

**GRAPHENE-COMPLEX OXIDE
HETEROSTRUCTURE**

by

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I. INTRODUCTION

A. MOTIVATION

B. INTRODUCTION TO LAO AND STO

Both LAO and STO have perovskite structure at room temperature. Lattice constant of LAO is $a = 3.791\text{\AA}$ [1], while lattice constant of STO is $a = 3.905\text{\AA}$. In each cubic unit cell of STO, the Ti atom is enclosed in octahedral cage of oxygen, and the octahedron is in the center of a cubic skeleton of Sr atoms (Figure 1). At $T = 105$ K, STO would go through a phase transition and oxygen octahedron pairs would rotate against each other so that the bonding lengths of Sr-O and Ti-O are optimized [2]. This ferroelastic transition would break the cubic symmetry and form tetragonal domains in STO, from different orientations of the tetragonal unit cells. At even lower temperature, the crystal symmetry may transit to orthorhombic and triclinic, but the effects on the property of STO are less significant than the tetragonal phase transition at $T = 105$ K.

At room temperature the STO is paraelectric, with a large dielectric constant ($\epsilon_r \sim 300$). When the temperature is lower than $T = 105$ K, the paraelectricity still persists. Although the elongation of unit cell in low temperature develops a double-well potential for Ti atoms, with potential minima at the oxygen at opposite sides of the the elongation axis, the Ti atoms do not displace towards the minima due to the quantum tunneling of oxygen atoms [2] between the minima. STO is one of the few materials that exhibit such *quantum paraelectricity* [3]. As a result, the dielectric constant of STO increases rapidly with decreased temperature. The increase is also cut off by quantum tunneling, leaves $\epsilon_r \sim 20,000$ [4]. This is especially important for gating experiment at low temperature, and more details will be

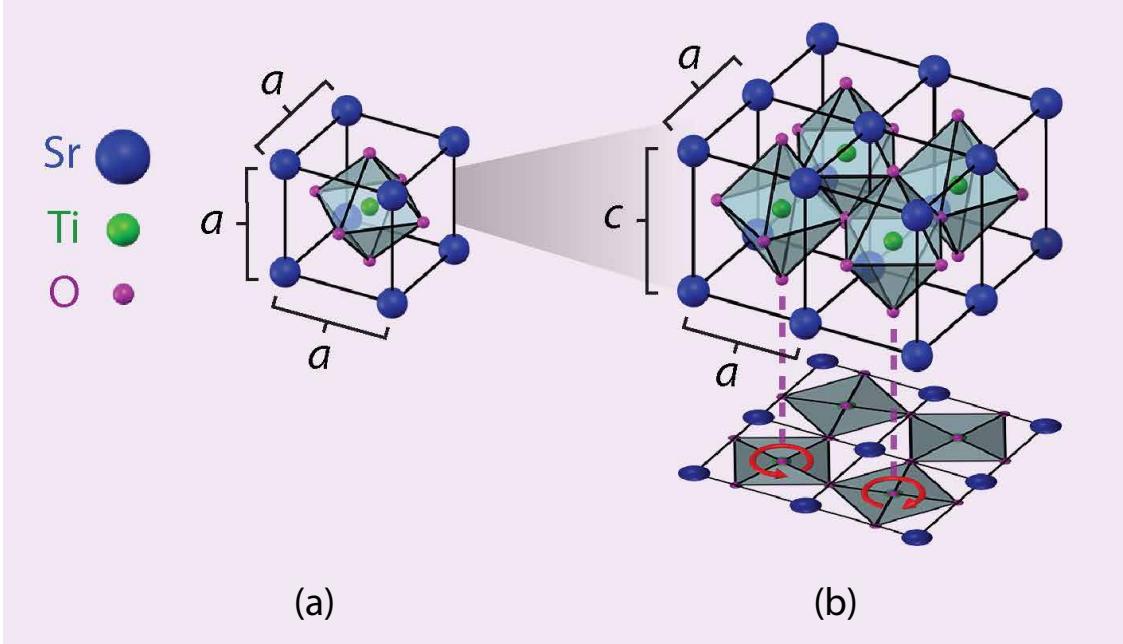


Figure 1: Ferroelastic transition of STO. (a) At $T = 300$ K STO has cubic perovskite structure. (b) At $T = 105$ K, the adjacent oxygen octahedrons would rotate in opposite directions and cause ferroelastic transition in STO. Domains will be formed for different orientations of unit cells. Adapted from [2].

discussed in the following chapters.

The band structure of STO is quite complex. As shown in Figure 2, the conduction band is derived from the $3d$ titanium orbitals and the valence band is from the $2p$ oxygen orbitals. The degeneracy of the five $3d$ orbitals is broken by the crystal structure of STO, and then they are grouped into high energy bands e_g (from $d_{3z^2-r^2}$ and $d_{x^2-y^2}$), and low energy bands t_{2g} (from d_{xy} , d_{yz} and d_{xz}). Ti d_{xy} , d_{yz} and d_{xz} orbitals are coupled to neighboring identical orbitals through the $2p$ orbitals of oxygen atoms in between. Therefore, the hopping matrix elements for in-plane are much greater than than for out-of-plane.

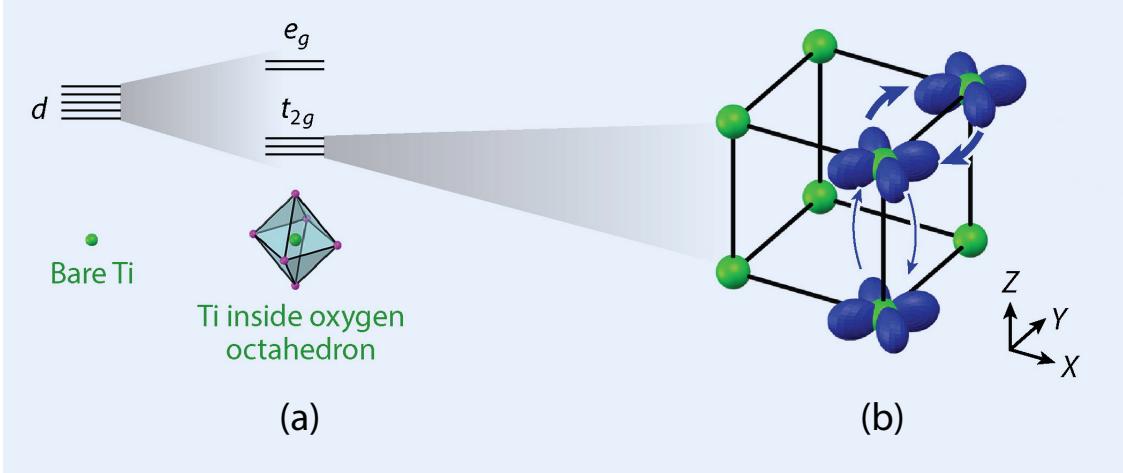


Figure 2: The band structure of bulk STO. (a) The conductive bands derive from the $3d$ orbitals of Ti. The degeneracy of the orbitals is broken by the octahedral cage of oxygen atoms, and the energy levels are grouped into e_g and t_{2g} . (b) The hopping of d_{xy} , d_{xy} and d_{xy} are much easier along in the plane directions, mediated by the $2p$ orbitals of oxygen atoms. Adapted from [2].

1. 2DEG on LAO/STO interface

Although STO is a band insulator, when LAO is grown epitaxially (the small lattice mismatch of 3% makes it possible) on TiO_2 terminated STO, the interface of LAO and STO becomes conductive and a layer of 2DEG is formed, first demonstrated by Ohtomo and Hwang in 2004 [5]. The origin of interface 2DEG is still under debate. There are several different theories about the formation of 2DEG on the LAO/STO interface: polar catastrophe [6], oxygen vacancy [7] and interfacial cation intermixing [8].

The most widely accepted explanation is the polar catastrophe. Unlike the $\text{Ti}^{4+}\text{O}_2^{2-}$ and $\text{Sr}^{2+}\text{O}^{2-}$ planes in STO which are charge neutral, the $\text{La}^{3+}\text{O}^{2-}$ and $\text{Al}^{3+}\text{O}_2^{2-}$ layer are polar, with a net charge of $+e$ and $-e$ respectively. When LAO is grown on TiO_2 terminated STO, the polarity will generate a positive electric field, that builds up as the thickness goes up, as shown in Fig 3(a). To avoid the divergence of potential, the electrons are transferred

from the surface to the interface and form 2DEG (Fig 3(c)). When LAO is grown on SrO terminated STO, a layer of hole gas will be formed in similar mechanism, as observed by Lee in 2018 [9].

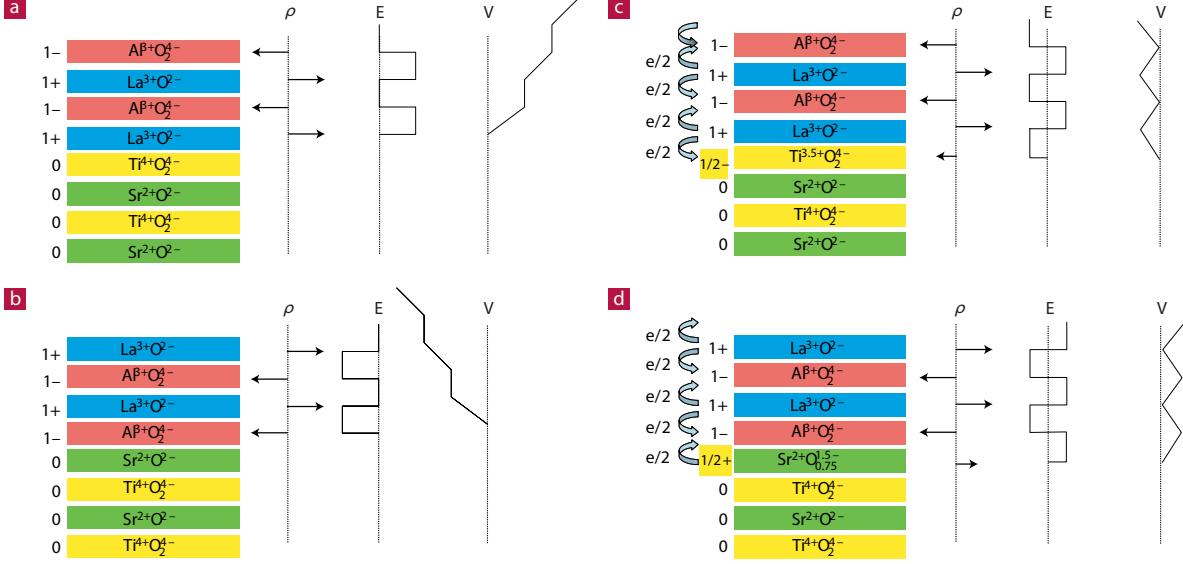


Figure 3: Polar catastrophe mechanism of interface conductivity of LAO/STO. (a) AlO_2 and LaO are not charge neutral and a non-zero potential is built up when LAO is grown on TiO_2 terminated STO. (c) Electrons are transferred from the top surface to neutralize the potential and therefore a layer of 2DEG is formed. (b) and (d) similar mechanism can explain the formation of hole gas on the interface. Adapted from [6].

However, there is a large discrepancy between the carrier density proposed by the polar catastrophe mechanism and measurement. In the polar catastrophe picture, each unit cell will donate half an electron, and result in carrier density of $3.2 \times 10^{14} \text{ cm}^{-2}$, while the observed values are in the order of 10^{13} cm^{-2} . Also, the formation of 2DEG on amorphous LAO on STO is contradicting to the polar catastrophe model.

Oxygen vacancy is another possible explanation of the origin of 2DEG [7], especially it is considered to be the source of conductivity of bulk STO [10]. Growth of LAO/STO sample under different oxygen partial pressure also shows that the carrier density is correlated to

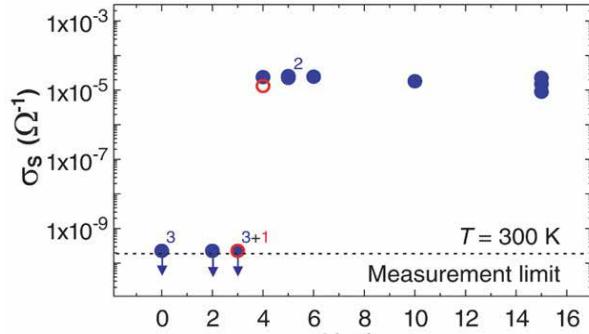
P_{O_2} , therefore the oxygen vacancies can at least partially explain the formation of 2DEG. The magnetism is also considered related to the oxygen vacancies in STO, which will be discussed in future sections. There are also TEM [6] and XRD [8] evidences support that cation intermixing across the interface can also explain the formation of 2DEG. The exchange of La^{3+} and Sr^{2+} provides extra electrons in the STO. However, this cannot explain the formation of hole gas formation with LAO grown on SrO terminated STO. So far, the polar catastrophe is the most widely accepted explanation of 2DEG in LAO/STO.

2. Metal-insulator transition and critical thickness

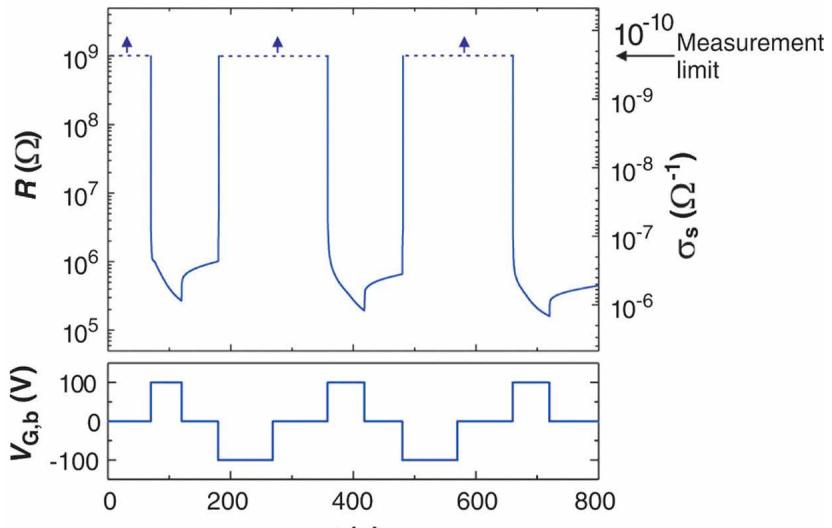
In 2006, Thiel et al. [11] reported that the interface of LAO/STO shows metal-insulator transition when the LAO is thicker than 4 unit cells. In Figure 4(a), when the thickness of LAO is over 4 u.c., the interface is conductive, otherwise the interface is insulating and the conductivity is below measurement limit. When LAO is slightly below the critical thickness (e.g. 3 u.c.), the conductivity on the interface is tunable, with a voltage applied to the backside of the sample. As Figure 4(b) demonstrates, when $V = +100$ V is applied, the interface becomes conductive. When the positive voltage is removed, the resistance is partially restored, but the interface is still conductive. However when $V = -100$ V is applied, the interface becomes insulating again. Similar phenomenon can be observed if the voltage is applied locally through a conductive AFM tip. More details are discussed in future chapters.

3. c-AFM lithography of 2DEG and “water-cycle” mechanism

Following the discovery of backgate tunable interface 2DEG, Cen et al demonstrated in 2008 that LAO/STO interface conductivity can also be induced with a gate voltage applied with a c-AFM tip on sample surface [12]. For a 3 u.c. LAO/STO sample, the previously discussed polar catastrophe mechanism is not strong enough to reconstruct the band structure and form 2DEG on the interface. With gate voltage locally applied with a nanoscale AFM tip, positive charge can be transferred on the surface of LAO and build up a potential to cause polar catastrophe. The threshold voltage on the tip is about $V_{thresh} \approx 6$ V [12]. The conductive channel created in this method is in the same order as the AFM tip, ~ 10 nm.



(a)



(b)

Figure 4: (a) When LAO is over the critical thickness of 4 unit cells, the interface is conductive, otherwise the interface is insulating. (b) When LAO is only slightly below the critical thickness (e.g. 3 unit cells), the conductivity on the interface is tunable with an external voltage applied to the backside. The as-grown sample is insulating. When +100 V is applied, the interface becomes conductive. When the voltage is removed, the conductivity still persists. When -100 V is applied, the interface becomes insulating again. The conductivity can be cycled with alternating voltages. Adapted from [11].

The process is reversible, and the positive charge can be removed with a negative voltage. An insulating gap can therefore be created on the nanowire. More experimental details are discussed in Section II.C.7.

The tunability of the LAO/STO with positive c-tip voltage can be explained with the “water-cycle” mechanism [13]. The water adsorbed onto LAO surface is dissociated into OH^- and H^+ . A positively biased tip removes the OH^- and leave excessive H^+ on LAO surface, which build up the polar catastrophe potential. In the erasing process, the negatively biased c-AFM tip removes the H^+ and restores $\text{OH}^- - \text{H}^+$ balance, and the interface becomes insulating. The water cycle mechanism is supported by the control c-AFM writing experiments performed in vacuum [13].

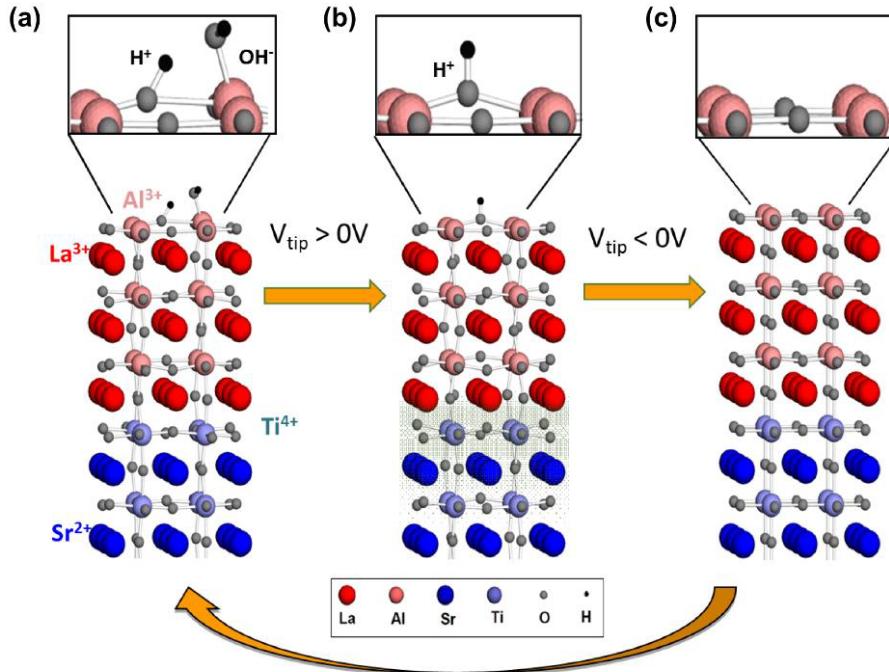


Figure 5: A positively biased c-AFM tip removes removes the OH^- and leave excessive H^+ on LAO surface, and the positive charges induce 2DEG on the interface underneath. A negatively biased c-AFM removes the H^+ , and restores $\text{OH}^- - \text{H}^+$ balance. Adapted from C. S. Hellberg's APS talk.

4. Superconductivity

Superconductivity has been found in STO since 1960s' [14]. Interface superconductivity on LAO/STO was first reported by Reyren et al in 2007 [15], with a phase transition temperature T_c of 200 mK. The in-plane and out-of-plane critical fields are around 1 T to 2 T and less than 1 T. Recently it was found that the electron pairing can persist up to a few T, much higher than the critical field of superconductivity, possibly induced by strong correlation between electrons [16].

5. Magnetism

LAO and STO are both non-magnetic materials, however in 2007 the signature of magnetism was discovered on the interface from Kondo-like behavior of interface resistance [17]. More characterization of the interface magnetism were conducted with torque magnetometry [18], scanning quantum interference device (SQUID) [19], and x-ray circular dichroism (XMCD) [20]. In 2014, Feng et al found that the interface ferromagnetism is electronically tunable at room temperature, from MFM measurement [21]. Optical measurements of the ferromagnetism will be discussed in Chapter IV.

C. GRAPHENE

Graphene is a single layer of carbon atom arranged in honeycomb structure and was first isolated and studied by Novoselov et al. [22]. It has proved to be a powerful and versatile platform for studying condensed matter phenomena due to the unique crystal structure and Dirac fermion behavior of electrons [23]. The Dirac cone band structure makes it possible to tune the carrier density continuously between electrons and holes. This duality of carriers in graphene results in many exotic properties of graphene, such as Klein tunneling [24–27], edge state mixing [28–31], and recently the “wedding cake” structure of quantum Hall states [32]. Bandstructure engineering of graphene has been successful using moire pattern [33,34], interlayer interaction between twisted graphene [35,36] and external periodic electric fields

[37]. More exotic phases such as Hofstadter butterfly [33, 34, 37], Mott insulator [35] and superconductivity [36] have been observed in graphene.

1. Graphene band structure and Dirac fermion

The band structure was first studied by Wallace et al. in 1947 [38]. The orbital structure of C atom is $(1s)^2(2s)^2(2p)^4$. The $2s$ and $2p$ orbitals hybridize into sp^2 orbitals that form three σ bonds with 120° angle, and a π bond that provides free electrons.

In the honeycomb lattice structure of graphene, there are two inequivalent sublattices that are mirror of each other, which can be labeled with A and B . The Bravais lattice is hexagonal, and the primitive lattice vectors can be chosen to be:

$$\mathbf{a}_1 = \frac{a}{2} (3, \sqrt{3}), \quad \mathbf{a}_2 = \frac{a}{2} (3, -\sqrt{3})$$

with $a = 1.42\text{\AA}$ being the spacing between two adjacent C atoms. Using the relationship between the real space lattice and reciprocal lattice $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$, the primitive reciprocal lattice vectors can be written as

$$\mathbf{b}_1 = \frac{2\pi}{3a} (1, \sqrt{3}), \quad \mathbf{b}_2 = \frac{2\pi}{3a} (1, -\sqrt{3})$$

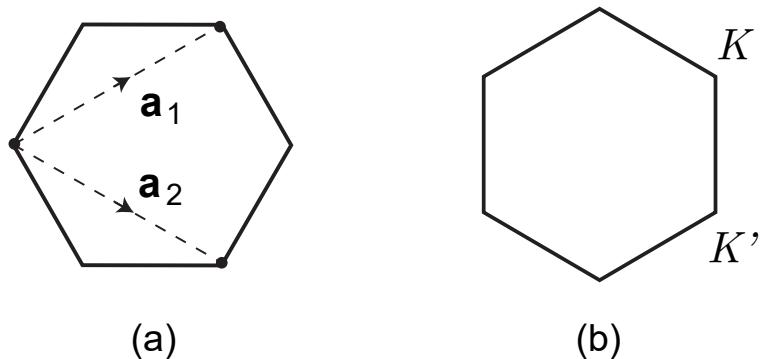


Figure 6: (a) Primitive vectors of Bravais lattice. (b) First Brillouin zone of graphene.

The first Brillouin zone is also hexagonal shape. There are two types of corners, K and K' , and their positions in the reciprocal space are:

$$\mathbf{K} = \frac{2\pi}{3a} \left(1, \frac{1}{\sqrt{3}} \right), \quad \mathbf{K}' = \frac{2\pi}{3a} \left(1, -\frac{1}{\sqrt{3}} \right).$$

The wavefunction of electron in graphene can be written as the superposition of states in the two sublattices A and B :

$$\Psi(\mathbf{k}, \mathbf{r}) = \sum_{\alpha=A,B} c_{\alpha}(\mathbf{k}) \Phi_{\alpha}(\mathbf{k}, \mathbf{r}),$$

and the wavefunctions for the sublattice states can be written as Bloch wave functions:

$$\Phi_{\alpha}(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{n}} \sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot\mathbf{R}} \phi_{\alpha}(\mathbf{r} - \mathbf{R}),$$

where ϕ_{α} is the wavefunction at each atomic site, \mathbf{R} is over the entire Bravais lattice, and n is the number of unit cells in the crystal.

