauc plots of $(\alpha E)^2$ versus $E$ were used to determine the nature and size of the bandgaps of C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$, which are shown as insets in Fig. 5-19b and Fig. 5-19c, respectively. It has to be noted that $(\alpha E)^{1/2}$ versus $E$ plots lead to negative band–gaps in both phases, which is unphysical and indicates a direct bandgap nature. The linear extrapolation of the $(\alpha E)^2$ versus $E$ curves to zero yields a direct band gap of 0.115 eV for R-Ti$_2$O$_3$ and 0.105 eV for C-Ti$_2$O$_3$, which are close to the reported value (0.1 eV) for corundum Ti$_2$O$_3$. As expected, the bandgaps for both Ti$_2$O$_3$ phases, achieved from the optical absorption, are consistent with the theoretical results.

![FTIR data used for band gap determination.](image)

**Fig. 5-20** FTIR data used for band gap determination.

Theoretical DOS calculations allowed us to assign that experimentally observed light absorption to the transitions between bands in the orthorhombic R-Ti$_2$O$_3$. In **Fig. 5-19d**, a
schematic band diagram is drawn based on the total DOS of R-Ti$_2$O$_3$, and possible optical transitions are proposed. Since the conduction band of R-Ti$_2$O$_3$ includes several sub-bands with hybridization, the low-energy absorption peaks a, b and c can be assigned to the $d$-$d$ transitions between the upper valence band and conduction band. However, in the high-energy range, the optical peak d could be assigned to the $p$-$d$ excitations from O 2$p$ (lower valence band) to the Ti 3$d$ (conduction band). Accordingly, the location of experimental peaks (a: 1.2 eV, b: 3.0 eV, c: 4.3 eV, d: 5.9 eV.) are consistent with the proposed theoretical transitions (a: 1.4 eV, b: 2.9 eV, c: 3.9 eV, d: 6.1 eV.).

![Figure 5-21](image)

**Fig. 5-21** Absorption characteristics comparison between Ti$_2$O$_3$ and other semiconductors. a) Light absorption comparison between Ti$_2$O$_3$ and Si at 300 K. b) Light absorption of Ti$_2$O$_3$ thin films at mid-infrared range, collected at 300 K. c) Optical absorption coefficient data for several Hg$_{1-x}$Cd$_x$Te alloy compositions, for photon energies near the fundamental absorption edge.
It is important to note that the bandgap of Ti$_2$O$_3$ (approximately 0.1 eV) is smaller than most other well-investigated semiconductors. For example, silicon has a bandgap of 1.1 eV, which is widely used for the electronics and solar cells. Furthermore, the large absorption coefficient in the range from UV to Near-Infrared indicates that Ti$_2$O$_3$ may find applications in wide-band solar energy harvesting photovoltaic and photothermal devices. In Fig. 5-21, we compare the absorption characteristics of Ti$_2$O$_3$ with other common narrow-bandgap semiconductors, and it is clear that Ti$_2$O$_3$ is an excellent light absorbing material with wider band absorption than Si and higher absorption coefficient than HgCdTe (MCT), which is a dominant candidate for mid-infrared photodetectors. Thus, Ti$_2$O$_3$ would also play an important role in the future environmental friendly mid-infrared (heat) imaging and remote sensing systems.

5.7 Magnetic Measurements and First-Principles Calculations

It is known that the ground magnetic state for Ti$_2$O$_3$ bulk (corundum) is antiferromagnetic, and a Hartree-Fock theory of itinerant antiferromagnetism was presented and applied to explain the observed electric and magnetic properties of Ti$_2$O$_3$ in the previous study. However, the magnetism in two different polymorphs of Ti$_2$O$_3$ have not been reported, yet. Thus, the magnetic properties of C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$ in this work could be different, since they have different lattice structures, and, besides, oxides are known to have strong structure-property correlation. In this work, magnetic property measurements were performed on the C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$ epitaxial films in a Quantum Design SQUID system.
Fig. 5- 22 Magnetic properties of Ti$_2$O$_3$ epitaxial thin films. a) $M$-$H$ data collected from C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$ samples at 300 K. A bare sapphire substrate was also measured. b) $M$-$H$ curves collected from R-2 from 300 K to 1000 K. The inset shows the enlarged central part of the $M$-$H$ curves. c) Substrate-subtracted $M$-$H$ curves for R-Ti$_2$O$_3$ from 300 K to 1000 K. d) Raman spectra taken before (R-Ti$_2$O$_3$) and after (“A-TiO$_2$”) HT-MH, up to 1000 K. e) $M$-$H$ curves taken before (R-Ti$_2$O$_3$) and after (“A-TiO$_2$”) HT-MH at 300 K. f) Temperature dependence of magnetization ($M_s$) for R-Ti$_2$O$_3$, obtained from c).
Fig. 5-23 More magnetic measurement performed at different temperatures. $M-H$ curves for a) Bare sapphire substrate, b) C-Ti$_2$O$_3$ powders, c) Sapphire+C-Ti$_2$O$_3$ and d) Sapphire+R-Ti$_2$O$_3$ samples, collected at different temperatures.