The tight-binding model assumes that the hopping is only allowed for the nearest and next nearest neighbors, and therefore the Hamiltonian can be written as [38, 39]:

$$\begin{aligned} \mathbf{H} = & -t \sum_{ij=\text{n.n.}, \sigma} (a_{i\sigma}^{\dagger} b_{j\sigma} + \text{H.c.}) \\ & - t' \sum_{ij=\text{n.n.n.}, \sigma} (a_{i\sigma}^{\dagger} a_{j\sigma} + b_{i\sigma}^{\dagger} b_{j\sigma} + \text{H.c.}), \end{aligned} \tag{I.1}$$

where t is the hopping energy, $a_{i\sigma}^{\dagger}$ is the creation operator for the state on the i th site of sublattice A with spin $\sigma \in \{+1, -1\}$, and $b_{j\sigma}$ is the annihilation operator for state on the j th site of sublattice B with spin σ . The summation is over all the nearest neighbors for the 1st term and next nearest neighbors for the 2nd term. For sublattice A , the three nearest neighbors in real-space are:

$$\delta_1 = \frac{a}{2} \left(1, \sqrt{3} \right), \quad \delta_2 = \frac{a}{2} \left(1, -\sqrt{3} \right), \quad \delta_3 = -a(1, 0),$$

and the next nearest neighbors are:

$$\delta'_1 = \pm \mathbf{a}_1, \quad \delta'_2 = \pm \mathbf{a}_2, \quad \delta'_3 = \pm (\mathbf{a}_2 - \mathbf{a}_1).$$

The resulting eigen energies are [38, 39]

$$E_{\pm}(\mathbf{k}) = \pm t\sqrt{3 + f(\mathbf{k})} - t'f(\mathbf{k}),$$

with

$$f(\mathbf{k}) = 2 \cos\left(\sqrt{3}k_y a\right) + 4 \cos\left(\frac{\sqrt{3}}{2}k_y a\right) \cos\left(\frac{3}{2}k_y a\right).$$

The plus sign is for the upper band and minus sign is for the lower band.

For \mathbf{k} close to \mathbf{K} (or \mathbf{K}'), set $\mathbf{q} = \mathbf{K} - \mathbf{k}$, with $|\mathbf{q}| \ll |\mathbf{K}|$, then the band energies can be approximated by a linear dispersion relation

$$E_{\pm}(\mathbf{q}) \approx v_F |\mathbf{q}|,$$

with \mathbf{q} being the momentum \mathbf{k} relative to \mathbf{K} (or \mathbf{K}'), and $v_F \approx c/300$ or 10^6 m/s. The Hamiltonian can be written as

$$\mathbf{H}(\mathbf{q}) = \hbar v_F \begin{pmatrix} 0 & q_x + iq_y \\ q_x - iq_y & 0 \end{pmatrix} = \hbar v_F \hat{\sigma} \cdot \mathbf{q} \quad (\text{I.2})$$

in the basis of *sublattice states*, with the components of $\hat{\sigma}$ operator being the usual Pauli matrices. The eigenvectors for states around \mathbf{K} and \mathbf{K}' are

$$\psi_{\pm, \mathbf{K}}(\mathbf{q}) = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-i\theta_{\mathbf{q}}/2} \\ \pm e^{i\theta_{\mathbf{q}}/2} \end{pmatrix}, \quad \psi_{\pm, \mathbf{K}'}(\mathbf{q}) = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{i\theta_{\mathbf{q}}/2} \\ \pm e^{-i\theta_{\mathbf{q}}/2} \end{pmatrix}. \quad (\text{I.3})$$

with

$$\theta_{\mathbf{q}} = \tan^{-1}\left(\frac{q_x}{q_y}\right)$$

The plus and minus signs are corresponding to states in the conductance and valence bands. Notice that when \mathbf{q} rotates around \mathbf{K} (or \mathbf{K}'), the phase of $\psi_{\pm, \mathbf{K}}$ (or $\psi_{\pm, \mathbf{K}'}$) only changes by π instead of 2π . Therefore the sublattice states are also called “pseudo-spin” states [39].

A significant difference between graphene and normal semiconductor is that, the electron and hole states are described by the same wavefunction, and both are obtained from a Hamiltonian of the form of a relativistic particle described by the 2D Dirac equation [39]. Therefore the electrons in graphene has the properties of Dirac fermions, such as handedness. Also notice that the spinors for \mathbf{q} around \mathbf{K} and \mathbf{K}' differ by a phase of π (equation I.3),

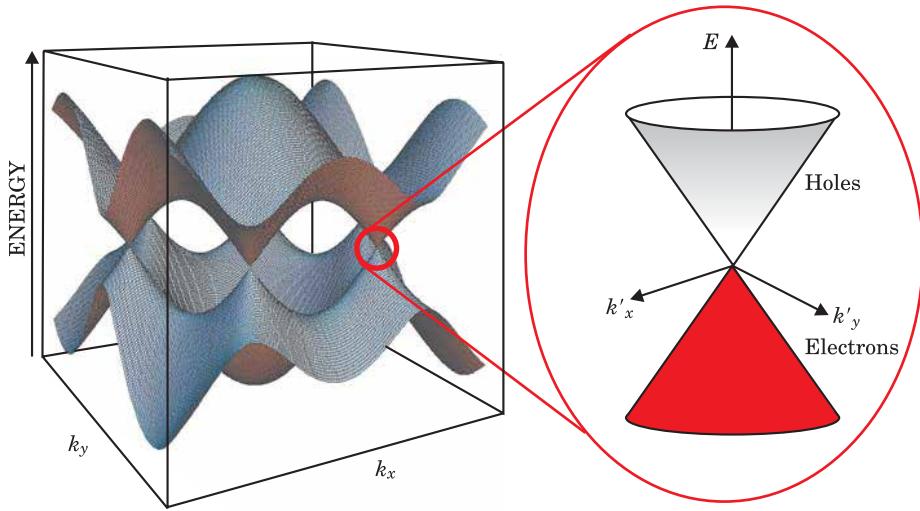


Figure 7: The band structure of Graphene. The low energy approximation around \mathbf{K} and \mathbf{K}' has linear dispersion relation. The conduction and valence bands are gapless and the electron behave like Dirac fermions. Adapted from [23].

therefore the states are opposite in handedness around \mathbf{K} and \mathbf{K}' . However, at \mathbf{K} and \mathbf{K}' the wavefunctions are still the linear combination of the two sublattice states, or the pseudo-spin states. This degree of freedom will introduce extra degeneracies and will be discussed in the following section.

2. Quantum Hall effect

Quantum Hall effect is one of the most important discovery in physics in the 20th century. In the classical Hall effect, a Hall voltage will be built by in the transverse direction of current in magnetic field. In the quantum Hall effect however, the Hall voltage built up by the magnetic field is quantized. This section will start from the classical behavior of electron in magnetic field, and discuss the unique quantum Hall effect in graphene.

a. Classical Hall effect In the classical Drude model, the electrons are colliding with scattering centers and the average velocity is zero without external electric field. When a field is applied, the drift velocity is

$$\mathbf{v}_d = -\frac{e\mathbf{E}}{m}\tau, \quad (\text{I.4})$$

where \mathbf{E} is the external field, and τ is the mean free time between two collisions. The current density can be written as

$$\mathbf{j} = -nev_d = \frac{ne^2\tau}{m}\mathbf{E},$$

where n is the carrier density in the conductor. The conductivity is

$$\sigma = \frac{\mathbf{j}}{\mathbf{E}} = \frac{ne^2\tau}{m} = n\mu e \quad (\text{I.5})$$

and $\mu \equiv \frac{e\tau}{m}$ is the mobility of carrier, which defines how fast the carriers move through a conductor. Usually when the scattering is less likely to happen, the mobility will be higher.

When a magnetic field is applied, the motion equation I.4 is modified as

$$\frac{m\mathbf{v}}{\tau} = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B}). \quad (\text{I.6})$$

Assume the motion is in x - y plane. The Ohm's law can be written as tensor form:

$$\mathbf{j} = \sigma \cdot \mathbf{E} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} \\ \sigma_{yx} & \sigma_{yy} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \end{pmatrix}.$$

The conductivity tensor σ can be solved using the motion equation I.6 and the definition of σ and \mathbf{j} :

$$\sigma = \frac{\sigma_0}{1 + \omega_c^2\tau^2} \begin{pmatrix} 1 & -\omega_c\tau \\ \omega_c\tau & 1 \end{pmatrix},$$

where σ_0 is the conductivity without magnetic field, and $\omega_c \equiv \frac{eB}{m}$ is the cyclotron frequency.

The resistivity tensor can be calculated from σ :

$$\rho_{xx} = \frac{1}{n\mu e}, \quad \rho_{xy} = -\frac{B}{ne} = R_H B, \quad (\text{I.7})$$

with the Hall coefficient $R_H = -\frac{1}{ne}$. The longitudinal resistivity ρ_{xx} and transverse resistivity ρ_{xy} are used to measure the carrier density and type n and mobility μ .

b. Quantum Hall effect of Graphene At low temperature and high magnetic field, the Hall resistance R_{xy} is quantized into plateaus

$$R = \frac{1}{\nu} R_k = \frac{h}{\nu e^2},$$

where $R_k = h/e^2 \approx 25812 \Omega$ is the von Klitzing constant, and the longitudinal resistance R_{xx} is suppressed. The conductivity tensor becomes

$$\rho = \begin{pmatrix} 0 & \frac{\nu e^2}{h} \\ -\frac{\nu e^2}{h} & 0 \end{pmatrix}$$

The quantum Hall effect can be understood semi-classically. In magnetic field, only the energy levels correspond to the quantized cyclotron orbits with integer flux are allowed:

$$E = \hbar \omega_c \left(n + \frac{1}{2} \right),$$

where ω_c is the cyclotron frequency and the orbitals are called Landau Levels.

The electrons that carry the current flow near the edge, while bouncing against the boundary and form chiral edge current channels. The backscattering is suppressed by the magnetic field, and therefore $R_{xx} = 0$ when the Fermi energy is between two Landau levels. The electrons in the bulk of the 2D conductor are trapped in the localized states induced by the scattering centers. When the Fermi energy is elevated to the next Landau level, the electrons start to fill the new localized states and the longitudinal resistance will be non-zero, while the Hall resistance transits to another plateau.

In graphene, the quantum Hall behavior was first observed by Novoselov et al. [40] and Zhang et al. [41] in 2005. The Hall conductance follows

$$\sigma_{xy} = \pm 4 \left(n + \frac{1}{2} \right) \frac{e^2}{h}.$$

The 4 is from the degeneracy of two spin degree of freedom and two pseudo-spin degree of freedom. The half-integer is the result Berry phase of electrons [41] in graphene.

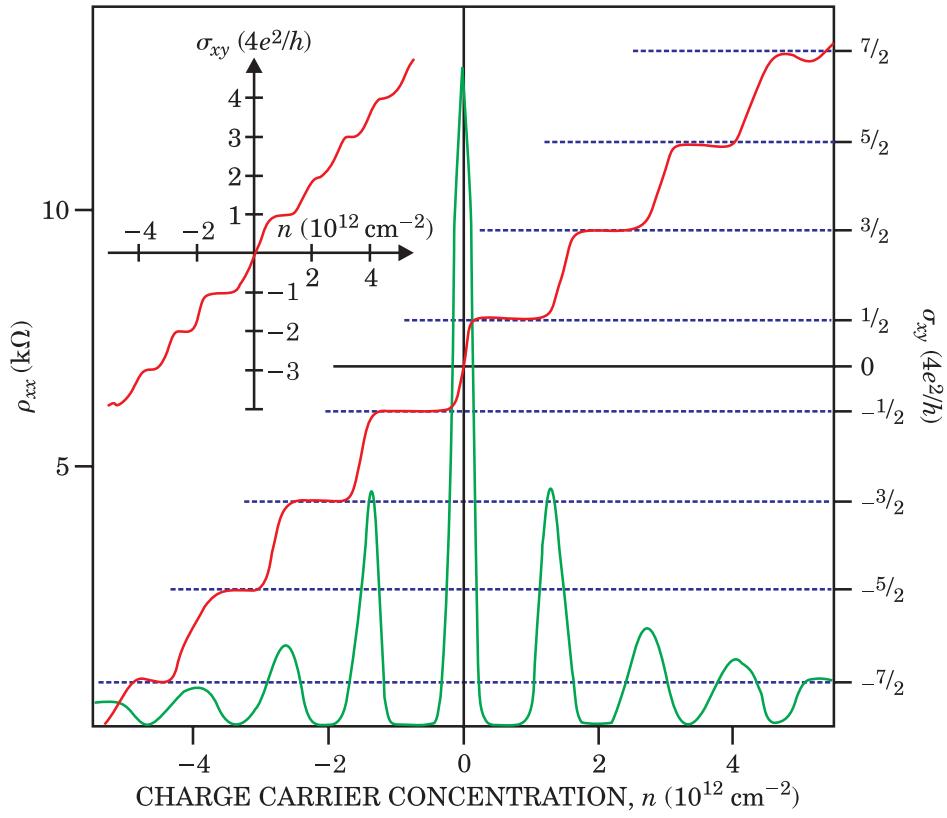


Figure 8: The quantum Hall effect in graphene. The Hall conductance (red line) follows $\sigma_{xy} = \pm 4 \left(n + \frac{1}{2} \right) \frac{e^2}{h}$, while the longitudinal resistance (blue line) shows peaks when the Fermi energy transits from one Landau level to another. Adapted from [40].

II. EXPERIMENTAL METHODS

A. SAMPLE GROWTH

1. LAO/STO growth

The properties of LAO/STO interfaces is extremely sensitive to growth conditions such as substrate temperature, background oxygen pressure, annealing conditions, etc [1]. The samples in my experiments are grown with pulsed laser deposition (PLD) by our collaborators at University of Wisconsin-Madison.

a. Pre-growth treatment STO (001) substrates are purchased from commercial crystal suppliers. The substrates have a carefully controlled mis-cut angle $< 0.1^\circ$, so that the width atomic terraces on STO surface is about 500nm (Figure 10(a)). It has been reported that the terraces on LAO/STO surface can affect the properties of the LAO/STO interface [2], therefore I would like to place the nano-devices on a single terrace. If the terraces are too wide however, the LAO cannot grow evenly on STO surface during the PLD process due to the high activation energy for atomic migrations, and end up forming holes on the sample (FIG. 11).

Before PLD growth, the STO (001) substrates are etched with buffered HF acid to remove SrO and become TiO_2 terminated. Then they are annealed at 1000°C for several hours, so that the surface will reconstruct and form crystal terraces [3]. Then the samples are etched in HF acid for a second time for a clean surface to start with.

b. PLD deposition In PLD deposition, KrF excimer laser ($\lambda = 248$ nm) pulses are focused on a LAO target and plumes of target material are deposited on the pre-heated STO substrates. Two growth conditions are used for LAO/STO samples: (a) STO substrate is heated at $T_{\text{STO}} = 550^\circ\text{C}$ and chamber background oxygen pressure $P(O_2)$ is maintained at 1×10^{-3} mbar, and sample is annealed in 1 atm of O_2 after growth. (b) STO substrate is heated at $T_{\text{STO}} = 780^\circ\text{C}$ and chamber background oxygen pressure $P(O_2) = 7.5 \times 10^{-5}$ mbar; sample is annealed at $T_{\text{STO}} = 600^\circ\text{C}$, $P(O_2) = 300$ mbar for 1 hour after growth, or the so called “Augsburg condition”. Samples grown in condition (a) are used for nano-scale device lithography (i.e. the sub-critical thickness 3.4 uc LAO/STO samples), while condition (b) favors the formation of oxygen vacancies and sample grown in such conditions are used for magnetism experiments [].

Figure 9 illustrates PLD epitaxial growth of LAO. The sample is loaded in an ultra-high vacuum chamber, backed filled with oxygen to the target pressure. Deep UV excimer laser is focused on the LAO crystal target through an optical window on the chamber. The target material is ablated off by the laser and forms a plasma plume. The STO substrate is heated up and placed on top of the target. As the plume expands, target material would condense on the substrate and forms atomic-thin films epitaxially. The high temperature of the substrate facilitates crystallization and epitaxial growth of the target material.

During the PLD growth, the reflection high-energy electron diffraction (RHEED) is used for *in-situ* monitoring the thickness of epitaxial layers. A beam of electron is generated from a source and reflected from the substrate as the film growth. Electron diffraction signal is collected by a detector on the other side (Figure 10(a) inset). The intensity of the diffraction oscillates as a function of film thickness. The thickness of LAO can be precisely controlled by counting the cycles of RHEED signal (Figure 10(b)).

2. Graphene growth

The two most popular methods to obtain single-layer/few-layer graphene are mechanical exfoliation and chemical vapor deposition (CVD).

The mechanical exfoliation isolate single layer graphene directly with adhesive tapes.

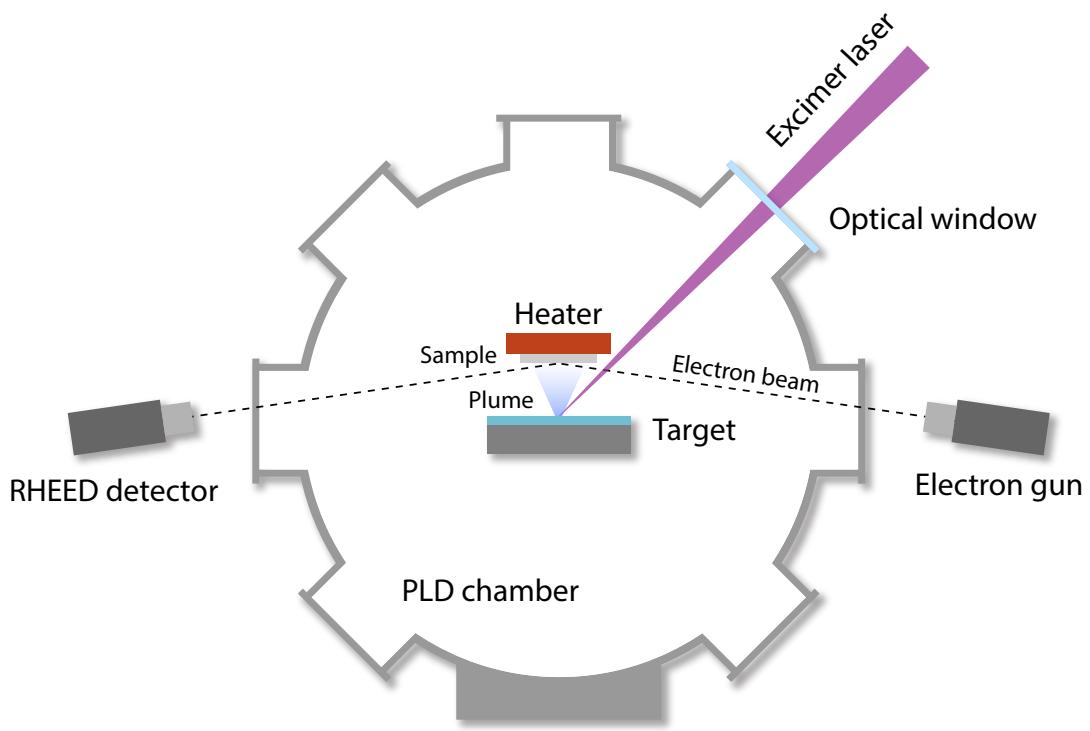
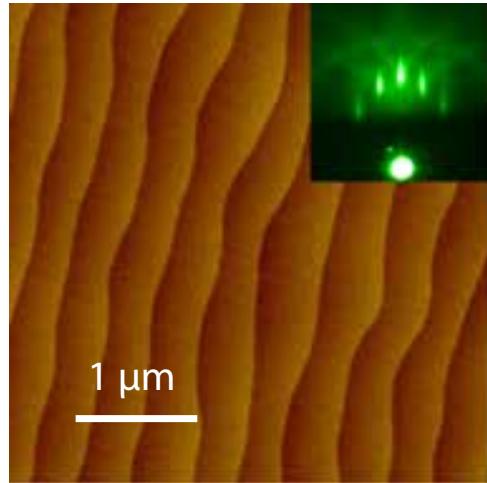
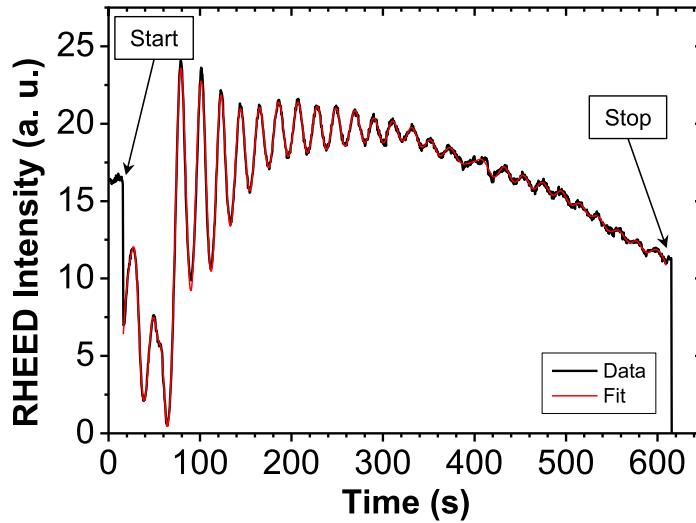


Figure 9: PLD epitaxial growth. The PLD chamber is back-filled with oxygen to the target pressure. A beam of pulsed deep-UV excimer laser is focused onto the LAO target. LAO is ablated off and a plume of plasma extends towards the heated substrate on top, and condensed into atomic layer films. RHEED signal is used to monitor the thickness of LAO.



(a)



(b)

Figure 10: AFM image of the sample after PLD growth and RHEED signal for PLD. (a) shows is the AFM Image. The stripes are the crystal terraces, with $h \approx 4\text{\AA}$. Inset of a is the raw diffraction sigal of RHEED. (b) is the RHEED signal oscillation during the film epitaxial growth. Each cycle indicates the completion of one unit cell. Adapted from [42].

Graphene is a type of Van der Waals material, which means that the carbon atoms within a layer are tightly bonded with covalent bond while the layers are bonded by the much weaker Van der Waals force. Adhesive tapes can easily separate graphene layers. After multiple exfoliation steps, single layer graphene flakes can be separated and identified [6]. One key aspect of the exfoliation method is choosing a proper substrate so that single layer graphene can be easily identified with optical microscopes. Although graphene has the highest absorption coefficient in the visible light regime [6], spotting a single layer graphene flake on a transparent substrate is still challenging, and is always assisted with other characterization methods such as Raman spectroscopy [6] to ensure the graphene is single layer. The most commonly used substrate is silicon wafer with 400 nm thick silicon oxide coating. The graphene on SiO₂ surface modifies the interference of visible light between the top and bottom layer of the coating, and make graphene layers distinguishable [6].

CVD is another method to obtain single layer graphene. Graphene flake from mechanical exfoliation is mostly a few micrometers or tens of micrometers; the size and shape cannot be well controlled. CVD on the other hand, can grow continuous graphene of wafer sizes [6], and then etch it into any desired shapes through post processing.

The CVD process uses gaseous organic molecules (methane, ethylene, etc) as carbon source, and graphene lattice-matching crystal such as SiC, Ni and Cu as substrate. In high temperature (about 1000 °C), the metal surface has highly reactive and can serve as a catalyst, so the gas molecules will react with the surface and carbon atoms are detached. At the high temperature, the carbon atoms will self-assemble into graphene. Over the entire process the substrate is in continuous gas flow so the gaseous byproducts are flushed away. Hydrogen is used to assist the growth. Without hydrogen molecules, graphene will grow simultaneously on the entire surface and form many small domains. Hydrogen will etch away the smaller domains while the larger domains are growing [6] until the domains meet or the process is terminated. If the hydrogen portion is too high however, the larger graphene domains will also be etched. CVD is a dynamic process of etching and growth. The ratio of methane and hydrogen need to be carefully controlled.

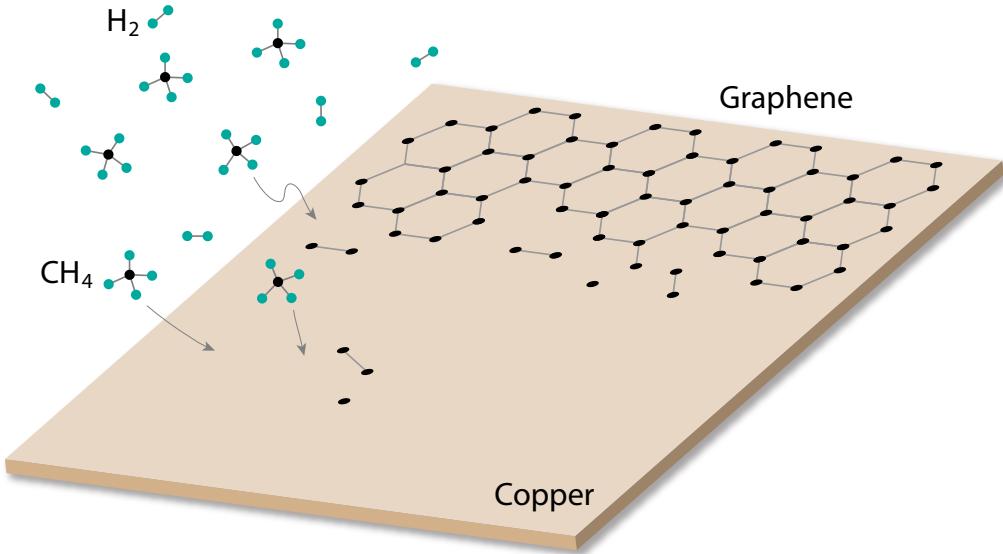


Figure 11: Graphene CVD growth. At a temperature $T \approx 1000$ °C, methane molecules will react with copper surface and leave carbon atom on the surface. Carbon atom will self-assemble into graphene due to lattice-match between graphene and copper super-cell. Hydrogen is used to etch away the smaller domain so that the final single layer graphene domains is as large as possible. If the hydrogen is too much, the larger domain will be etched as well. Ratio of methane and hydrogen has to be carefully controlled.

a. Copper substrate preparation Various materials are used for graphene growth, most commonly SiC, Ir, Ni and Cu. Cu is the most common choice due to the low carbon solubility scalability [43]. Compared to other substrate materials, copper is also easy to be etched with wet chemicals. In CVD growth, the carbon atoms form into graphene following the shape of the substrate. Therefore, the graphene quality is directly related to the substrate. Surface roughness and contaminants on copper provide nucleation centers for graphene, and can cause polycrystalline structure and multi-layer growth [44]. The issue

of surface roughness can be addressed with electrochemical polishing [43], or mechanical polishing. In my experiment I used a graphene substrates polishing procedure developed by Dr Brian D'Urso's graduate students, by using diamond turning machine to reduce the roughness from several hundred of nanometer to a few nanometers [45]. Compared to electrochemically polished substrates, this method can produce surface 50 time smoother and the copper domain sizes are 5 time larger.

Diamond turning machine (DTM) is commonly used for high precision manufacturing, such as laser reflective mirrors. The DTM works like a lathe, where the workpiece is fixed on a turning spindle, and the cutting tool approaches the workpiece and shape or polish the surface by steps. Figure 12 shows the DTM at work. The cylindrical metal piece in 12(a) is the spindle of DTM. Copper piece is fixed on the spindle by vacuum and spins at 2000 rpm. The diamond tool approaches the copper surface from the opposite side. 12(b) is an image taken in the middle of a cutting step. Mineral spirit is sprayed from a nozzle from the left, cools down the surface and blow away the metal debris to the right. Reflection of the tool shows a flat finishing.

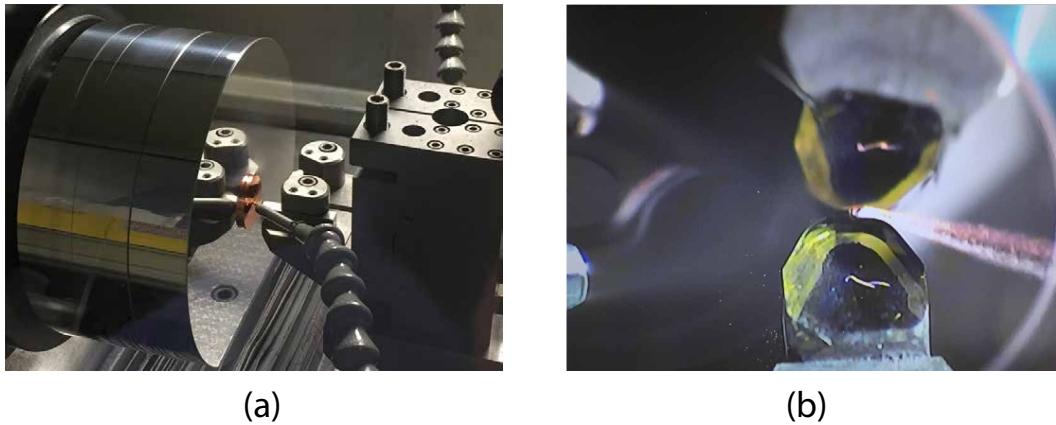


Figure 12: Diamond turning machine at work. (a) Copper is fixed onto a turning spindle with vacuum. (b) Mineral spirit is sprayed to the tool and cutting spot, to cool down the surface and blow away the debris.

Instead of using high-speed-steel tool, the DTM uses a curved-edge (radius of curvature $r = 1.5$ mm) diamond tool for cutting (Figure 13). By reducing the incremental step to 10 μm , as shown in Figure 14, the roughness of the finishing surface can be smaller than 2 nm. The diamond tool sometimes have dents on the surface, which can leave a trace after each revolution.



Figure 13: (a) Diamond cutting tool. (b) Magnified image of the tool tip. The radius of curvature $r = 1.5$ mm.

Other than surface roughness, the copper domain size is another limiting factor for large single domain graphene growth. Although it was not clear the effect of copper substrate domains on the graphene quality [46–48], larger copper domain sizes gives us a chance to grow larger graphene single crystals. Annealing the copper at high temperature will reconstruct and merge the polycrystalline domains into larger domains, but mechanical processing will introduce defects and break the single domains, therefore the substrate needs to be re-annealed several times before graphene growth starts.

The procedure of making copper rods into copper foils for graphene growth is shown in Figure 15. 1' long oxygen-free high thermal conductivity copper (OFHC) rods with ultra high purity (99.99%) are purchased from McMaster Carr. The rod is first annealed at $T = 1050^\circ\text{C}$ for 24 h, and the polycrystalline domains will merge into larger domains within

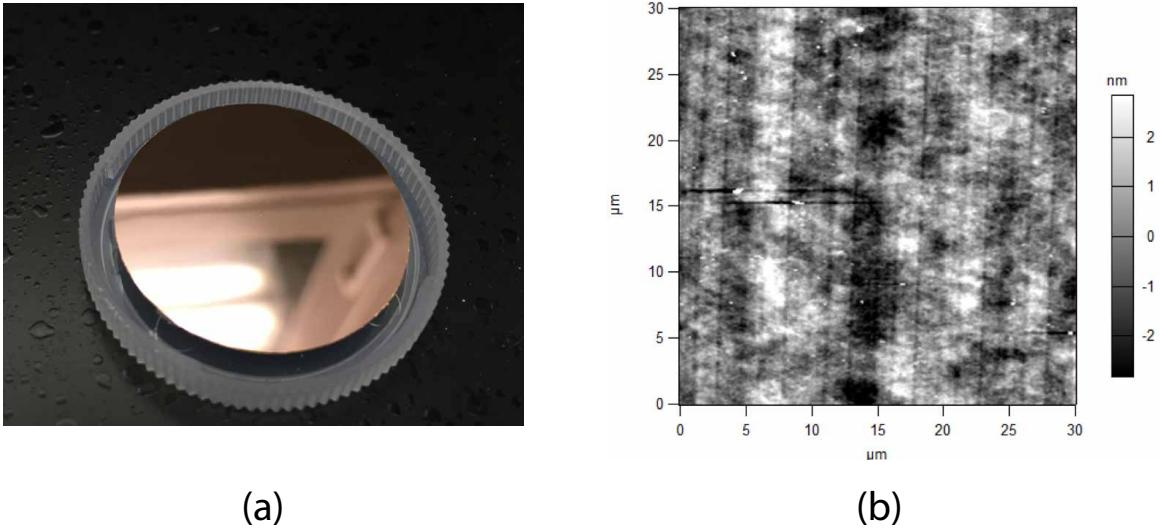


Figure 14: (a) The copper foil after DTM thinning and polishing. The final thickness is about $100 \mu\text{m}$. (b) The AFM image of the copper foil surface. The roughness is within 2 nm. Some nanoscale particles can be seen. They will serve as nucleation centers for graphene CVD growth. Reducing the density of surface contaminants will reduce the density of nucleation centers and enlarge the domain size. The vertical grooves are left by the dents on the diamond tool for each revolution. The spacing between grooves is the same as the approaching speed of the tool towards the center. The copper is annealed at $T = 1050^\circ\text{C}$ for another time before growth starts and the surface will reconstruct, possibly remove those grooves.

the rod. Then the rod is cut into copper discs of 2 mm thick in the machine shop. The mechanical cutting process will break the domains and introduce surface contaminant, so the surfaces copper discs are cleaned on the DTM, and then annealed again at 1050 °C for 8 h. After annealing, the domain re-formation in the disc will cause corrugation on the surface. Therefore, the copper surface is cut with DTM for a second time. Then the copper discs are cut into 100 μm foils, by 10 μm steps. During the thinning procedure, the copper will expand on the cutting face and cause deformation, and eventually break the vacuum sealing between the disc and spindle on the backside. Therefore the copper disc needs to be flipped

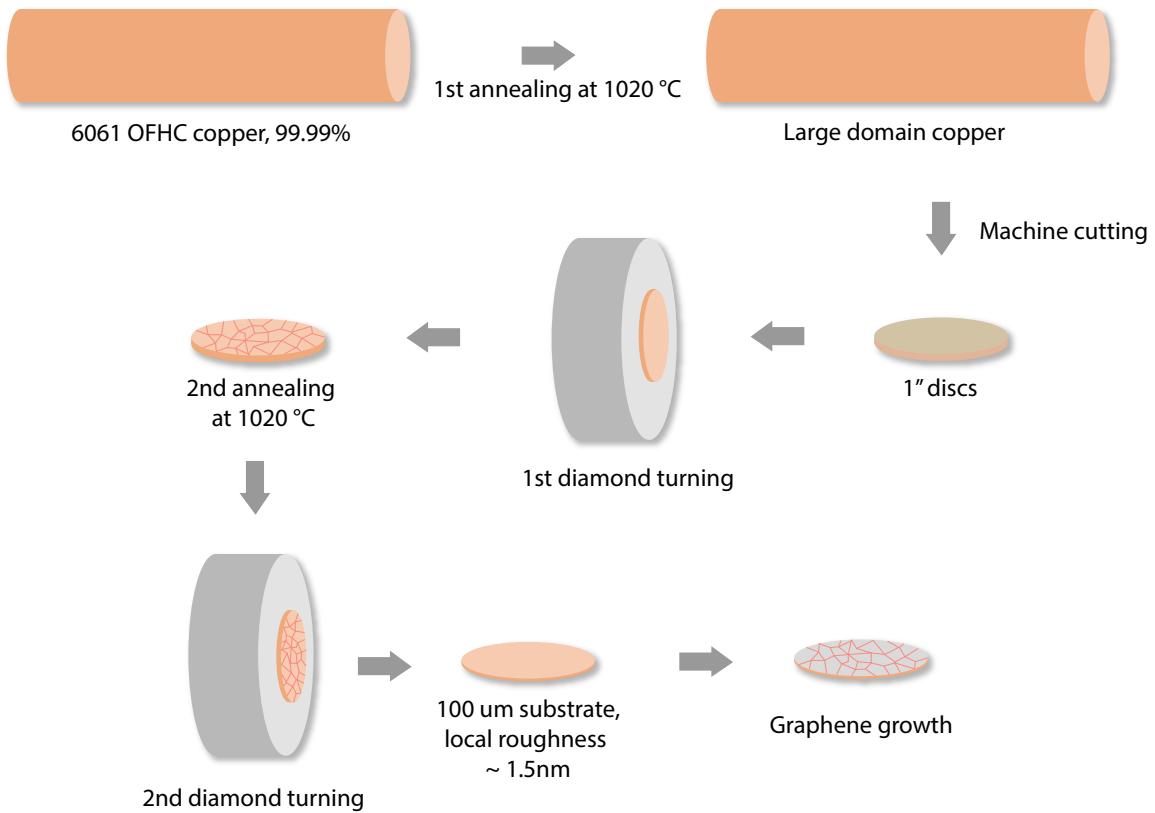


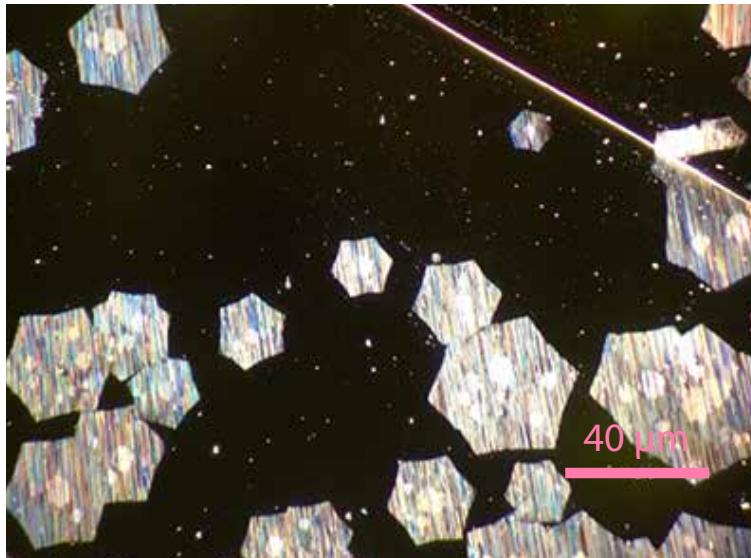
Figure 15: Procedure of cutting copper rods into $100\mu\text{m}$ foils for graphene growth. High purity OFHC copper rods are purchased from McMaster Carr. The rod is first annealed at 1050°C for 24 h so that the polycrystalline domains merge into larger domains. Then the rod is cut into 2 mm thick copper discs in the machine shop. The discs are cleaned with DTM and then annealed again to “heal” the domains broken by the mechanical cutting. Domain re-formation would cause surface corrugation, therefore the copper disc surface is cleaned with DTM and then cut into $100 \mu\text{m}$ foils and ready for graphene CVD growth.

several times to balance out the expansion and keep it flat when thinned from 2 mm to 100 μm . The process takes about 5 h.

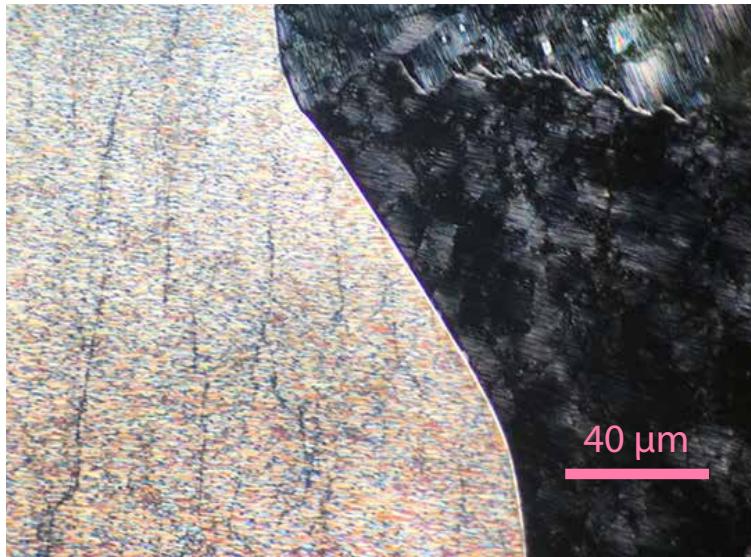
b. CVD growth The CVD graphene growth can be performed in low pressure (LPCVD) or atmospheric pressure (APCVD). LPCVD grows graphene at a pressure lower than 100 mTorr, in continuous flow of pure hydrogen and methane and 1000 °C substrate temperature. The problem with LPCVD is that the melting point of copper ($T_m = 1085^\circ\text{C}$) is close to the growth temperature. As a result, the copper will evaporate severely and contaminate the furnace [49]. Also the pure precursor gases bring fire hazard. APCVD can eliminate those difficulties associated with the low pressure and improve the graphene quality [49, 50]. Instead of using pure hydrogen and methane, APCVD uses gas mixture of 2.5 vol % H₂, balance Ar and 0.1 vol % CH₄, balance Ar. The furnace is pumped into low vacuum, and then back-filled with hydrogen and methane mixture with argon to atmospheric pressure. The pressure from argon will suppress the evaporation of copper at annealing and growth temperature. The growth procedure are as follows [50].

- The furnace is pumped down to ~ 10 mTorr.
- Backfill the furnace with H₂/Ar mixture at 186 sccm, up to ~ 100 Torr.
- Start the furnace temperature controller to ramp up to $T = 1050^\circ\text{C}$, and let the furnace stay at this temperature for 1 h.
- Start flowing mixture of CH₄/Ar at 14 sccm into the furnace, and let the copper foil stay in graphene CVD growth condition for 1.5 h.
- Cool down the system to room temperature. The flow of CH₄/Ar mixture is turned off at $\sim 650^\circ\text{C}$. H₂/Ar mixture keeps flowing overnight until the system is below 50°C.

In Figure 16 the dark-field mode of optical microscope clearly shows the CVD graphene on copper substrates. In 16(a) the copper substrate is partially covered with graphene. Growth process was terminated before graphene fully covered the substrate. Hexagonal shape of single domain graphene flakes can be identified. Some double layer can also be observed. On the top right corner of 16(a) a copper domain boundary can also be identified. 16(b) is the image of graphene grown in another run. The substrate is fully covered with graphene.



(a)



(b)

Figure 16: Dark field mode microscope images of CVD graphene on copper substrates. (a) The copper substrate is partially covered with graphene. Hexagonal shape single domain graphene can be observed. Growth was terminated before graphene fully covered the substrate. (b) Graphene covers the entire copper substrate. Copper domains of two different orientations can be observed.

The image shows two copper domains with different orientations, and therefore the graphene grown on the two domains look different. Wrinkles on graphene can be observed, resulting from different thermal expansion coefficient of copper and graphene.

B. LAO/STO SAMPLE PROCESSING

One of the challenges with experiments on LAO/STO interface is to make good electrical contact from the bonding pads to the interface. A major part of my research is process the samples before the c-AFM writing can be performed, or graphene can be transferred. The processing methods have to be carefully chosen, so that the 2DEG and interface switchability will not be affected. Sample cleanliness is another concern. Any nano-particles introduced in the processing would affect sample quality, considering that the dimensions of devices are also nanoscale. The procedure has those steps. Details of each steps can be found in the following subsections.

- **Initial cleaning:** the sample is cleaned with acetone and isopropanol alcohol (IPA) in ultrasonic cleaner so that the particles introduced in shipping are cleaned. Usually I do not use deionized-water (DI-water) for cleaning. Proton from the water can get adsorbed on sample surface and affect the interface [].
- **Photolithography:** the sample is patterned with standard UV photolithography procedures, either with optical mask and UV lamp or with direct laser writer, for further processing. The finest features in my design are $2 \mu\text{m}$ wide.
- **Ion milling:** after the desired patterns are developed on the photoresist, the sample is bombarded with Ar^+ ion flow so that the LAO/STO interface is exposed for electrical contact.
- **Deposition:** titanium and gold are used for making contact with the exposed LAO/STO interface either by electron-beam evaporation or sputtering.
- **Lift-off:** the excessive metal outside the patterns are removed by the lift-off process following the metal deposition. Like the initial cleaning process, I use IPA and acetone and do not use water as solvent.

- **Oxygen plasma cleaning:** the sample is covered with residue from liquid and photoresist, until it is cleaned with oxygen plasma cleaner. Then the atomic steps can be seen with AFM.

1. Photolithography

Photolithography is a commonly used technology in semiconductor industry. The substrate is covered with a thin layer of photosensitive material, and exposed under UV with designed pattern. UV would change the solubility of photoresist, and the pattern can be developed in buffered base solution after exposure. The modern state-of-the-art photolithography technology can reach resolution of 10 nm, and is the pillar of support for the semiconductor industry. There are two types of photoresists: positive and negative. Positive photoresist will be washed off after been exposed to UV, while negative photoresist is stabilized by UV and the unexposed parts are removed by developers. In my experiment, three types of positive photoresists are used: AZ4620, AZ4210 and AZ4110. For each sample, a 3" carrier wafer is used as a fixture, because dimensions of the sample ($5\text{ mm} \times 5\text{ mm} \times 1\text{ mm}$) is non-standard and most photolithography instruments are designed for 3" or 4" wafer in the university facility. AZ4620 is used to fix the sample to the carrier wafer during spin-coating, exposure and other steps, as a cleanroom-safe "epoxy".

a. **Spin-coating** There are two limiting factors of the feature resolutions in photolithography: diffraction limit of light and photoresist thickness. Spin-coating is a standard technique to keep the photoresist thin and uniformly covering the sample surface. When the sample is spinning at a speed between 1000 rpm and 6000 rpm, the photoresist solution on sample surface would spread out. The liquid will be finally in equilibrium of viscosity, roughness of sample surface and centrifugation from spinning. After the spin-coating the sample is baked at a temperature around 100°C to vaporize the remaining solvent in photoresist and stabilize the film before UV exposure. In my experiment, the spinning speed is 4000 rpm. Thickness of AZ4210 and AZ4110 are $2.1\text{ }\mu\text{m}$ and $1.1\text{ }\mu\text{m}$, respectively. These two types of photoresists have the same chemical composition. They have different concentrations so

Photoresist	AZ4210	AZ4110
Spinning speed	4000 rpm	4000 rpm
Spinning time	30 s	30 s
Baking temperature	95 °C	95 °C
Baking time	60 s	60 s
Thickness	2.1 μm	1.1 μm

Table 1: Spin-coating conditions for AZ4210 and AZ4110

they end up with different thickness at the same speed. Usually thinner films will have more stable performances for fine features (2 μm , to be specific). In the cases where photoresists are consumed in the processing, such as reactive ion etching, thicker photoresist will be a better option.

The spin-coating conditions are listed in Table 1.

b. UV exposure The UV exposure is to use short wavelength photon to change the solubility of photoresist, so that the following developing step can selectively remove the photoresist. Like all optical system, the resolution of exposure is limited by diffraction limit of light. Historically, mercury gas-discharge lamp is used, and 436 nm (“g-line”), 405 nm (“h-line”) and 365 nm (“i-line”) are selected as UV source. Besides Hg lamp, solid state laser and excimer laser with shorter wavelengths are also commonly used UV source. Samples are exposed with two different methods: mask exposure and direct laser writing.

Mask exposure is performed by a mask aligner (Suss MJB3 or MA6, see Figure 18). Incoherent and collimated UV is generated from a Hg lamp and an area of 4” \times 4” is exposed with UV at constant intensity of 10 mW/cm². The sample is covered with a photomask (Figure 17), a square piece of soda glass (to reduce UV absorption) coated with chromium on one side. The desired pattern is pre-printed on the chromium by chemical etching. The patterns on photoresist will be the copy of the patterns on the photomask.

Direct laser writing uses focused laser beam to write micro-patterns directly on photoresist.