Fig. 5-24 Dynamic SIMS. (a) Depth profiling spectra of the R-Ti$_2$O$_3$/Al$_2$O$_3$ heterostructure. (b) Mass spectra over the mass range of 45-70 amu, collected from the R-Ti$_2$O$_3$ film.
The magnetic field \((H)\) dependence of magnetification \((M)\) measured up to 10000 Oe for C-Ti\(_2\)O\(_3\) (C-1) and R-Ti\(_2\)O\(_3\) (R-1) films, collected at 300 K, are shown in Fig. 5-22a, with the bare sapphire substrate as a reference. Surprisingly, an unexpected ferromagnetic loop was observed in the R-Ti\(_2\)O\(_3\) sample, while the bare sapphire substrate shows a straight line with diamagnetism. For the C-Ti\(_2\)O\(_3\) sample, there is no hysteresis loop observed in the \(M-H\) measurements, which is in line with its antiferromagnetism\(^{154}\).

Additionally, more \(M-H\) curves collected at different temperatures (< 300 K), from bare sapphire substrate, C-Ti\(_2\)O\(_3\) powder, C-Ti\(_2\)O\(_3\) and R-Ti\(_2\)O\(_3\) thin film samples are shown in Fig. 5-23. For the C-Ti\(_2\)O\(_3\) thin film sample, only straight lines were observed, when the weak antiferromagnetic signal of C-Ti\(_2\)O\(_3\) film must be drawn in the strong background signal from the diamagnetic substrate. However, ferromagnetic hysteresis loops were consistently obtained down to 10 K in R-Ti\(_2\)O\(_3\) (R-1) sample. To rule out any magnetic contamination issue, secondary ion mass spectrometric (SIMS) were performed, as shown in Fig. 5-24, and no evidence of any magnetic element such as Fe, Co, Mn, Ni or Cr exists in the sample.

Furthermore, a thicker sample (R-2: 112 nm) was used to further confirm the ferromagnetism in R-Ti\(_2\)O\(_3\) at high temperatures. As shown in Fig. 5-22b and Fig. 5-22c, the ferromagnetism in R-Ti\(_2\)O\(_3\) was disappeared above 900 K. Suprisingly, the R-Ti\(_2\)O\(_3\) was converted to Anatase TiO\(_2\) (A-TiO\(_2\)) after the high temperature \(M-H\) (\(HT-MH\)) measurements in SQUID, up to 1000 K. As shown in Fig. 5-22d, the R-2 sample was turned to be white (“A-TiO\(_2\”)”), and no ferromagnetic loop could be observed again at 300 K (Fig. 5-22e), which confirmed the emergent ferromagnetism was induced in the
orthorhombic R-Ti$_2$O$_3$ matrix. In order to ascertain the phase transition, from R-Ti$_2$O$_3$ to A-TiO$_2$, annealing of R-Ti$_2$O$_3$ in the SQUID chamber from 500 K to 900 K was performed. As shown in Fig. 5-25, the R-Ti$_2$O$_3$ was converted to A-TiO$_2$ above 800 K, and the impurity was observed at 700 K. Fig. 5-22f shows the temperature dependence of magnetization ($M_S$) for R-Ti$_2$O$_3$ (R-2), with the phase transition. The ferromagnetism observed up to 600 K is confirmed to be induced from the orthorhombic R-Ti$_2$O$_3$ matrix. Combing with the electrical property (carrier behavior), we speculate the ferromagnetism in R-Ti$_2$O$_3$ originates from the oxygen vacancies, which is similar to that observed in the reduced or doped TiO$_2$.[155-159]

![Raman spectra](image)

**Fig. 5-25** Annealing in SQUID chamber for R-2. Raman spectra taken from the sample annealed in the SQUID at different temperatures.