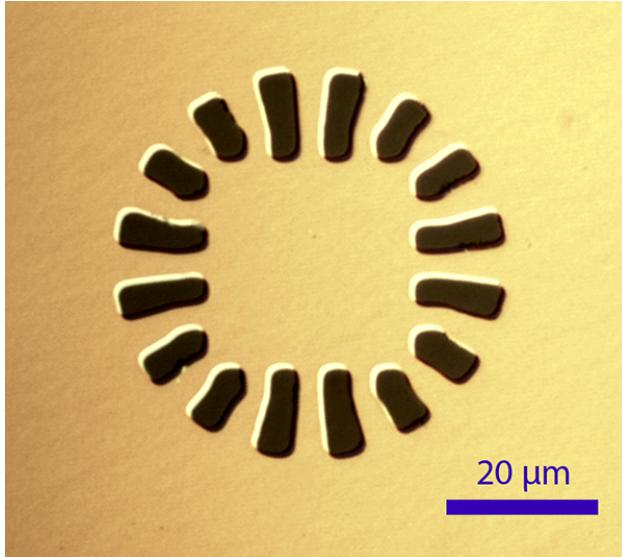


Figure 17: Mask for photolithography. The dark parts are transparent, while the bright parts are covered with chromium. Sample will be exposed where UV is not blocked by chromium. The figure shows the electrodes of a canvas for writing. The pedal shape area to be exposed will be etched away on the sample, and filled with titanium and gold to make contact with the LAO/STO interface.

sist, without using a mask. This is usually how the photomask is manufactured, but it can also be used to pattern samples. In my experiment I use Heidelberg MLA100 (Figure 19), with 405 nm wavelength UV generated from a solid state laser. The laser is expanded and filtered with a pinhole, and focused on the sample with a high-NA objective. The focusing objective is fixed, and the sample is placed on a piezostage controlled with computer, to follow the designed pattern. The UV dose is determined by both the laser power and laser spot dwell time. It is important to keep the sample surface horizontal, so that laser spot will not defocus while moving through the entire sample surface. Sometimes, especially when the critical dimension is close to $2 \mu\text{m}$, the photoresist patterns are not evenly developed, and it is caused by sample tilting and laser defocussing. Focusing quality can be checked with a real-time CCD image, while the sample is illuminated with red light from a second diode.

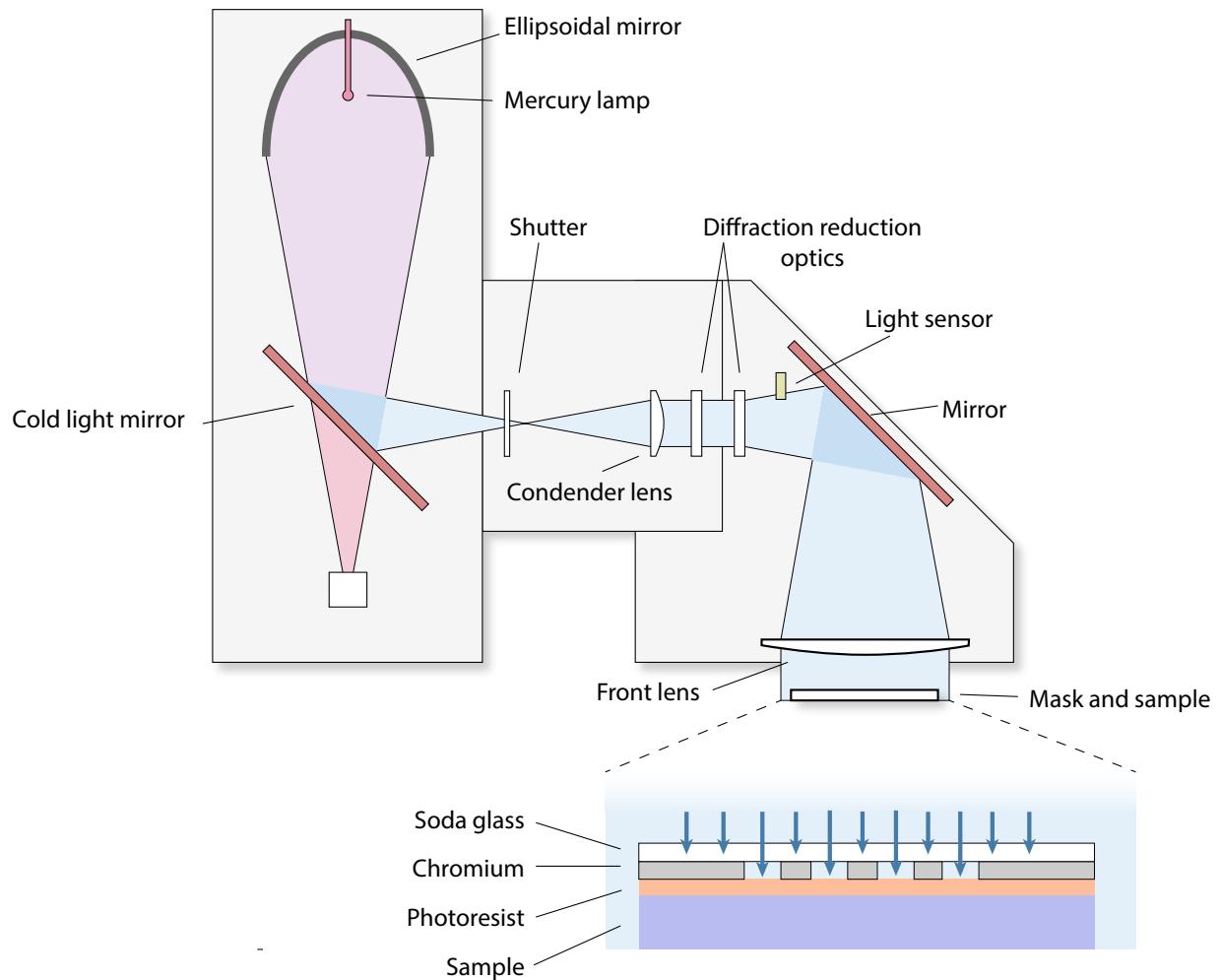


Figure 18: Suss UV mask aligner. The mercury lamp generates broad band light from arc. The light is reflected by an ellipsoidal mirror and focused on a cold light mirror, where the UV is selected. The exposure time and dose is controlled by a shutter. The UV is collected by a condenser lens and diffraction reduction optics for collimation and resolution enhancement. Finally, the UV is shed on the sample with a folding mirror and front lens. The sample is in close contact with a mask, where chromium is partially removed. UV exposes the photoresist on sample and print the mask pattern on it.

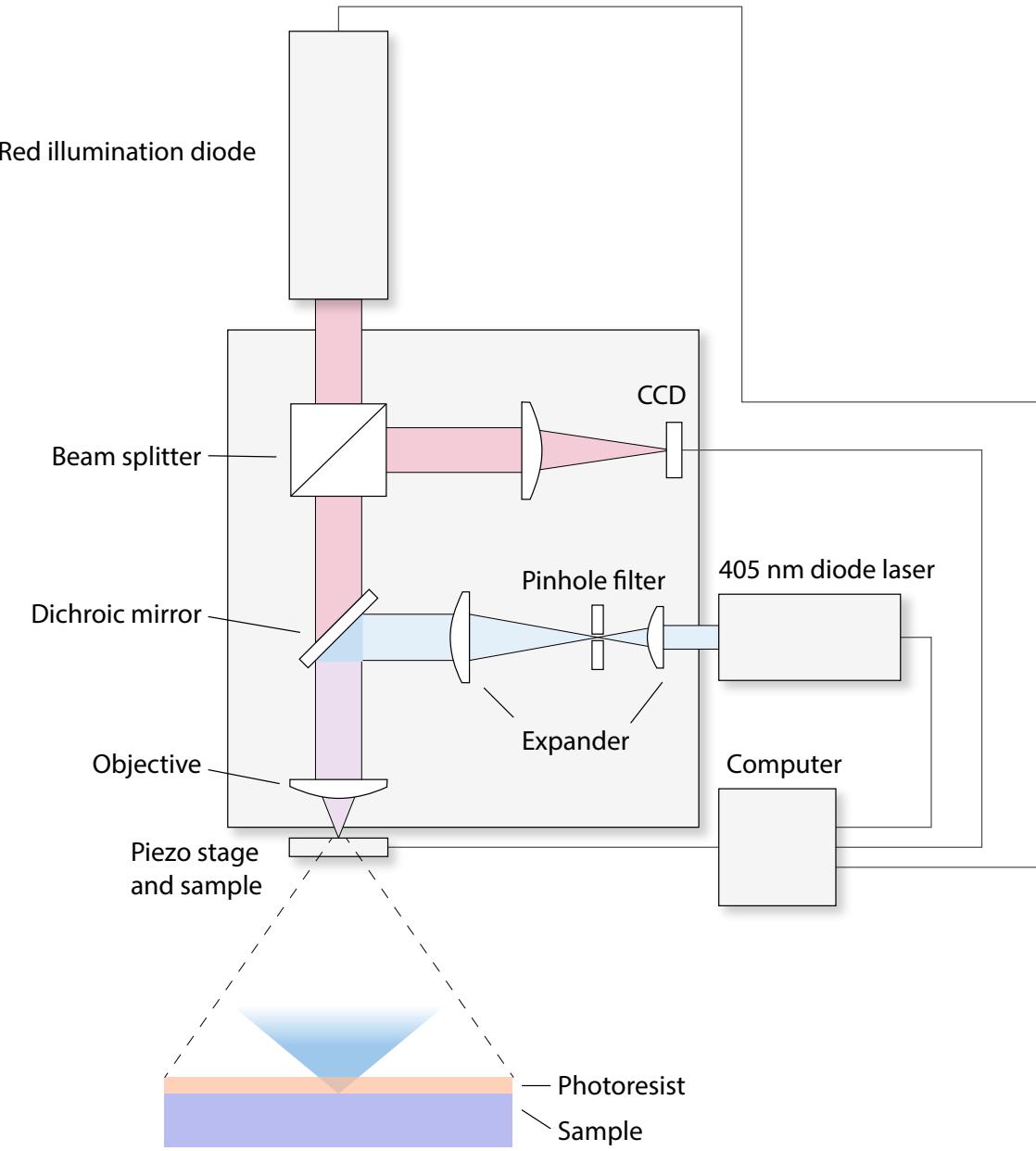


Figure 19: Heidelberg direct laser writer. The sample is illuminated by red light from a diode, and realtime image of sample surface can be monitored with a CCD. UV with $\lambda = 405$ nm is generated from a laser diode. The laser is expanded and filtered, and focused on the sample surface with a high-NA objective. The sample is fixed on a piezo-driven stage. The CCD image, laser power, sample movement and layer alignment are all controlled with computer, so that the laser path and dose control is fully automatic.

c. Developing Developing is the process using buffered base solution to washed away the unwanted parts of photoresist after exposure and reveal the pattern on sample, for future processing steps. Depending on the type of photoresist, either the exposed parts (positive photoresist, such as AZ4210) or unexposed parts (negative photoresist, such as AZ5214) are removed. In my experiment I use AZ400K (potassium borate) for developing. The developer is diluted with DI-water, by 1:3 or 1:4 ratio. Different concentration will maintain different pH level and developing speed. The sample is washed with DI-water after developing, to remove the excessive developer.

A picture of sample after UV exposure and developing is shown in Figure 20. Photoresist in the bright area are washed away while the rest of the sample is still covered with photoresist. Note that the edges of the pattern are less sharp than the mask, because of the resolution limit from diffraction.

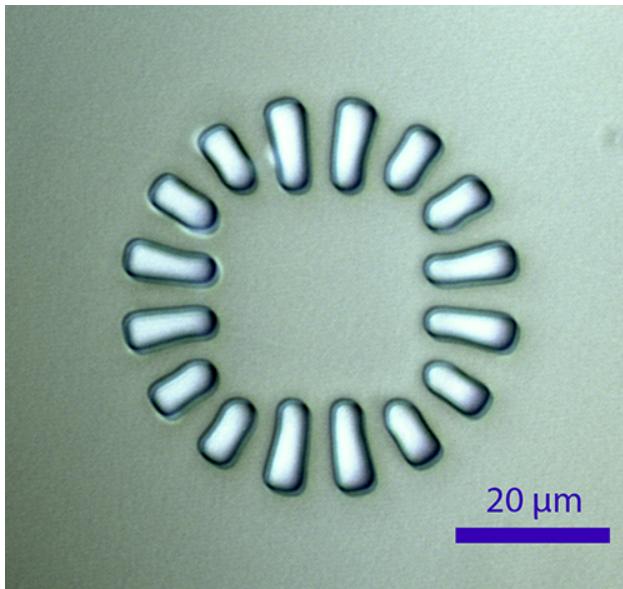


Figure 20: Exposed and developed sample. The bright regions are free of photoresist while the rest of the sample is still covered.

The conditions for exposure and developing are listed in Table 2.

Photolithography is the part that has the most uncertainty in the entire processing, and can affect some samples (like graphene/LAO/STO) more significantly. This will be discussed

Photoresist	AZ4210	AZ4110
UV Dose	170 mJ	100 - 120 mJ
Developer : Water	1 : 4	1 : 4
Developing time	120 - 180 s	120 - 180 s
Resolution	3 - 5 μm	2 μm

Table 2: UV exposure and developing conditions for AZ4210 and AZ4110

in future sections.

2. Ion milling

LAO/STO interface is buried underneath LAO, so if contact need to make with the interface the LAO has to be etched. Usually there are three methods for etching: wet chemical etching, dry plasma etching and ion milling. Wet chemical etching using reactive chemical solutions (such as HF, HCl) to etch away the materials. This is cheaper but less controlled, and etching is isotropic. Plasma etching, uses the plasma or free radicals of active gas molecules (such as O₂, SF₆, etc) to react and remove materials, at pressure between 0.1 and 5 Torr. It is better controlled in etching rate and directionality, but the instrument is more expensive, and finding the right gas to selectively etch the target material while keeping the protecting layer intact is not always feasible. Although there are mature industrial solutions for silicon, alumina and silica etching with plasma, there is not a good solution to etch complex oxides like LAO/STO with our facility plasma etcher. Ion mill uses accelerated ionized argon plasma to physically bombard sample. The etching rate is slower than the previous two methods, but performs well on most inorganic materials including LAO/STO. Also, the etching is more directional. In Table 3 is a comparison of the three etching methods.

Ion mill accelerates Ar ions to a certain kinetic energy and physically etch samples with bombardment. As shown in Figure 21, Ar⁺ is generated from the discharge chamber. The entire chamber is pumped to high vacuum ($< 10^{-6}$ Torr), and back filled with Ar gas to

Method	Chemical etching	Plasma etching	Ion milling
Cost	low	high	high
Directionality	anisotropic	anisotropic	isotropic
Selectivity	high	high	low
Speed control	poor	good	good
Target material	inorganic	organic or inorganic	inorganic
Environment	aqueous, ambient	0.1 - 5 Torr, vacuum	$< 10^{-4}$ Torr, vacuum

Table 3: Comparison of etching methods.

10^{-4} Torr. On the right-hand-side of the figure, a filament is heated up and a biased voltage is applied between the filament and chamber wall. Electrons are extracted from the filament and ionize the argon molecules. Usually a magnetic field is applied through a solenoid to increase the path and ion yield before the electrons reach the chamber wall. At the opening side of the discharge chamber, there are two or three layers of electrically isolated screen grids (made of sputter-resisting materials like Mo or W). A voltage of 500eV is applied between the grids so that Ar^+ can be accelerated to the same energy. The pores on the grids are aligned so that the Ar^+ flow is collimated. Right after the Ar^+ exits the chamber, it is mixed with free electrons from a neutralizer filament, so that flow will not be diverged by coulomb attraction between Ar^+ before they reach the sample. The sample is 20° to 30° off the normal direction, to create undercut and facilitate electrical contact between the interface and the electrodes. The kinetic energy of the plasma is converted to heat on the sample surface. Either the sample is cooled down with flowing water inside the chuck, or the plasma flow is shutoff with a duty cycle so that the sample can cool down by radiation. Temperature over 150°C will cause phase transition of the photoresist on the sample, and make hard to remove by lift-off.

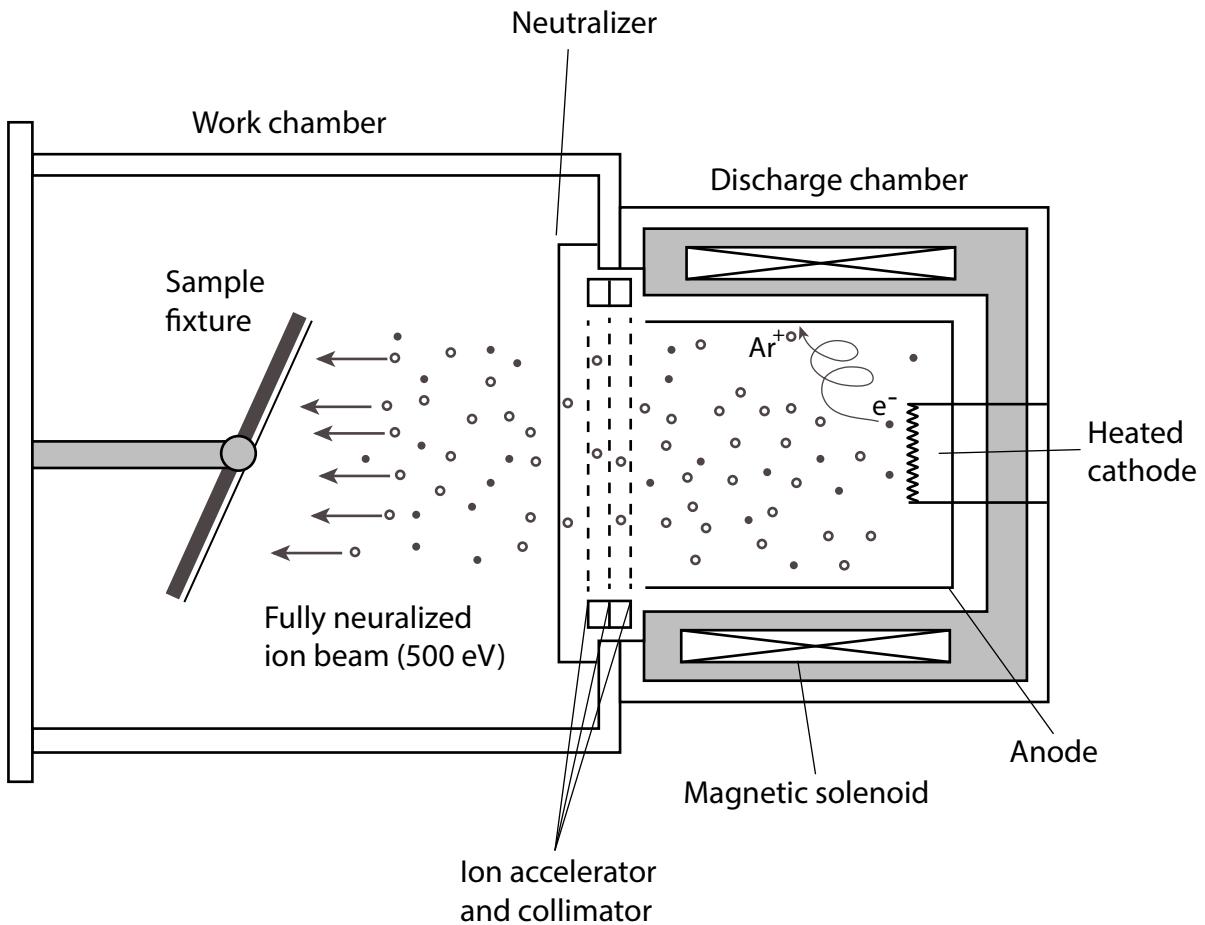


Figure 21: Simplified view of ion mill. The argon ions are generated from the discharge chamber on the right hand side. Electrons are extracted from the heated cathode and ionize Ar molecules before they reach the chamber, which works as an anode cup. A magnetic field is applied through a solenoid to increase electrons' path. Ar^+ are accelerated and aligned by the grids to 500 eV. Electrons from the neutralizer are mixed with the Ar^+ plasma flow so that the collimation can be maintained. Sample is tilted by an angle of 22.5°.

3. Deposition

Titanium and gold are used for making contact with the interface of LAO/STO. I use two methods to deposit the material: sputtering and electron-beam (e-beam) evaporation. Sputtering is similar to ion milling, but instead of using Ar^+ plasma flow to bombard and etch the sample, it is directed towards the target materials (Ti, Au, etc). The binding energy of the target material atoms is much smaller than the kinetic energy of Ar^+ , and are ejected from the target and deposit onto the sample surface. E-beam evaporation (Figure 22) controls electron-beam to heat up the target material and vaporize it. The vapor is thrown through a long distance ($> 10 \text{ cm}$) before it reaches the sample. Compared to sputtering, the e-beam evaporation is more directional, because of the long throw-distance of evaporated material, compared to sputtering.

As can be seen in Figure 22, a beam of electron is accelerated by a high voltage of 10 kV. The direction and shape of the beam is controlled by magnetic field. The material is loaded in a crucible and heated up by the e-beam, and evaporated. The material is thrown upward, towards the loading chamber where the sample is located. A shutter is used to control the deposition time of material. Deposition rate is controlled by the e-beam current. The sample can be tilted if needed, to improve the electrical contact to the interface.

The pressure of the chamber is maintained at $< 10^{-6} \text{ Torr}$ to avoid any oxidation of material during deposition. Also, when titanium is used to make contact between gold bonding pads and LAO/STO interface, a pre-deposition evaporation of 10 minutes is required. The evaporated titanium can trap the remaining oxygen molecules in the chamber, and further reduce the oxidation on the target metals.

4. Lift-off

When the sample is patterned with photolithography and coated with metal, the photoresist and the excessive metal need to be removed. Photoresist can dissolve in organic solvents such as acetone. Acetone has high vapor pressure, so it is not suitable to be heated up to increase solubility of photoresist. Also, when acetone dries up on sample it forms streaks. Therefore the sample needs washed with IPA to remove the acetone residue. When the photoresist

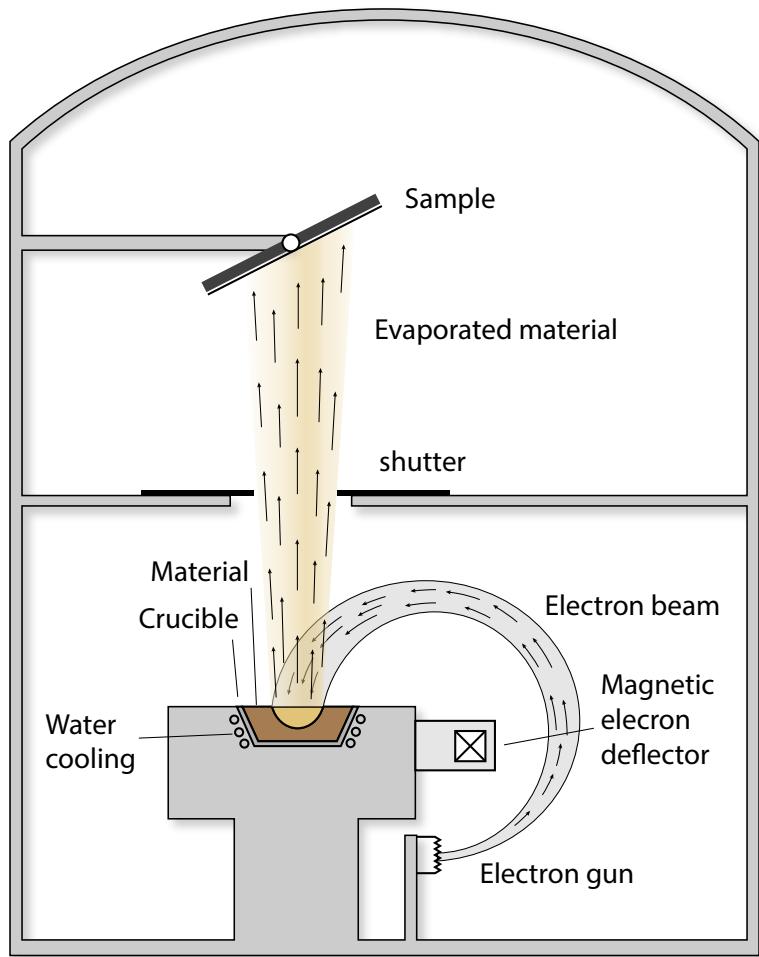


Figure 22: E-beam evaporator. The electron beam is generated from an electron gun on the bottom. The beam is deviated and shaped by magnetic field, towards the material. Them material is loaded in a crucible and heated up to melting point. The vapor of the material is thrown towards the sample on top. Deposition time is controlled by a shutter.

is heated up to 140 °C, it will cross-link and its solubility in will decrease. 1165 remover (1-methyl-2-pyrrolidone, or NMP) need to be used for lift-off in such cases. It has low vapor pressure and can be heated up to 80 °C. If 1165 still cannot fully remove the photoresist after sample is immersed in it for 24 hours, oxygen plasma cleaner is needed.