To shed light on the ferromagnetism observed in R-Ti$_2$O$_3$, first-principles calculations were performed.[160-163] First, the physical properties of the non-defective structure (see Fig. 5-26a), including the magnetism and electronic structure, have been
calculated. To determine the ground state, several possible magnetic orders have been tested, as shown in Fig. 5-27. The AFM-III state has the lowest energy. The corresponding local magnetic moment is ±0.636 μB/Ti (shown in Fig. 5-28) and the net magnetic moment is zero. According to the total DOS and element-resolved DOS, as sketched in Fig. 5-26e, the band gap is ~0.26 eV and the bands near the Fermi level are mostly from Ti 3d orbitals.

Fig. 5-26 First-principles calculations of R-Ti$_2$O$_3$ with different vacancy configurations. a) – d) Schematic presentation of different vacancies in R-Ti$_2$O$_3$ considered in the calculations. e) – h) Corresponding total DOS and atomic pDOS of R-Ti$_2$O$_3$ with none vacancy, O1 vacancy, O2 vacancy and Ti vacancy, respectively, calculated using the HSE method.

Second, to investigate the effect of vacancy defects, both Ti and O vacancies are considered. As shown in Fig. 5-26h and Fig. 5-28, for Ti vacancy (one Ti missing per 2 u.c.’s, ~12.5%), although the net magnetic moment is nonzero (~0.167 μB/per Ti), the
system is metallic with finite DOS at the Fermi level, which disagrees with the experimental measurements. For oxygen ions, there are two different sites [O1: between Ti1 (Ti2) and Ti4 (Ti3), O2: between Ti1 (Ti3) and Ti2 (Ti4)] in R-Ti₂O₃, as shown in Fig. 5-26b and Fig. 5-26c. For the O1 vacancy (one missing O per u.c., ~16.7%), the net magnetic moment is still zero with a band gap of ~0.322 eV. In contrast, the net magnetic moment for the O2 vacancy is ~0.188 μB/per Ti, with a narrow band gap of ~0.095 eV, which is in agreement with the experimental value. In addition, the energy of O2 vacancy is lower than O1 case ~0.35eV/Ti. Therefore, it is reasonable to argue that the ferromagnetism observed in R-Ti₂O₃ is induced by the O2 vacancy. The details of magnetic moments of Ti atoms are listed in Fig. 5-28.
Details of DOS calculation on R-Ti$_2$O$_3$. a) Various types of possible magnetism in R-Ti$_2$O$_3$. FM: ferromagnetic; NM: non-magnetic; AFM: antiferromagnetic. b) Energy comparison between those possible magnetic orders for non-defective R-Ti$_2$O$_3$. c) Details of the structure of R-Ti$_2$O$_3$. d) Calculated band gap of R-Ti$_2$O$_3$ with different defects.
For comparison, the magnetic and electronic properties of C-Ti₂O₃ are also calculated. As shown in Fig. 5-29, the magnetic ground state is AFM-I, which is robust against the vacancies (at least in our calculations). Different from R-Ti₂O₃, there is only one type of oxygen site in C-Ti₂O₃. The band gaps for the state with single O vacancy per u.c. (~5.6%) and Ti vacancy per u.c. (~8.3%) are ~0.249 eV and ~0.17 eV, respectively.
Fig. 5-29 DFT Results of C-Ti$_2$O$_3$. a) Various types of possible magnetism in C-Ti$_2$O$_3$. b) d) f) Energy comparison between those possible magnetism, with none vacancy, O vacancy, and Ti vacancy induced in C-Ti$_2$O$_3$. c) e) g) DOS and pDOS calculated using HSE for none vacancy, Ti vacancy and O vacancy, respectively.
To summarize, a new orthorhombic phase of Ti$_2$O$_3$ thin films were epitaxially stabilized on Al$_2$O$_3$ (001) single crystal substrates and show high temperature ferromagnetism with n-type semiconducting behavior distinct from the trigonal bulk phase (C-Ti$_2$O$_3$). Multilateral comparison, including semiconducting carrier behavior, structure, magnetic property, and role of defects, between C-Ti$_2$O$_3$ and R-Ti$_2$O$_3$, demonstrates selective stabilization of polymorph phases could provide a new way to engineering carrier behaviors and magnetisms in semiconductors with same composition, which is significant to both electronic fabrication and the solid state physics.
Chapter 6 Conclusion and Outlook