5. Oxygen plasma cleaning

The oxygen plasma cleaner activates oxygen molecules with a high frequency voltage (kHz to MHz) in low pressure, and forms plasma or oxygen radicals when electrons recombine with oxygen ions. The mixture is highly reactive and interactive with organic materials like photoresist residue on sample surface. Oxygen plasma cleaning can be categorized as a form of RIE (as discussed in Section II.B.2), but it usually operates at high end of 100 mTorr and the etching is less directional. Compared to chemical solvent, oxygen plasma removes the photoresist residue at a much lower speed (about 10 nm/min), but the finishing is much cleaner, while less invasive compared to RIE. Therefore, oxygen plasma is used as a final step for sample processing.

C. ATOMIC FORCE MICROSCOPE

The atomic force microscope (AFM) is a type of instrument that uses a nanoscale probe to interact with the surface, and characterize the properties (topography, coulomb interaction, conductivity, etc) of a sample. It was invented in IBM lab by Bin, Quate and Gerber [1] in 1986 and later commercialized in 1989. The development of AFM technology benefited from the advancement of STM and precise closed-loop spatial control using piezoelectric effect. However, AFM was invented to overcome the drawback of STM — only conductive or semi-conductive samples can be measured. AFM can measure various types of interaction between the probe and surface, such as surface potential, magnetic force, Van de Waals force, etc. Also, unlike the scanning electron microscopy (SEM) or tunneling electron microscopy (TEM), the AFM can be operated in various environment (aqueous, ambient, vacuum or

cryogenic), and does not require the sample to be pre-treated (such as metal coating) or being conductive. The robustness and non-invasive nature of AFM make it a powerful tool for studying surface phenomena including charge density, magnetic dipole moment, capacitance, chemical bonding, nano-device lithography, and even biomacromolecules. AFM can also be integrated with other techniques, such as infrared spectroscopy []. The limitation of AFM is that the imaging cannot be as fast as SEM or TEM, as it relies on the physical movement of the tip.

1. Working principle

The AFM is mainly consist of three parts, as shown in Figure 23, AFM tip, laser optics, and piezoelectric scanning system. The AFM tip has a sharp end, with a radius of curvature in nanometer scale. A laser is reflected from the top surface the AFM tip and collected by a quad detector. The quad detector determines the position by

$$\begin{aligned} I_{\text{sum}} &= I_A + I_B + I_C + I_D \\ I_{\text{vdiff}} &= (I_A + I_B) - (I_C + I_D) \\ I_{\text{hdif}} &= (I_A + I_C) - (I_B + I_D), \end{aligned} \tag{II.1}$$

where I_A , I_B , I_C and I_D are the intensities on the four quadrants of the detector. I_{sum} is the total intensity. I_{hdif} and I_{vdiff} are the horizontal difference and vertical intensity difference. Assume the laser spot has Gaussian distribution. When the center of laser spot changes, the distribution of intensity on the four quadrant would change. The detector can monitor the movement by the horizontal and vertical differences in intensities.

When the interaction between the tip and sample surface changes and the tip is slightly deformed, the laser spot would move on the quad detector. The deformation of tip follows Hooke's law:

$$F = -k \cdot x$$

Where x is the amount deformation, and k is the spring constant of the tip cantilever. k is mostly between 1 N/m and 100 N/m, depends on the type of the tip. In my experiment I use tips with spring constant $k = 3$ N/m. The interaction between the AFM tip and sample

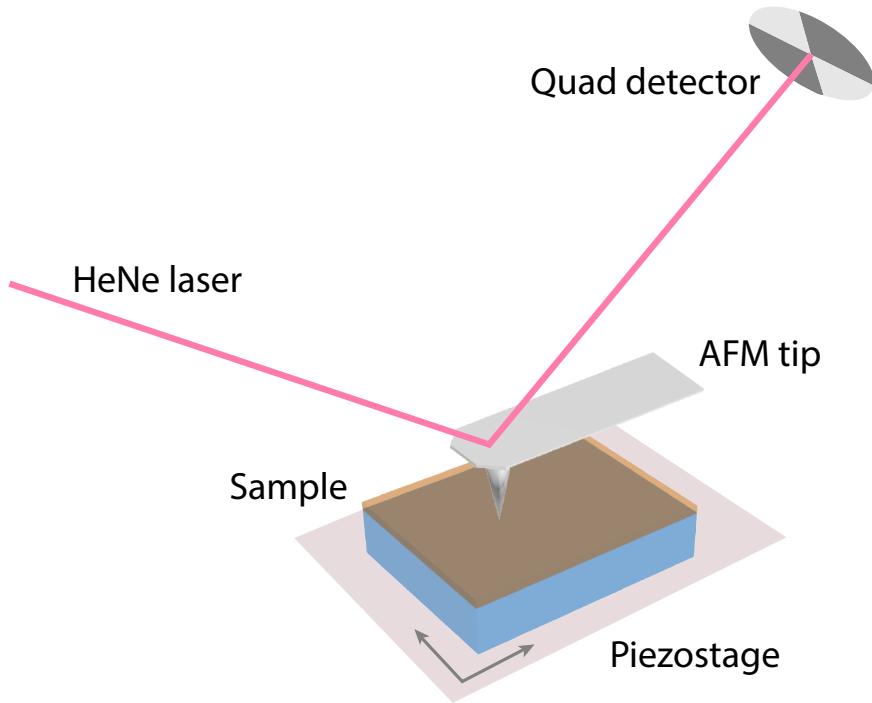


Figure 23: The schematics of AFM. A laser is reflected from the top surface of the AFM tip, and collected by a quad detector. A small amount of deformation would cause the center of laser spot to move on the quad detector, and measured as a change of differential voltage.

surface is a function of distance. The attractive interaction decays slower than the repulsive interaction, therefore the total interaction follows the curve in Figure 24.

The sample is located on the piezoelectric scanning stage. The movement of the sample and the tip, and signal from the laser optics system are controlled and monitored by a computer. The type of signal depends on the working mode of AFM and nature of the interaction it is targeting. More details are discussed in the following sections.

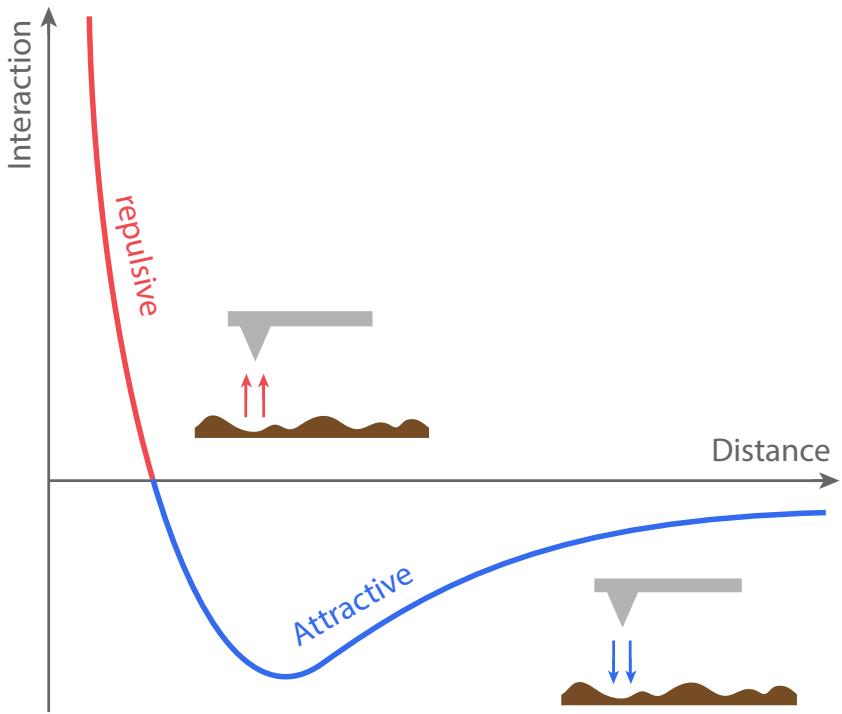


Figure 24: The interaction between tip and the sample surface. At long distance the interaction zero. When the tip moves towards the sample, the interaction is attractive. As the tip gets closer, the interaction would switch from attraction to repulsion, and gets larger and larger the tip moves closer.

2. Contact mode

In contact mode, the AFM tip is in close contact with the sample. The distance between the tip and sample is controlled by a piezoelectric actuator. As shown in Figure 25, When the tip approaches the sample surface, repulsion from the sample would deform the tip and changes the reflection angle of laser spot. The intensity difference on the quad detector would also change, in terms of a voltage signal. When the sample is driven by the piezostage and cause the tip moves relative to the sample, the repulsive force between the tip and sample surface is regulated by a feedback loop between voltage on the piezoelectric actuator, and the voltage

difference on the quad detector, so that the amount of tip deformation and repulsive force is a constant.

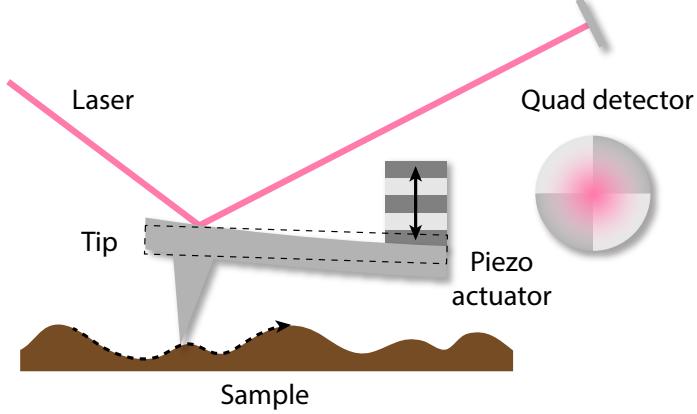


Figure 25: AFM contact mode. The tip is pressed to the sample surface by the piezoelectric actuator. The deformation of the tip is monitored by the quad detector. The voltage of the piezoelectric actuator is controlled with a feedback loop with the deflection voltage on the quad detector.

3. AC mode

In AC mode, the AFM tip is driven by a sinusoidal electrical signal on the tip piezoelectric actuator, as shown in Figure 26. The electric frequency is close to the resonance frequency of the tip (10 kHz - 500 kHz). The driving frequency is not exactly at the resonance frequency, so that the gradient of amplitude change is maximized and the system is most sensitive to the interaction change. The laser spot and difference signal also oscillates at the same frequency. When the tip approaches the sample surface, the interaction between the tip and surface will cause the resonance frequency to shift and change the amplitude A and phase θ of the tip oscillation and monitored by the differential voltage signal on the quad detector. The measurement can be integrated with lock-in amplifier technique for noise reduction. When the tip scan through the surface, A and θ are recorded for each position on the sample surface and mapped onto a 2D image. The voltage on the piezoelectric actuator (z voltage)

is controlled by a feedback loop so that the amplitude A is maintained at a set point. During the scan the tip is not continuously in contact with the sample surface, but “tapping” the sample with oscillations, therefore AC mode is sometimes called “tapping mode”. Compared to contact mode, in the AC mode the tip does not scratch the sample surface, so it has less effect on the sample.

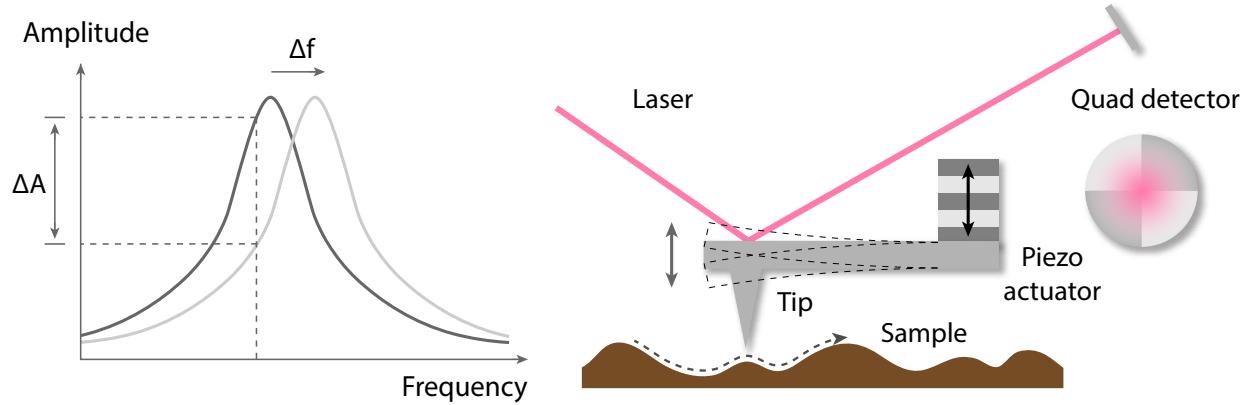


Figure 26: AFM AC mode. Left: the tip is driven at a frequency close to the resonance frequency. When the resonance frequency shifts as the interaction between the tip and the sample changes, the Change of oscillation amplitude is monitored by the quad detector and sent to the computer.

4. Non-contact mode

In the non-contact mode, the tip is maintained at the attractive regime so that the sample does not have direct contact with the tip. The tip and the sample is maintained at distance that the interaction is always attractive while the tip is scanning through the sample (Figure 27). This is especially important for biomacromolecules and organism.

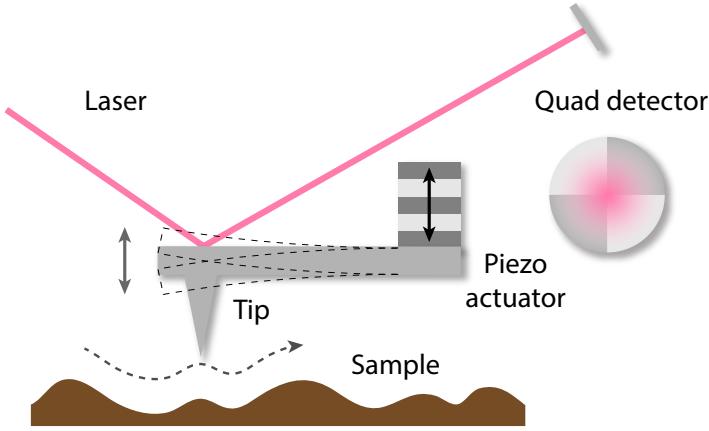


Figure 27: AFM Contact mode. The tip is kept at a distance from the sample so that the interaction is always attractive. The tip does not have direct contact with the sample during the scanning.

5. Magnetic force microscopy

When the tip is coated with ferromagnetic materials (e.g. Co, Fe), the AFM is able to measure the magnetic interaction with magnetic force microscopy (MFM). Similar to AC mode, the tip is driven by an oscillating AC voltage close to the resonance frequency (about 100 kHz in my experiments), and the change of interaction is monitored by the amplitude A and phase θ of the differential voltage on quad detector. The challenge of MFM is that the magnetic and Van der Waals interactions are coupled together. The two-pass technique is used to solve this problem, considering that Van der Waals interaction is short-ranged and decays much faster than the magnetic interaction. First, the tip scans the sample close to the surface, and measures the topography. Second, the tip is lifted and maintained at a constant distance (such as 50 nm) from the sample surface using the height information obtained from the previous scan, so that the Van der Waals interaction is negligible, and the spatial gradient of magnetic force can be measured [51]:

$$\Delta A \approx \frac{2A_0Q}{3\sqrt{3k}} \cdot \frac{\partial F_z}{\partial z}, \quad \Delta\phi \approx \frac{Q}{k} \cdot \frac{\partial F_z}{\partial z}, \quad \Delta f \approx -\frac{f_0}{2k} \cdot \frac{\partial F_z}{\partial z}, \quad (\text{II.2})$$

where ΔA , $\Delta\phi$ and Δf are the change of amplitude, phase and resonance frequency; A_0 and f_0 are the original amplitude and frequency; Q and k are the resonance quality factor and cantilever spring constant. $\partial F_z/\partial z$ is the spatial gradient of magnetic force.

Like contact and AC mode of AFM, the resolution of MFM is limited by the tip radius of curvature. Ferromagnetic coating of the MFM tip is about 40 nm in my experiments, so the resolution is in the same order of magnitude.

The advantage of MFM is that, the resolution and sensitivity is higher than other methods such as magneto-optical effect imaging. Also, like contact and AC mode AFM imaging, MFM does not require special treatment on the sample. The downside of MFM is that the imaging speed is limited by the raster scanning speed. The two-pass method takes twice as long as usual AFM AC scanning. Also, as equation (II.2) shows, MFM signal is not determined by the absolute value of magnetic force, but is proportional to the spatial gradient of the force $\partial F_z/\partial z$, therefore the scanning speed would also affecting the signal. The field from the AFM tip can also affect the magnetic dipoles on the sample, and MFM image can change after each scan. Other long range interaction such as coulomb interaction cannot be eliminated by the two-pass method, and need to be taken care of. More details are discussed in the next chapter. In spite of these disadvantages, the MFM is still a power tool to study surface magnetism for its robustness and simplicity of operations.

6. Piezoresponse force microscopy

The high sensitivity and extendability of AFM make it a versatile tool to measure different types of interactions between the tip and sample. One important variant is piezoresonse force microscopy (PFM). Piezoelectric effect is the phenomenon when an external stress or strain is applied to a piezoelectric material, the deformation will induce electric dipole moments and build up an internal electric potential across the sample. Inversely, the external electric field can also induce mechanical deformation. Depending on the properties of the material, the deformation can be either expansion or contraction. The effect can be described with

$$X_i = d_{ki}E_k,$$

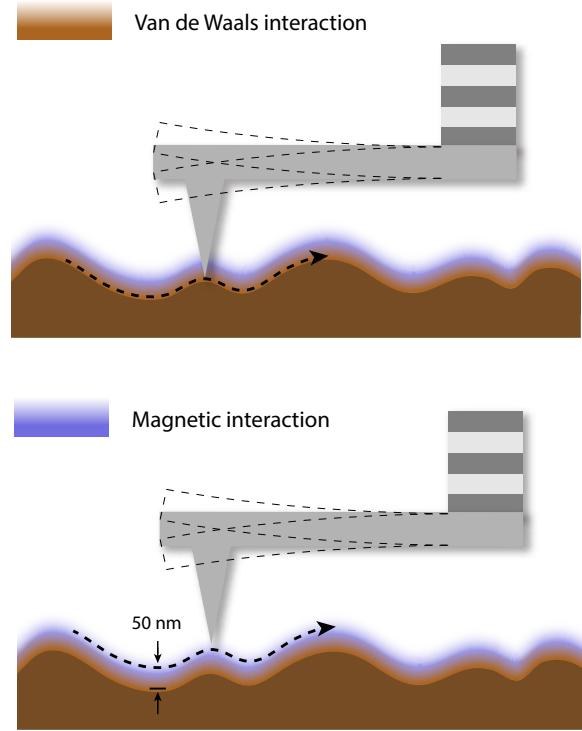


Figure 28: MFM mode. The first scan is close to the sample surface, so that the topographical information can be obtained. In the second scan the tip is lifted to a constant distance from the sample surface, so that the Van der Waals interaction is negligible and only the long-ranged magnetic interaction is measured.

where X_i is the strain tensor, d_{ki} is the piezoelectric tensor and E_k is the electric field. For a tetragonal system,

$$\begin{bmatrix} X_1 \\ X_2 \\ X_3 \\ X_4 \\ X_5 \\ X_6 \end{bmatrix} = \begin{bmatrix} 0 & 0 & d_{31} \\ 0 & 0 & d_{32} \\ 0 & 0 & d_{33} \\ 0 & d_{15} & 0 \\ d_{15} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix}$$

When a field is applied in E_3 direction, the resulting non-zero strain terms are $X_1 = d_{31}E_3$, $X_2 = d_{32}E_3$ and $X_3 = d_{33}E_3$. Therefore, an electric field in the c-axis of the crystal will cause elongation in the c-axis and contraction in the other two orthogonal directions, or vice versa. The piezoresponse of sample can bring insights of the sample properties such as carrier concentration [6], ferroelectric domain orientation [6], domain boundary [6], etc. The piezoresponse of the LAO/STO system can be used to characterize the carrier density change on the interface. More details will be discussed in the following section.

In PFM measurement, a conductive tip made of doped silicon or coated with metal is in contact with the sample and a sinusoidal voltage signal is applied to the tip. For a sample with piezoresponse, the electric field will cause a deformation of the sample topography sinusoidal in time. Since the sample is in contact with the tip, the topographical change of sample will cause slight change of tip deformation and the change is recorded by the differential voltage on the quad detector. The sample deformation is usually in the order of 10 pm/V (e.g. 85.6 pm/V for BaTiO₃ [6]). Therefore, PFM signal is measured with lock-in technique for the best signal-to-noise ratio. As shown in Figure 29, If the sample contract in the direction of the electric field, the piezoresponse signal will be in phase with the electric signal; if the sample elongate in the direction of the field, the signal will be out of phase.

7. LAO/STO nano-device c-AFM lithography

Other than performing surface characterization, the main application of AFM in our lab is to create nano-scale structures on the interface of LAO/STO. As discussed in Section ??, the “water-cycle” mechanism [13] and surface protonation [6] are central for the reversible AFM lithography on LAO/STO interface. In contact mode, the AFM tip is in direct contact with the LAO/STO sample surface. When a positive voltage is applied to the conductive AFM tip, and $V_{tip} > +6V$ [12], the electric field from the tip will dissociate the water molecules between the tip and sample surface, and leaves a trace of proton, as the tip scans through the LAO surface.

As shown in Figure 30, the golden regions are a pair of electrodes connected to the LAO/STO interface. An AC voltage of ± 100 mV is applied to one electrode, while the

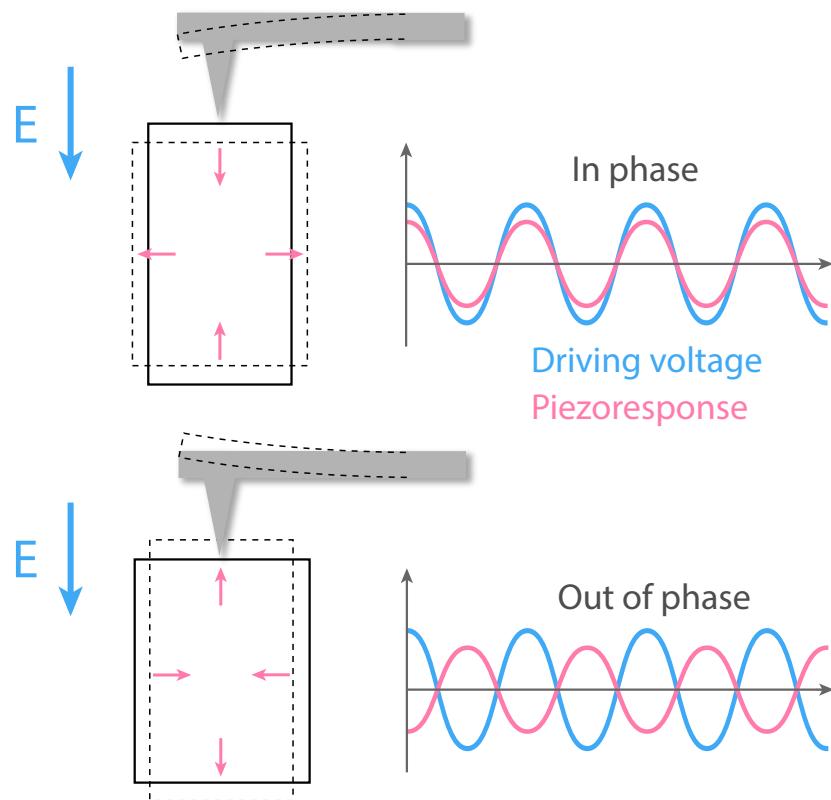


Figure 29: PFM measurement. The external electric field is applied on the sample through a conductive tip. The sample deforms and slightly bend the tip, and the deformation signal is monitored with a quad detector (not shown). If the sample contract in the direction of the field, the deformation signal is in phase with the driving voltage (above); if the sample elongate in the direction of the field, the signal would be out of phase with the driving voltage (below).

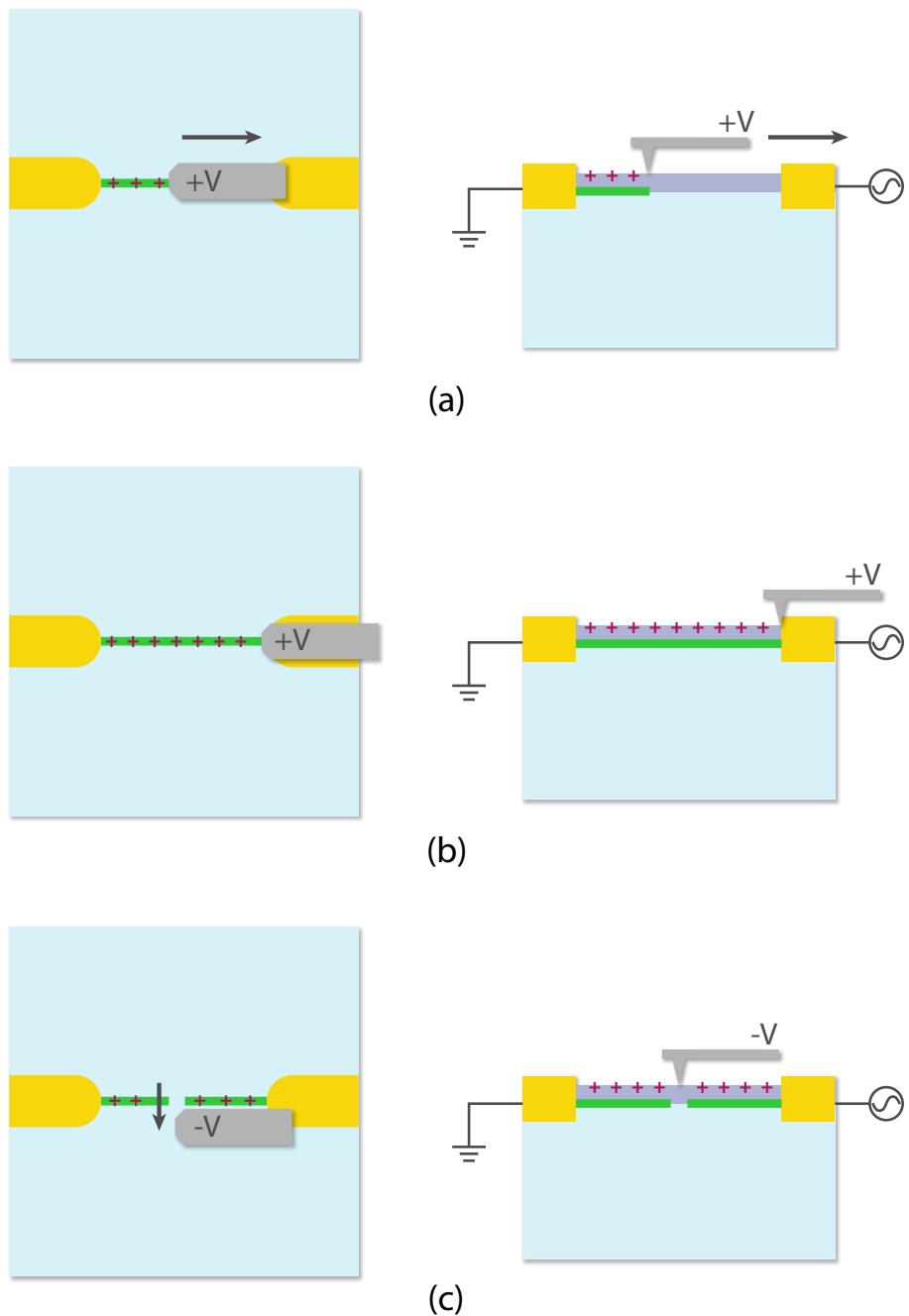


Figure 30: AFM lithography on LAO/STO. (a)(b) The AFM is set in contact mode. A positive bias voltage is applied to the tip. A trace of proton is left on the path of AFM tip, and 2DEG is formed underneath the path. Conductivity of the two interface electrodes are monitored, and a conductance jump will be observed once a closed loop is formed. (c) A negative voltage can remove the proton and cut the nanowire previously written.

other one is grounded. Before the c-AFM lithography starts, the interface between the two electrodes is insulating. The current between them is monitored in real-time as the c-AFM tip scans through the surface (zero before lithography starts). A positive voltage is applied, and protons are dissociated from the water meniscus and left behind the tip (plus signs in the Figure). 2DEG is formed under the protonated region and makes the interface conductive (green region). Once the two electrodes are connected by the conductive channel, a conductance jump can be observed. When a negative voltage on the tip is applied, the protons will be removed from the surface and make the interface insulating again. A typical resistance of the nanowire right after the writing is about $200 \text{ k}\Omega/\mu\text{m}$, and the width is in the same order of magnitude as the c-AFM tip [12].

The sample is patterned in such a way that I can do AFM lithography and electrical measurement in real-time. Figure 31 show the pattern of a typical LAO/STO sample for c-AFM lithography. The dimension of the sample is $5 \text{ mm} \times 5 \text{ mm}$. There are two layers of metals. The blue layer is in direct contact with the LAO/STO interface. The sample is first etched with Ar ion mill and the etched areas are backed-filled with 4 nm of Ti and 25 nm of Au (as discussed in II.B.2). The orange regions are for electrical connections and wire-bonding. 4 nm of Ti and 50 nm of Au are directly coated on the LAO surface without etching. The orange crosses on the corners indicate the corners of the sample. the blue crosses and triangle are guidance for alignment. The zoomed-in image shows the region where c-AFM lithography is performed. The patterns are written inside the $20 \mu\text{m} \times 20 \mu\text{m}$ area, and connected with the interface electrodes.

D. GRAPHENE/LAO/STO DEVICE FABRICATION

Current state-of-the-art high quality graphene devices are fabricated from mechanically transferred exfoliated graphene encapsulated with hexagonal boron nitride (h-BN) [52], where the mean-free-path of the electron can exceed the dimension of the device [53] (tens of micrometers). For applications requiring an arbitrary substrate and graphene shape like my experiment, graphene grown from CVD method and transfer in liquid (“wet-transfer”)

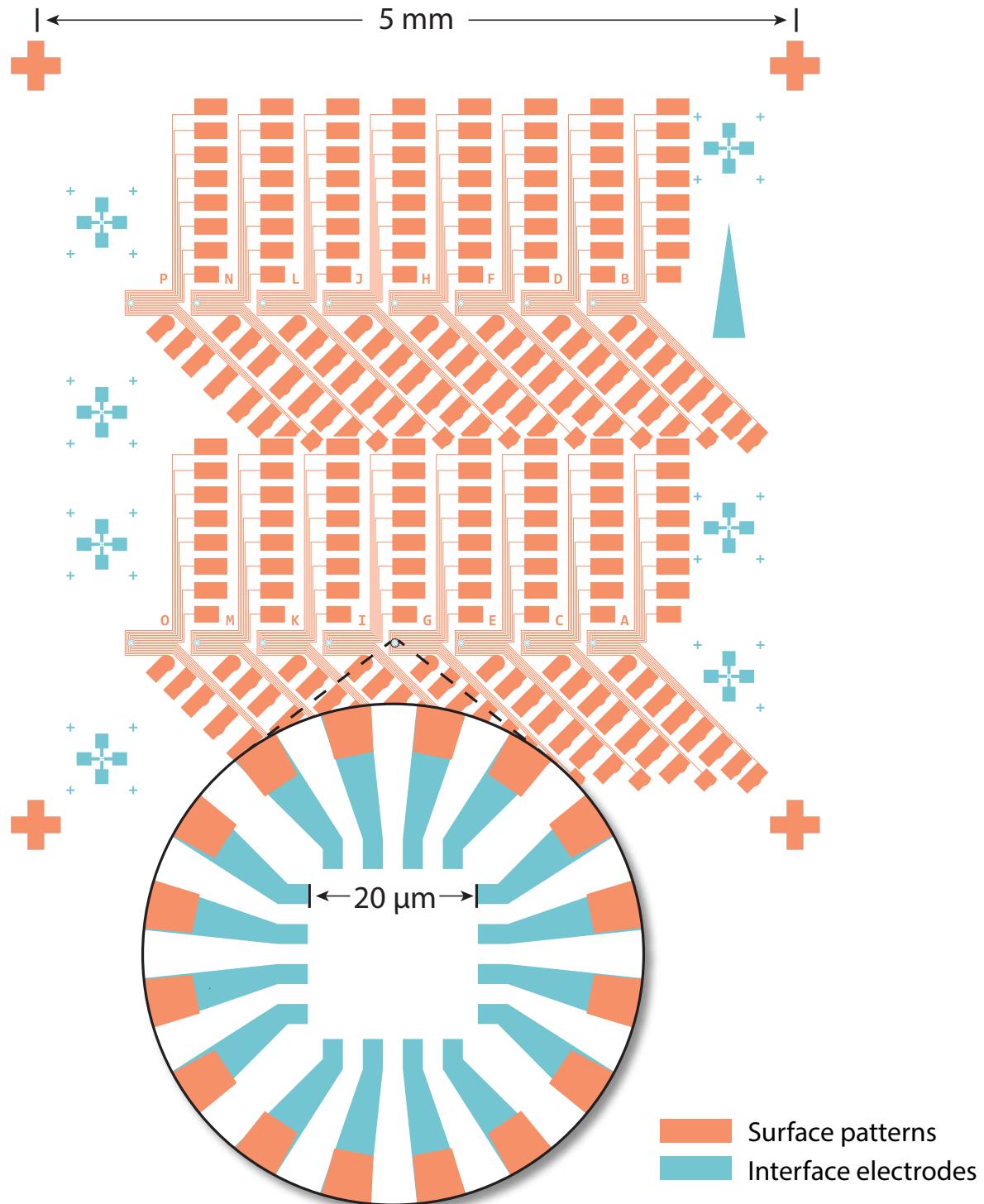


Figure 31: LAO/STO sample pattern for c-AFM lithography. The sample size is 5 mm × 5 mm. Canvas are 20 μm squares.

is preferred. The basic idea of wet-transfer is to use wet chemical etchant such as nitric acid, hydrochloric acid, FeCl_3 or ammonium persulfate (AP) to etch away the metal substrate while the graphene is floating on the liquid surface. The graphene is then scooped out and rinsed in DI-water for several times while floating on water. The substrate is then immersed in the DI-water and used to catch the graphene piece from the bottom. Conventionally, the wet-transfer needs polymers like poly(methyl methacrylate) (PMMA) a scaffold layer to support graphene on the liquid surface before it is transferred onto the substrate [54–56]. The PMMA is then patterned with deep UV exposure or e-beam lithography, so that graphene can be etched in to the designed shape. In the end the PMMA is cleaned with organic solvent. The procedure of using PMMA to transfer and pattern graphene shown in Figure 32.

The issue with PMMA as transfer medium is that, the residual PMMA is known to be a source of electron scattering, and would significantly reduce the electron mobilities [57–59]. Annealing the sample in H_2/Ar environment proves to partially remove the residue, but the process can also introduce structural defects to graphene [58], or increase coupling between graphene and the substrate and result in extrinsic doping and deterioration of mobility [59].

Another drawback of using PMMA as a transfer medium is that LAO/STO substrate is susceptible to PMMA contaminants. Figure 33 shows the AFM AC phase image of LAO/STO with a graphene piece transferred and patterned with PMMA. The inside the circular region is graphene. On the LAO/STO surface, contamination particles can be seen. Many experiments in my project require tuning the 2D electron gas on the interface of LAO/STO with c-AFM (will be discussed in Section II.C). Most of the LAO/STO samples were found to lost the interface tunability after the graphene transfer with PMMA.

A replacement for PMMA is a type of perfluoropolymer Hyflon from Solvay. Our collaborator Brian D’Urso has used Hyflon for hydrodynamic experiment, and suggested it might work as a perfect protection layer for graphene. Hyflon is a type of perfluorinated polymer (similar to Teflon), and is highly hydrophobic and chemically stable. Hyflon has been reported to be widely used in membrane applications such as fuel cells, due to the inertness of C-F bonds [60–62]. It has also been reported that the Hyflon membrane between graphene

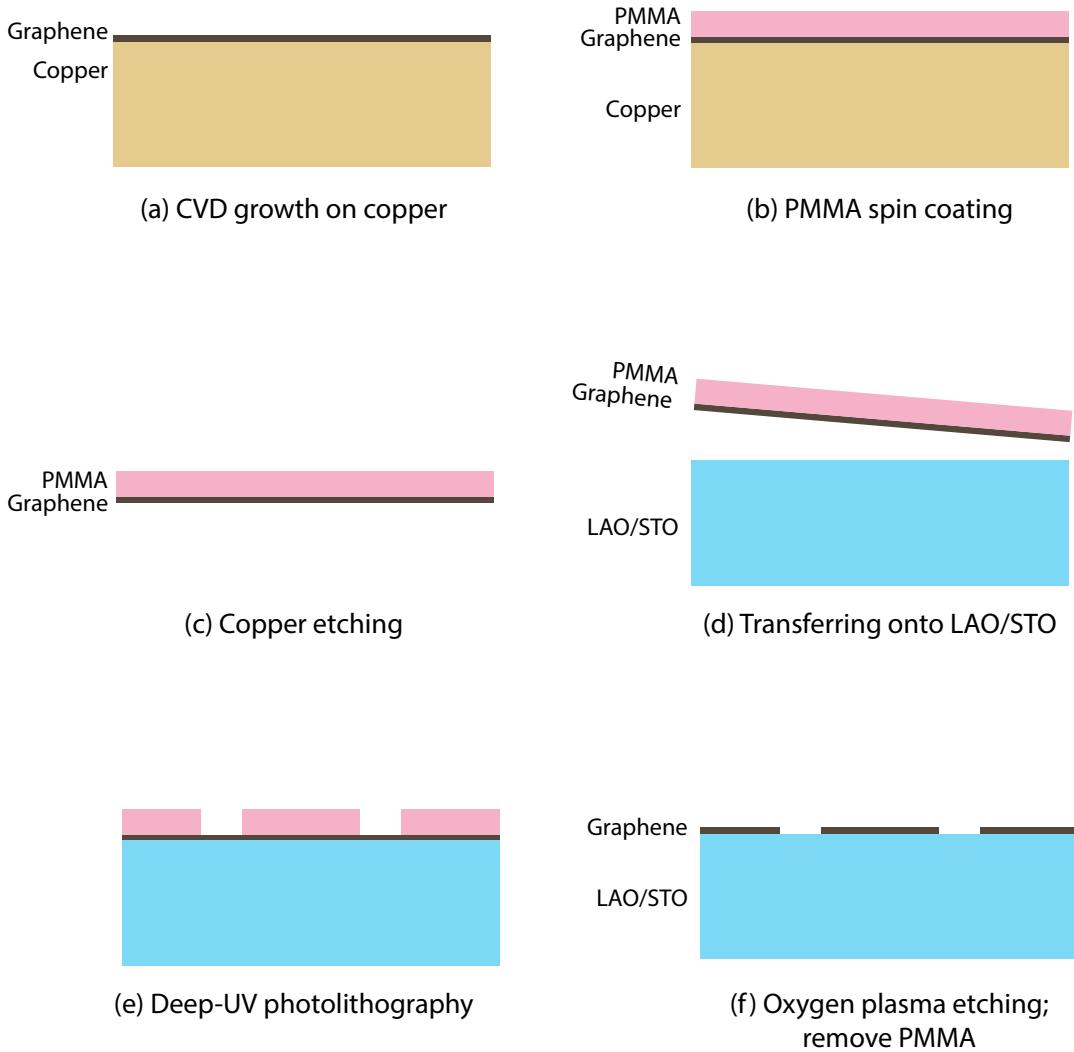


Figure 32: CVD graphene transfer and patterning with PMMA. (a) Graphene is grown on copper with CVD. (b) PMMA is spin-coated onto graphene surface. (c) Copper is etched chemically, while graphene floats on the liquid surface. (d) Graphene is transferred onto LAO/STO, using PMMA as a supporting layer. (e) PMMA is patterned with deep-UV lithography. (f) Graphene is etched with oxygen plasma and then PMMA is removed with organic solvent.

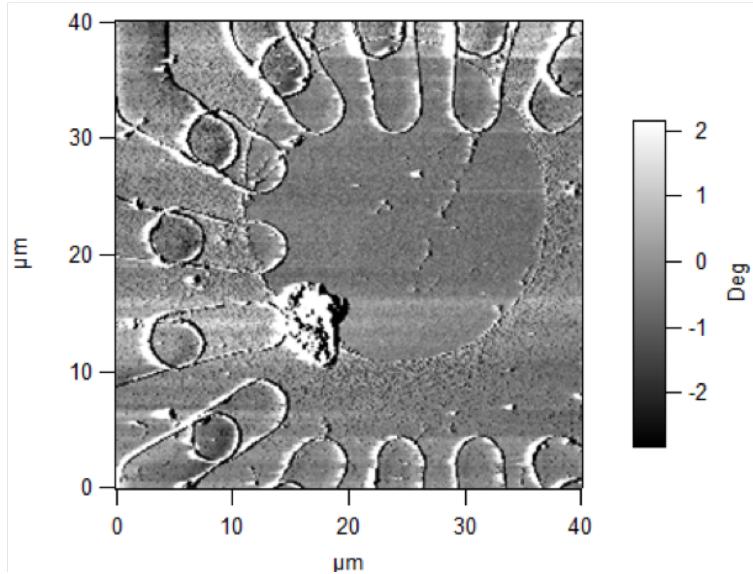


Figure 33: AFM phase image of graphene on LAO/STO, transferred with PMMA. The circular region is graphene. Particles can be seen outside graphene, on LAO/STO surface. Other features are the metal electrodes for graphene and interface contact.

and substrates like SiO_2 can reduce the extrinsic p-type doping in graphene by preventing water molecule adsorption to the dangling bonds on the substrates [63]. It means that, unlike PMMA that leaves residue and deteriorate graphene quality, Hyflon can actually preserve the graphene while used as a transfer medium. Hyflon is also high selectivity to solvent. Most of the organic or inorganic solvent such as acetone, IPA or DI-water cannot dissolve Hyflon, which makes it a perfect protection layer for graphene.

The commercially available Hyflon is in powder form. It is only soluble in a few types of perfluorinated solvent. In my experiment I used FC-40 to make Hyflon solutions. There are different types of Hyflon available, mainly Hyflon AD 40 and Hyflon AD 60, with different molecular weights and phase transition temperature. I have tested both types, and found that graphene transferred with Hyflon AD 60 has higher quality. Although AD 40 has smaller molecular weight and easier to be dissolved, the sample soft-baking temperature is higher than the phase transition temperature of AD 40, and would cause cross-linking of the

polymer chains. This makes Hyflon AD 40 hard to be removed and affects graphene quality as a result.

1. Overview of the Hyflon transfer method

The procedure for graphene transfer with Hyflon is similar to the PMMA transfer method. As shown in Figure 34, the graphene on copper is spin coated with Hyflon. The Hyflon film is only 50 nm, therefore a second supporting layer, photoresist, is spin-coated on top of the Hyflon. The copper is etched with ammonium persulphate while graphene with Hyflon and photoresist floats on the surface of chemical. The graphene is then rinsed 4 to 5 times and then transferred onto a pre-patterned LAO/STO substrate, and soft-baked to remove the DI water between graphene and LAO. The photoresist is then removed, and another layer of photoresist is spin-coated. The sample is patterned into Hall bars with standard photolithography. Excessive graphene is etched away with oxygen plasma, along with the Hyflon covering it. The patterned graphene/LAO/STO sample is rinsed with acetone to remove the photoresist, and then Hyflon is removed with FC-40. The particles left on the patterned graphene surface is cleaned by AFM in contact mode scans.

2. Hyflon solution preparation and spin-coating

Hyflon solutions in FC-40 are made by adding 2.5 grams of Hyflon powder into 100 ml FC-40 (nominally 2.5%). The solution is shaken at 100 rpm for 48 hours. Before spin-coated on sample, the Hyflon solution needs go through a series of filters of 450 nm, 200 nm and 100 nm in size to remove any undissolved particles. When spin-coated at 3500 rpm, the thickness of Hyflon film is about 50 nm. In the past I also used 0.5% Hyflon solution and spin-coated at 1000 rpm to make coatings of 50 nm, but it turned out that higher concentration of Hyflon solutions spin-coated at a higher speed would yield more uniform films on graphene samples.