Semiconductors have been the workhorse of a wide range of modern technologies owing to their favorable and tunable physical properties. Semiconductors with bandgap larger than 1 eV are known to dominate technological applications, such as UV photodetector, light-emitting diode (LED), solar cell, photocatalysis and so on. Some oxides, particularly titanium dioxide (TiO$_2$), also have promising application in technologies such as photocatalysts, but its bandgap of 3.3 eV is too large. Extensive efforts have been devoted to improve the catalytic efficiency of TiO$_2$ by enhancing the light absorption through reduction/doping. In reduced TiO$_{2-x}$, Ti$^{3+}$ ions play the crucial role to reduce the effective band gap and enhance the light absorption in the visible range. Incidentally, Ti$^{3+}$ was also reported to play important roles in triggering the emergence of conduction, superconductivity and magnetism of the 2D electron gas at the LaAlO$_3$/SrTiO$_3$ interface. However, in these prior examples, the amount of disordered Ti$^{3+}$ ions within the Ti$^{4+}$ background is limited, and their effect is weak and unreliable. The quest of a pure Ti$^{3+}$ (3$d^1$) system led us to titanium sesquioxide Ti$_2$O$_3$, a narrow band gap semiconductor.

In this dissertation, we mainly focused on the synthesis, structural, physical and optical properties of titanium sesquioxide Ti$_2$O$_3$. We examined various forms of Ti$^{3+}$ containing materials including interface, nanoparticles, and epitaxial thin films. Our main conclusions are as follows:

- **Interface:** Microstructure of the Ti/SrTiO$_3$ interface was investigated by high resolution S/TEM. Furthermore, the chemical and valence evolution was characterized and analyzed by S/TEM and EELS line scan across the interface.
One unit cell thick of cubic perovskite Ti$_2$O$_3$ was observed at the Ti/STO interface. And oxygen diffusion depth of ~3.2 nm was observed and confirmed at the sample fabricated at room temperature. Besides, oxygen vacancy domains in the SrTiO$_3$ substrates was observed and characterized by LAADF and EELS.

- **Nanoparticles:** Corundum Ti$_2$O$_3$ nanoparticles (~100 nm) were fabricated by ball milling process. The size distribution, structural, optical and physical properties were studied. Strong light absorption and high performance of photothermal properties had been observed in the Ti$_2$O$_3$ nanoparticles. 
  
  a): Seawater desalination was investigated on the Ti$_2$O$_3$ nanoparticles, based on its excellent photothermal property (with Prof. Xiaodong Chen, NTU).
  
  b): Graphene/Ti$_2$O$_3$ hybrid mid-infrared (4.5-10 μm) photodetectors were fabricated on SiO$_2$/Si substrates (with Prof. Qijie Wang, NTU), based on its strong absorption at the mid-infrared range. Extremely high responsivity was achieved.
  
  c)*: Used as light absorbing material for water splitting and CO$_2$ reduction……

- **Epitaxial thin films:** Several different phases of Ti$_2$O$_3$ epitaxial thin films were stabilized on Al$_2$O$_3$, Si, SrTiO$_3$, LaAlO$_3$, TiO$_2$……
  
  a): Emergent superconductivity at 8 K was discovered in the new stabilized orthorhombic Ti$_2$O$_3$ (R-Ti$_2$O$_3$) epitaxial thin films. The electrical and magnetic transport of V-doped R-Ti$_2$O$_3$ epitaxial thin films are under investigating.
b): Different carrier behavior and magnetism was observed and studied in the corundum and orthorhombic Ti$_2$O$_3$ thin films. Emergent ferromagnetism was observed in the R-Ti$_2$O$_3$ with n-type semiconducting behavior, while C-Ti$_2$O$_3$ is antiferromagnetic and p-type semiconducting.

c): Mid-infrared photodetectors would be fabricated on the Ti$_2$O$_3$ thin films.

Based on the observed physical and optical properties of Ti$_2$O$_3$ nanoparticles and epitaxial thin films, high performance solar energy harvesting photovoltaic devices, photothermal devices, and mid-infrared photodetectors could be achieved using Ti$_2$O$_3$. Besides, we provided a new material system for studying the emergent superconductivity and ferromagnetism in oxides, which is critical for solid states physics research. As future works, we think the narrow bandgap and ultrahigh conductivity can be further explored for advanced catalytic, energy conversion and energy storage technologies. Improvements of the synthesis of Ti$_2$O$_3$ based nanomaterials and thin films with well controlled morphology and composition are the prerequisites for realizing new technologies. Furthermore, besides integrating with graphene, composites of Ti$_2$O$_3$ with other functional materials can be explored to enhance device performances.
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