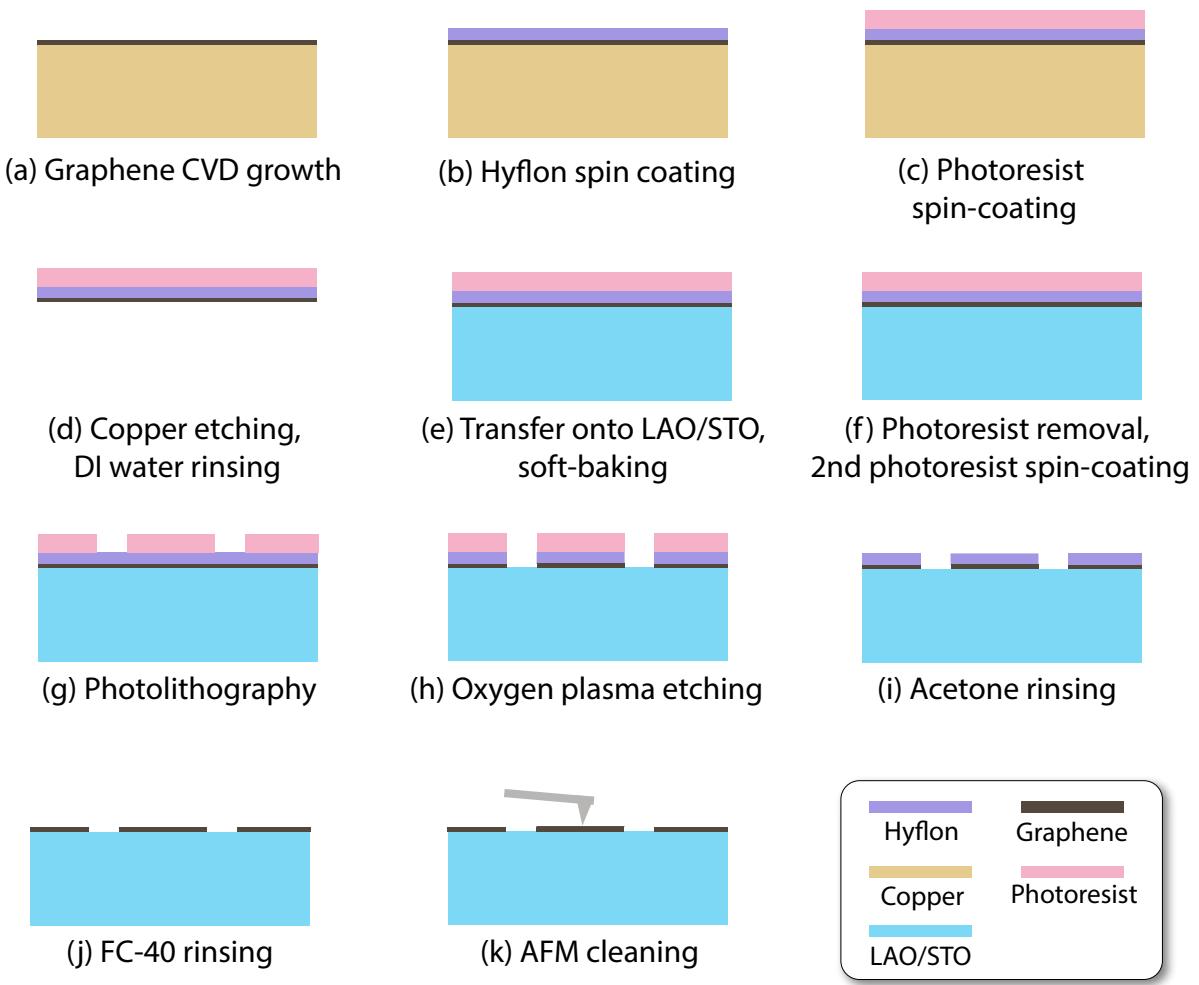
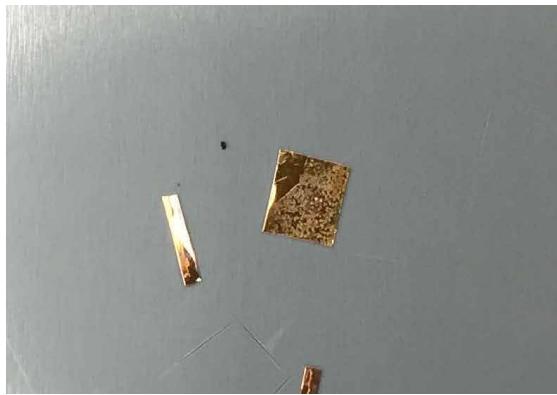
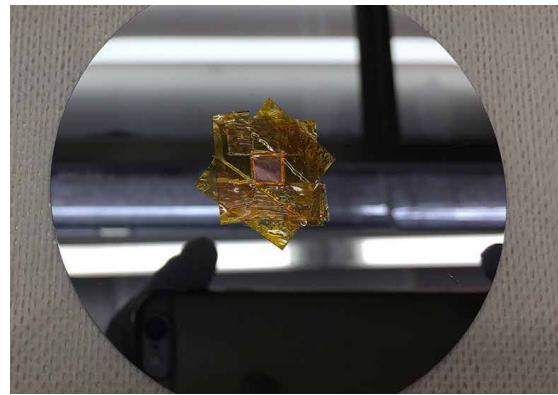


Figure 34: Hyflon transfer and patterning procedure. (a) Graphene is grown with CVD on a copper substrate. (b) Hyflon is spin-coated on graphene. (c) A layer of photoresist is coated on Hyflon as a supporting layer for wet-transfer. (d) Copper substrate is etched with ammonium persulphate; graphene is rinsed in DI-water for several times. (e) Graphene is transferred onto LAO/STO surface. (f) Photoresist for transfer assistance is removed; another layer of photoresist is coated. (g) Standard UV photolithography. (h) Oxygen plasma etching on the excessive graphene. (i) Photoresist removal with acetone. (j) Hyflon removal with FC-40. (k) Residue particle cleaning with AFM.



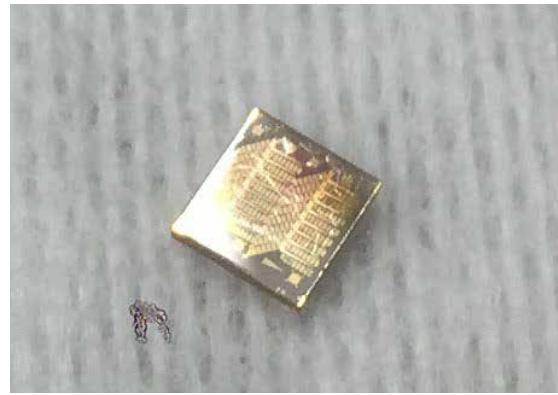
(a)



(b)



(c)



(d)

Figure 35: (a) The graphene with copper foil is cut into squares. The graphene single domains can be seen. (b) copper foil with CVD graphene is fixed onto a silicon wafer as a spin-coating carrier. The edges of the copper foils are carefully sealed with Kapton tape to prevent Hyflon solution leaking into the space between copper and silicon substrate. (c) After the copper is fully etched by ammonium persulfate, the graphene flake with Hyflon and photoresist floats on the surface of the liquid. (d) Graphene transferred onto pre-patterned LAO/STO. Liquid between the graphene LAO is evaporated in an oven or on a hot plate.

3. Graphene preparation, copper etching and wet transfer

The as-grown CVD graphene is on 100 μm thick circular copper foil. The LAO/STO substrates that graphene will be transferred on are 5 mm \times 5 mm squares. Therefore, the graphene on copper needs to be cut into 5 mm \times 5 mm shape with a razor blade as shown in Figure 35(a). Graphene single domains can be seen in the Figure. The square shape copper foil is then fixed onto a 3" silicon wafer for spin coating, with Kapton tapes, prepared for Hyflon spin coating. The edges of the graphene need to be carefully sealed, so that the Hyflon solution will not leak into the space between the copper and silicon wafer. In the past, I used to leave the edges open, and the Hyflon will be left on the backside of the copper. After copper etching and graphene transferred onto the LAO/STO, the Hyflon on the backside will be trapped between graphene and substrate and impossible to be removed.

Transferring graphene with only the 50 nm Hyflon proved to be very hard. To address this issue, an additional layer of AZ4210 photoresist is spin-coated on Hyflon. However, since the Hyflon is highly hydrophobic, the photoresist solution cannot stick to the surface and form a film of 2.1 μm thick, as it usually does on hydrophilic surfaces. A mild oxygen plasma etching is performed to modified the Hyflon surface and improve surface hydrophilicity. The parameters of plasma etching need to be carefully tested. Etching will not only change the Hyflon hydrophilicity, but also change the solubility of Hyflon in FC-40. In the last step where Hyflon is removed by FC-40 from graphene, if the previous Hyflon surface treatment is too strong, the modified Hyflon can cross-linked and hard to be fully removed from graphene. In practice, etching the Hyflon for only a few nanometers would drastically improve the hydrophilicity and make photoresist spin-coating possible.

After spin coating, the copper foil is taken off the silicon substrate. 1 mol/L concentration ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) DI-water solution is prepared beforehand. Ammonium persulfate is a type of oxidation agent widely used as copper etchant in printed circuit board industry. Compared to other chemicals like ferric chloride, ammonium persulfate does not leave metal ion to graphene, which is critical for experiments on magnetism or transport. The ammonium persulfate solution also needs to go through a 450 nm polymer filter before the copper foil is place on the surface of it. Copper etching usually takes 3-4 hours.



Figure 36: (a) Without copper substrate backside cleaning, the graphene transferred onto LAO/STO has contaminant trapped. (b) The graphene on LAO/STO is much cleaner if the backside is cleaned.

After the graphene transferred onto the LAO/STO, the sample is sometimes found dirty, and the contaminants seemed to be introduced by the transfer procedure. AFM scanning showed that the contaminants were trapped between graphene and LAO. One possibility was that the contaminants were the graphene grown on the backside of the copper. When the copper was etched away by ammonium persulfate, the backside graphene did not sinked into the etchant, but transferred with the topside graphene onto the sample and got trapped between graphene and LAO.

The *two-step etching* procedure can be used instead. After the copper top surface is coated with Hyflon, it is placed on the surface of ammonium persulfate solution and left inside an ultrasonic cleaner for 15 minutes. While the backside of the copper is been etched, it is also scratched by the ultrasound wave so that the backside graphene can be removed. After 15 minutes, the backside is washed by spraying DI-water on it. The graphene on the topside is protected by Hyflon, and will not be affected by the backside cleaning. Then

the copper foil is placed back on the surface of ammonium persulfate. After 3–4 hours the copper foil is fully etched, and the graphene with Hyflon and photoresist would float on the surface, as shown in Figure 35(c). The gray color of the floating flake is from the AZ4210 photoresist. The dark spot on the lower-left corner of the flake is a piece of contaminant.

The graphene flake is then scooped out with e mesh and place on the surface of DI-water, repeated for 4–5 times to make sure the ammonium persulfate is washed off the backside of the flake. Then the LAO/STO substrate is immersed in the DI-water where the flake is floating. The substrate is slowly lifted up towards the flake on the liquid surface, and catch the flake when it comes out of the water. The substrate with the graphene flake on surface is then baked in an oven pre-heated to 50°C, or on a hot plate at 70°C for 5–10 minutes so that the DI-water between graphene and substrate is evaporated and graphene firmly adheres to LAO (Figure 35(d)).

4. Graphene/LAO/STO sample pattern

The metal electrodes and bonding pads on LAO/STO are patterned before graphene is transferred. Therefore, electrodes are making contacts with graphene from below. The patterns are slightly modified from the one in Section II.C.7, so that there are electrodes dedicated for making contacts to graphene. As shown in the zoomed-out image in Figure 37, the graphene Hall bars are located on the canvas for c-AFM lithography. The graphene is in direct contact with the metal electrodes on LAO/STO surface (orange in color), while LAO/STO are in contact with the interface electrodes (blue in color). Therefore, the two layers can be measured separately.

5. Photolithography and etching

The graphene transferred onto LAO/STO is patterned with standard UV photolithography, as discussed in Section II.B.1. Although there is already photoresist on graphene flake to assist wet transfer, it needs to be washed off and re-coated, because it is exposed to UV and chemical etchant. Unlike the photolithography for LAO/STO electrodes, patterning graphene into Hall bars need to wash off the photoresist outside of the Hall bars and leave

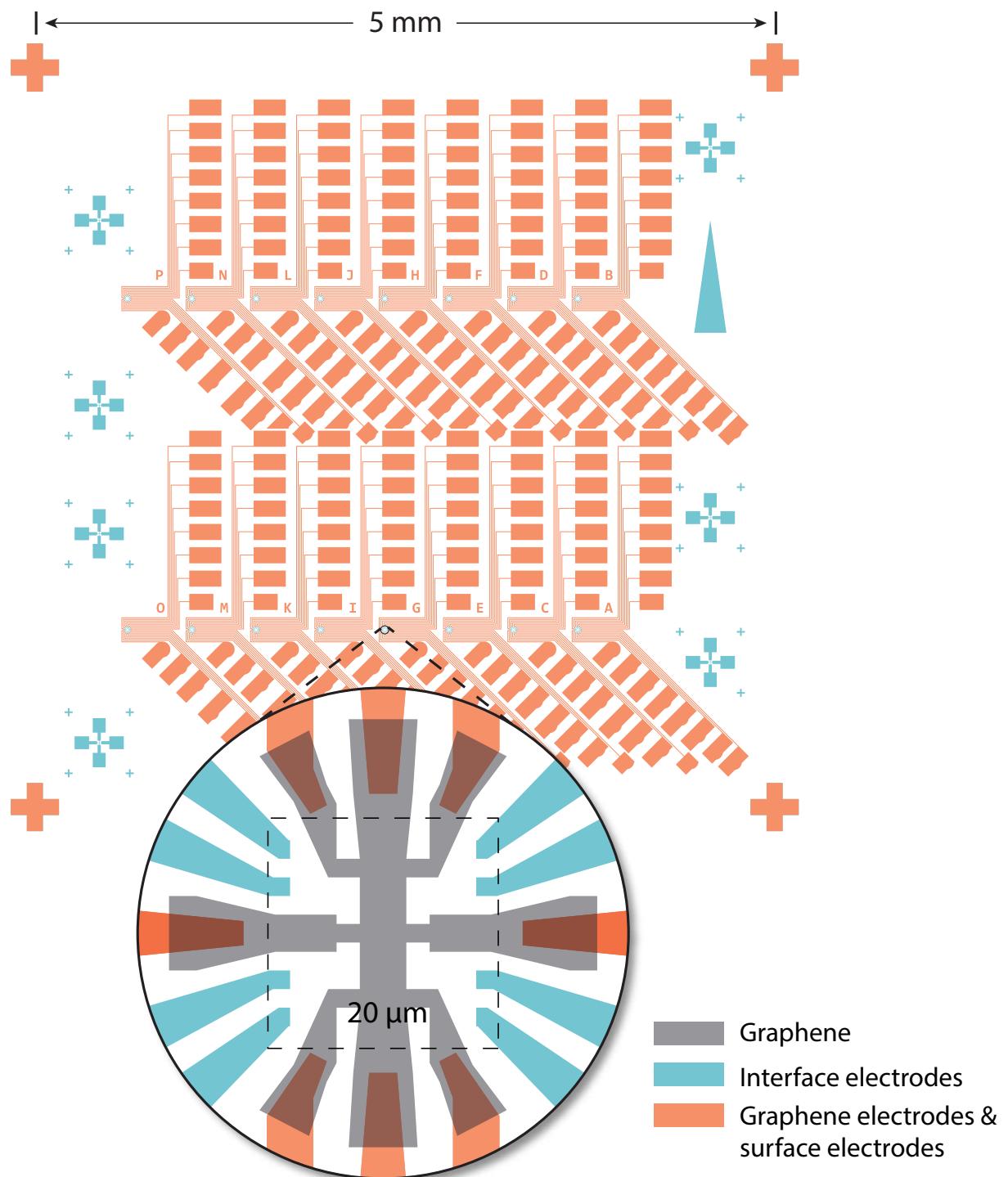


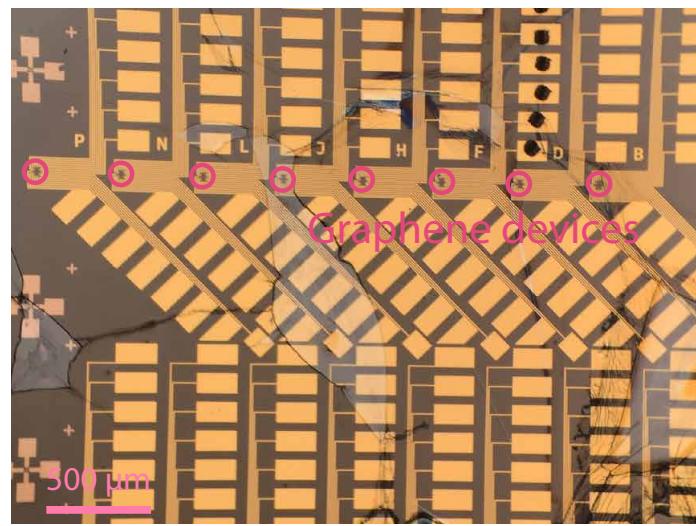
Figure 37: Patterns for graphene/LAO/STO. Two sets of electrodes are patterned separately, for interface and graphene contact.

the Hall bar region covered with photoresist, so that the graphene is protected from oxygen plasma etching. The oxygen plasma barrel etcher and RIE proved to be effective for patterning graphene. However, other than the Hyflon and graphene, there are usually contaminant introduced by wet-transfer procedure that need to be cleaned with RIE as well (Figure 38).

a. One-step etching Before 2018 I was using the one-step etching method (as shown in Figure 34), that is to etch the graphene and clean the contaminants with RIE in one step. Figure 38 shows the image of a sample before and after the RIE etching. In Figure 38(a), it can be seen that bubbles or foldings introduced from the wet transfer covers the entire sample. Fortunately in my experiments, most of the graphene transferred on LAO/STO needs to be etched away, and only the graphene device inside red circles in Figure 38(a) need to be covered with graphene. A zoomed-in image is shown in Figure 39, with graphene covered with Hyflon. The metal patterns are contact electrodes for graphene and LAO/STO interface. Wrinkles on graphene can be seen, which are following the corrugations on the copper substrate during CVD growth. The patterns for the entire sample are designed in the way that there can be as many graphene devices fit in the sample as possible, so that there are higher chances of finding a clean graphene device. The contaminants are etched away with an aggressive RIE procedure (listed in Table 4).

As shown in Figure 38(b), the single-step RIE etching can completely clean the contaminants on LAO/STO. However, the etching can be problematic for the LAO/STO interface. As shown previously in Figure 37, the graphene Hall bar locates inside the $20\ \mu\text{m}$ canvas area. When the graphene outside the Hall bar and surface contaminants are etched with the same aggressive RIE recipe, the bombardment would damage the LAO/STO interface and it would be impossible to write nanowires with c-AFM in some cases. However if I etch the sample with a milder recipe, the contaminants cannot be fully cleaned in some cases.

b. Two-step etching To address the interface-damaging issue, I started to use the two-step etching method. The basic idea is to separate sample cleaning and graphene etching steps. As shown in Figure 40. In the first step of etching, the Hyflon and graphene are protected by photoresist in a square shape, that covers the Hall bar devices to be pattern



(a)



(b)

Figure 38: Contaminants can be introduced by wet transfer. The source can be photoresist, copper etchant, or liquid trapped in the bubble formed from transferring. (a) Contaminants can be seen after graphene transfer. Only the graphene inside the red circles (zoomed-in image in Figure 39) need to be protected with photoresist, and rest of the graphene can be removed along with the contaminants by RIE procedure. (b) Sample surface is clean after RIE procedure.

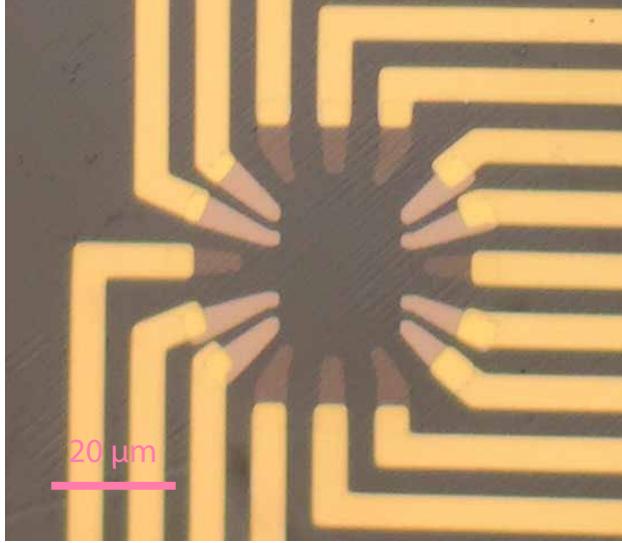


Figure 39: The graphene area of interest on pre-patterned LAO/STO sample. The patterns are for graphene and LAO/STO interface contact.

in the next step and the LAO/STO canvas region. The rest of the sample is etch with an aggressive RIE step so that the contaminants on bonding pads and connection patterns are fully removed. After the etching the photoresist is washed away with acetone and IPA. In the second step, another layer of photoresist is spin-coated, and patterned into graphene Hall-bar device shape. Then the graphene and Hyflon outside the Hall bar region but covering the LAO/STO canvas are etched away with a much weaker oxygen plasma, so that the LAO/STO interface will not be damaged.

The detailed procedures are shown in Figure 41. Right after graphene is transferred onto LAO/STO and the supporting photoresist is washed off, it is spin-coated with AZ4210. The square-shape is patterned with photolithography to protect the canvas. Then the sample is etched with RIE, until all the contaminants are cleaned. In some cases, the contaminants needs long etching time, and photoresist may be etched through. Multiple photolithography and RIE etching steps will be needed. For the same reason, AZ4210 (2.1 μ m thick) is preferred than AZ4110 (1.1 μ m thick). After that, AZ4210 is washed off, and AZ4110 is spin-coated. Photolithography on AZ4110 has higher precision. One thing I noticed was that

Instrument	RIE
Gas	Oxygen
Flow rate	19 sccm
Power	50 W
Pressure	300 mTorr
Time	60 - 180 s

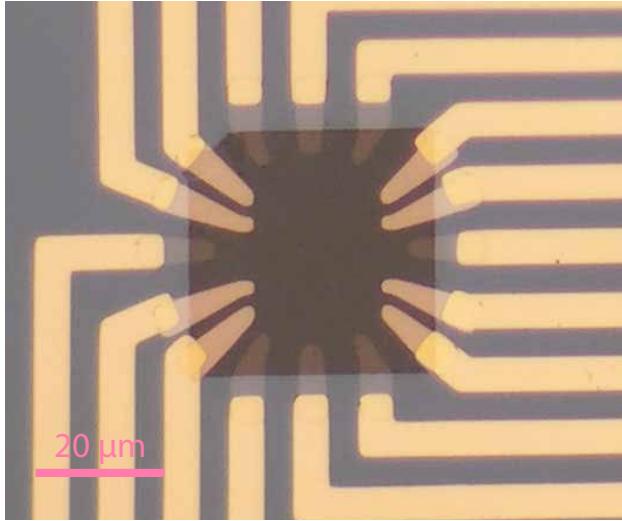
Table 4: One-step RIE etching recipe.

the developing time required for AZ4110 is much longer than usual, possibly because the previous RIE etching changed the surface hydrophilicity and make the exposed photoresist harder to be washed off. After the Hall bar is patterned with inverse pattern, the sample is etched with a weak oxygen plasma barrel etching recipe, and shape the graphene and Hyflon into Hall bars (Figure 40). The recipe for photolithography and etching are listed in Table 5 and Table 6.

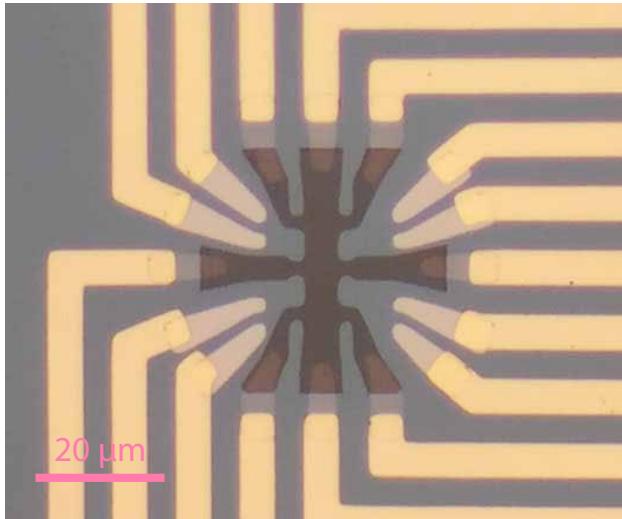
6. Hyflon removal

Over the entire processing, the graphene is covered with Hyflon until the last step. The Hyflon is only solvable in perfluorinated solvent such as FC-40. On one hand, this makes it possible for Hyflon to serve as a protection layer for all the other chemicals like acetone, IPA or photoresists. On the other hand, it also make Hyflon hard to be fully removed. I used two recipe for Hyflon removal.

a. High temperature method FC-40 heated up to 165 °C in a beaker. The boiling point of FC-40 is about 175 °C and it decomposes into HF, therefore I keep the temperature lower than that. Once the sample is placed in FC-40, the beaker is taken off the hot place and left on a shaking stage at 100 rpm, and the sample is shaken in FC-40 for 12 hours while it cools down to room temperature. Then the sample is taken out and dried with nitrogen.



(a)



(b)

Figure 40: Two-step graphene etching. (a) A square shape region is protected by AZ4210 photoresist. Outside of the square region the sample is etched with an aggressive RIE process to remove the contaminants introduced by wet-transfer. The figure shows the graphene with Hyflon. Photoresist has been washed off. (b) A second step of photolithography is performed and a Hall-bar shape region is protected by AZ4110 photoresist. Outside of the Hall-bar the Hyflon and graphene is etched away with a mild oxygen plasma barrel etching recipe, and the LAO/STO interface is still writable. The figure shows the graphene Hall-bar covered with Hyflon.



Figure 41: Two-step graphene etching. (a) AZ4210 is spin-coated on Hyflon. (b) The photoresist is patterned into square-shape protection layer for the canvas. (c) An aggressive RIE process is used to fully remove the contaminants outside the canvas. (a) to (c) might be repeated if necessary. (d) AZ4110 is spin-coated. (e) Hall bar shape is patterned, to protect the Hyflon and graphene on the regions of interest. (f) A weak oxygen plasma etching step is used to remove the unwanted Hyflon and graphene. (g) AZ110 is washed off by solvents. (h) Hyflon is removed by FC-40.

Photoresist	AZ4210 (step 1)	AZ4110 (step 2)
Spin-coating	4000 rpm	4000 rpm
Baking	95 °C	95 °C
UV dose	170 mJ	100-120 mJ
Developer : DI-water	1 : 4	1 : 4
Developing time	120 s	240 - 600 s

Table 5: Two-step etching photolithography recipe. First layer of AZ4210 is used to protect the canvas against the aggressive RIE for contamination removal. Second layer of AZ4110 is for graphene Hall bar protection, and only need to resist mild oxygen plasma etching.

Instrument	RIE (step 1)	Barrel etcher (step 2)
Gas	Oxygen	Oxygen
Pressure	300 mTorr	~ 600 mTorr
Power	50 W	100 W
Time	200 - 400 s	300 s

Table 6: Two-step etching recipe. Although it seems that the barrel etcher is running at higher power, the structure of the instrument make the etching much less invasive compared to RIE.

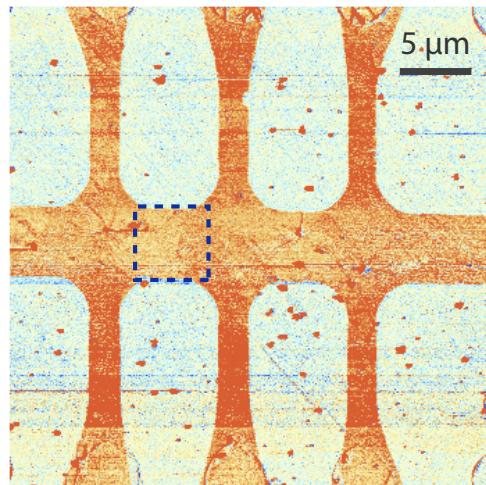
b. Low temperature method FC-40 is heated up to 70 °C in a beaker. After the sample is immersed in FC-40, the beaker is shaken at 100 rpm while the temperature is kept at 70 °C for 12 - 24 hours. Then the sample is taken out and dried with nitrogen. I started to use this method since 2017.

It is hard to determine which method is more preferable. The room temperature method does seem to be less harsh, and might affect the graphene and LAO/STO. However, the residue on graphene is more than the high temperature method. There was a period of time (about a year) when I could not produce high quality graphene/LAO/STO sample. Whether or not it is related to switching from the high temperature method to low temperature method for Hyflon removal is still uncertain.

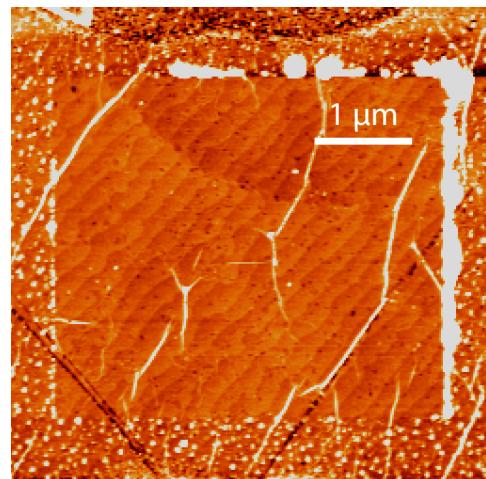
7. AFM cleaning of graphene

From the past experiences, all the solvents including DI-water, IPA and FC-40 would leave a layer of nano-particles on sample surface, until cleaned by oxygen plasma. For graphene/LAO/STO sample, even a weak recipe of oxygen plasma etching can potentially cause structural damage to the graphene. Therefore, the nano-particles from solvents, especially FC-40, and the residues of Hyflon are cleaned with AFM contact mode scanning, as a final step of processing.

Figure 42 shows the AFM images of graphene before and after cleaning. Figure 42(a) is the AFM AC mode phase image. The Hall bar shape in orange is the graphene, and the LAO surface is in cyan. As can be seen, particles of different sizes can be observed. Larger particles (~ 100 nm) are probably from the the FC-40, while the smaller particles ($\downarrow 100$ nm) are the residues of Hyflon. Figure 42(b) is the zoomed-in image of the squared region in 42(a), after the center is been scanned with AFM in contact mode. Particles are pushed to the edges of the square, and it can be seen that the scanning is bottom to up, left to right. Inside the clean region, terraces ($h = 4\text{\AA}$) of the LAO/STO substrate can also be observed. Wrinkles of the graphene are formed during the transfer or AFM contact scan process. Mechanical strength of graphene is high enough [] to withstand the contact



(a)



(b)

Figure 42: AFM cleaning of graphene. (a) The organ Hall bar region is the graphene, after Hyflon removal in FC-40. Particles on graphene can be observed. (b) Zoomed-in image of the square region in (a). The center has been scanned in AFM contact mode. Particles are pushed to the top and right edges. Terraces of LAO/STO and wrinkles can be observed.

scanning, however it is possible that graphene is broken by the AFM tip, especially when the raster scan speed is too fast and large amount of resilient contaminants are present on graphene (and a large contact force has to be applied), or when the AFM tip is scanning from the LAO to graphene from the edge with a large contact force. Typical cleaning recipes with on models of AFM are listed in Table 7, with which the graphene does not break.

AFM model	Asylum MFP3D	Asylum Cypher
Tip spring constant	3 N/m	3 N/m
Deflection set-point	0.05 – 0.5 V	0.1 – 1.0 V
Contact force	40 – 400 nN	20 – 200 nN
Scanning speed	10 $\mu\text{m}/\text{s}$	10 $\mu\text{m}/\text{s}$
Line separation	10 – 20 nm	10 – 20 nm

Table 7: Graphene cleaning recipes on Asylum MFP3D and Cypher.

To prove that the sample is clean after AFM cleaning, an room temperature STM measurement is performed. Tunneling currents are measured from graphene surface to a tungsten tip. From the AFM image the graphene atoms can be identified, which proves that the graphene on LAO/STO is atomically clean.

8. Graphene/LAO/STO nano-scale device lithography

The experiments on graphene, such as Klein tunneling [24–27], edge state mixing [28–31], band structure engineering using superlattice [37], rely on the Dirac cone band structure and tunability of carriers from electrons to holes. The ability to control the charge neutrality point is central to controlling these exotic properties of graphene. c-AFM writing is proved to be a powerful tool to create nanostructures on LAO/STO interfaces. Pattern nano-scale devices on graphene/LAO/STO reversibly with c-AFM is one of the major techniques I have been trying to develop in my research.

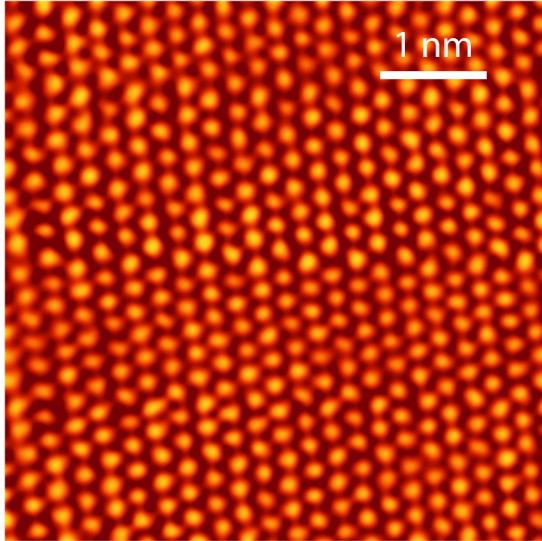
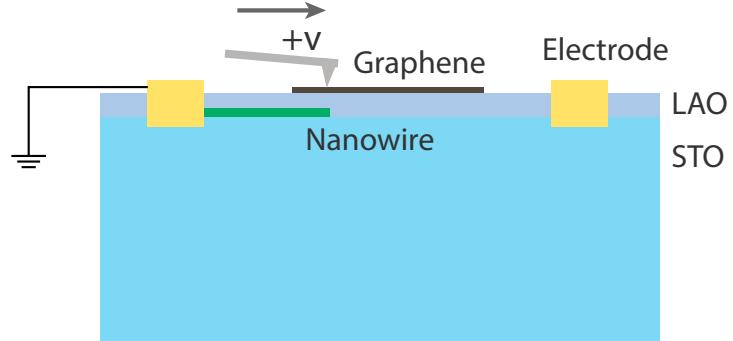


Figure 43: STM image of graphene on LAO/STO after AFM cleaning.

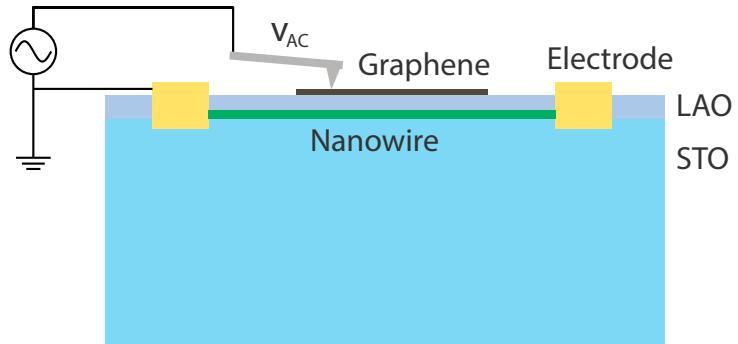
9. c-AFM lithography and PFM imaging

Figure 44 demonstrates the setup of c-AFM lithography on graphene/LAO/STO, and the subsequent PFM imaging of the nanowire underneath the graphene. The setup of c-AFM lithography is similar to bare LAO/STO samples. The interface electrodes is grounded or measure. A positive voltage $V_{\text{tip}} > +6V$ is applied to the c-AFM tip, while the tip sketches between the two interface electrodes. A protective resistor of $1 \text{ G}\Omega$ is connected in series with the tip and voltage source (not shown in Figure 44). The graphene is disconnected and floating in this experiment. The tip goes through the graphene covered area before two interface electrodes are connected. The typical voltage applied to the AFM tip is $+15 \text{ V}$, and the tip moving speed is $0.5 - 1 \mu\text{m}/\text{s}$, but can be as high as $10 \mu\text{m}/\text{s}$ in some cases. Contact force is about $20-80 \text{ nN}$. A sudden increase of conductance between two electrodes can be observed (inset of Figure 44(c)), indicates that a conductive channel has been created.

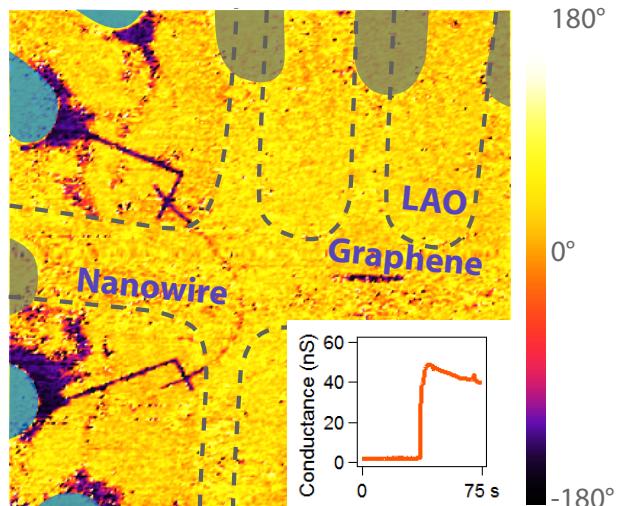
A subsequent PFM measurement is performed. An AC voltage (with modulation frequency f close to the PFM resonance frequency of the sample) is applied to the c-AFM tip, while the tip scans in contact with the sample. The alternating voltage from the tip



(a)



(b)



(c)

Figure 44: (a) c-AFM lithography of graphene/LAO/STO nanowire. (b) PFM measurement setup. (c) PFM image of the nanowire on LAO/STO interface, underneath the graphene. The inset shows the sudden jump of conductance after the two interface electrodes are connected.

modulates the carrier density on the LAO/STO interface, and the carrier density change will cause deformation of STO through the Jahn-Teller effect [6]. The area that previously written with nanowire would respond differently to the AC tip voltage, causes contrast on the PFM image. Figure 44(c) shows the PFM phase image of the nanowire written. The region colored in blue are the interface electrodes, and the region in gray are electrical contact with graphene. The graphene covered regions are enclosed with dashed lines. The narrow path in dark purple color is the nanowire previously written with c-AFM. The path under the graphene regions is dimmer than the outside sections, indicating the shielding effect of graphene against both the c-AFM lithography voltage and the PFM AC voltage on tip.

10. More about the c-AFM writing conditions on graphene and damage thresholds

The graphene on LAO/STO makes the c-AFM lithography more complicated than on bare LAO/STO. As discussed in Section II.C.7, the lithography and erasure of nanowire on the interface relies on the water-cycle and protonation induced by c-AFM tip voltage. It was also found that the surface conditions of LAO can affect the interface 2DEG [6]. Graphene on LAO also changes the critical thickness of LAO/STO [64].

The LAO/STO is fairly robust under the writing and erasing with c-AFM. The graphene however, can be damaged by a high negative voltage on the tip, from the anode oxidation effect [6]. It was reported [6] that the graphene damaging threshold voltage on the c-AFM is about $V_{\text{damage}} \approx 6V$. This voltage is dependent on whether the graphene is floating or grounded and how much current is flowing between the tip and graphene. Figure 45 is an AC phase image of damaged graphene. The light color paths are from AFM sketching with -15 V on the tip, at 400 nm/s speed and 75 nN contact force. The contrast clearly shows the oxidation on graphene. The upper and lower regions of the graphene are electrically disconnected. To avoid oxidation damage to graphene, the tip voltage is limited to -5 V when the graphene is grounded, and -8 V when the graphene is floating while performing c-AFM on graphene with a negative voltage. From my experience the damaging thresholds

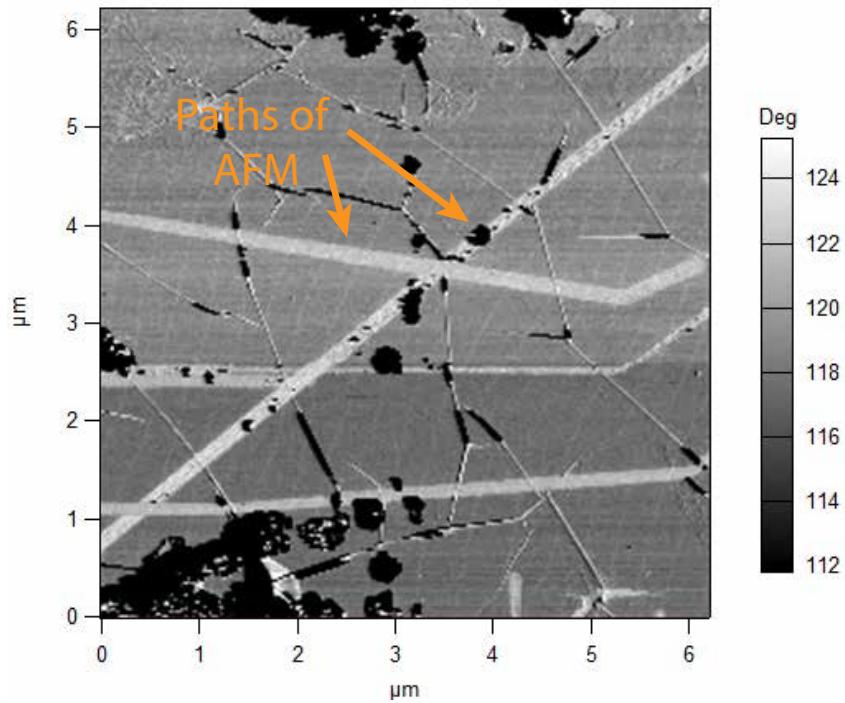


Figure 45: Damages on graphene from c-AFM lithography. On the AFM paths the graphene is oxidized and show contrast on the phase image.

are also related to the AFM tip condition or graphene surface roughness, but in general under these voltages the graphene damage can be avoided. The AFM lithography parameters are listed in Table 8.

	Writing	Erasing
Tip spring constant	3 N/m	3 N/m
Deflection set-point	0.05 - 0.5 V	0.1 - 1.0 V
Tip voltage	+10V to +20V	-5V (graphene grounded) to -8V (graphene floating)
Contact force	80 nN	80 nN
Tip speed	0.4 - 10 μ m/s	0.4 - 10 μ m/s

Table 8: c-AFM writing and erasing parameters on graphene/LAO/STO samples.

III. GRAPHENE/LAO/STO HETEROSTRUCTURE DEVICE

This chapter is about the transport properties of graphene device on graphene/LAO/STO. It is also found that graphene can be reversibly doped with c-AFM lithography technique, similar to the nanostructure lithography on bare LAO/STO. Two experiments are discussed in details: edge-state mixing on graphene *p-n* junctions and graphene superlattice.

A. TRANSPORT MEASUREMENT IN GRAPHENE

The properties of graphene on LAO/STO is different from SiO_2 or hBN substrates due to the unique properties of the LAO/STO substrate. This section will discuss the transport properties of graphene/LAO/STO samples.

The geometry of the sample is illustrated in Figure 46. The graphene on LAO/STO is patterned into Hall bar shapes, with the procedure discussed in previous chapters. Gold electrodes make contact to the graphene from the surface of LAO. The bottom of the sample is pained with silver epoxy, and backgate voltage is applied to the bottom to control the global chemical potential of graphene. Current flows through the main channel of graphene, with a typical $I = 100 \text{ nA}$. Longitudinal and transverse voltages are measured from the leads shown in Figure 46(b).

1. Charge-neutrality point

The tight binding model determines that the density of state of graphene near the Dirac point is zero [39], as Figure 47 shows. The resistance of graphene would have a maximum

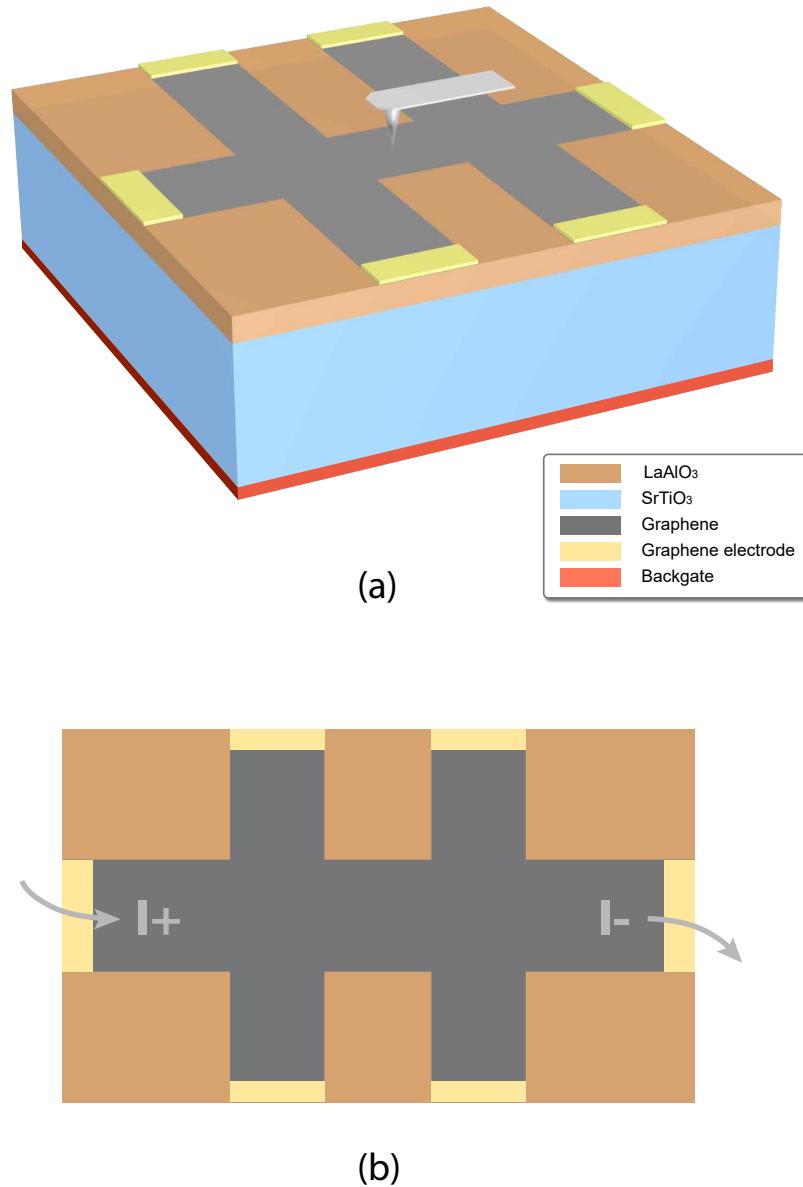


Figure 46: (a) The graphene on LAO/STO is patterned into Hall bar shape. The bottom of the LAO/STO is painted with silver epoxy for applying backgate gate voltages and control the chemical potential of graphene. c-AFM tip is used to shift the local charge neutrality point of graphene. (b) The current flows through the main channel of graphene, while the longitudinal and transverse voltages are measured.

as the Fermi energy gets close to the Dirac point. In Figure 48, the resistance of graphene is measured as a function of the backgate voltage V_{bg} , which is applied to the bottom of the sample. The graphene sample is transferred and patterned on LAO/STO substrate. The thickness of the substrate is 5 mm. At $T = 2$ K, the dielectric constant of STO $\epsilon_r \sim 20,000$, as discussed in previous chapters. Therefore, the gate voltage applied to the bottom of STO can still effectively tune the chemical potential of graphene on top surface. When the chemical potential reaches the Dirac point, a maximum of resistance can be observed. Away from the Dirac point the resistance would decrease, due to the increase of density of state.

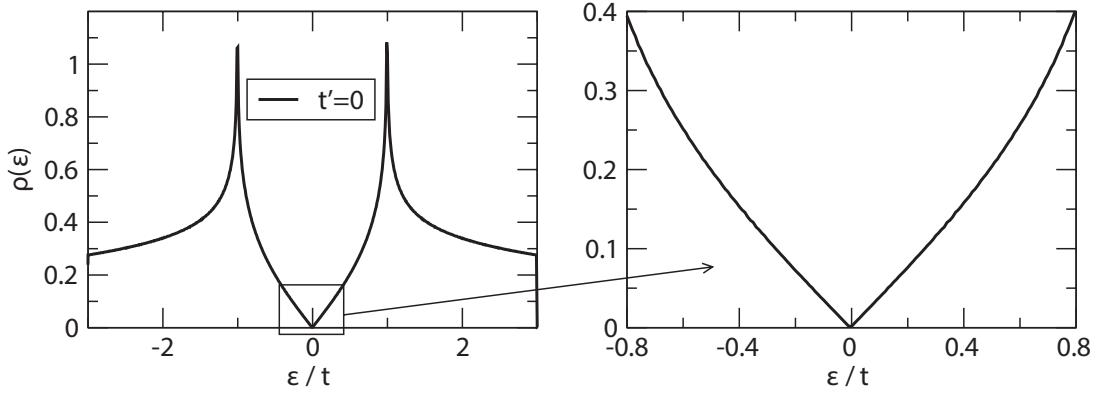


Figure 47: The density of state of graphene near the Dirac point, assuming the hopping energy between the second nearest neighbor t' is zero. ϵ is the Fermi energy, t is the hopping energy in the tight binding model. Adapted from [39].

The effect of STO dielectric constant change as the temperature changes is critical for graphene devices on LAO/STO, as discussed in literatures [65]. Figure 49 demonstrates the change of resistance as a function of V_{bg} . As the temperature drops, the dielectric constant of STO increase from 300 to 20,000, about two order of magnitude. Therefore the effective gating range under the same backgate sweeping range (-15 V to $+15$ V in this figure) also drastically increases. Therefore, at low temperature ($T < 10$ K) gating through 1 mm of STO is still effective.

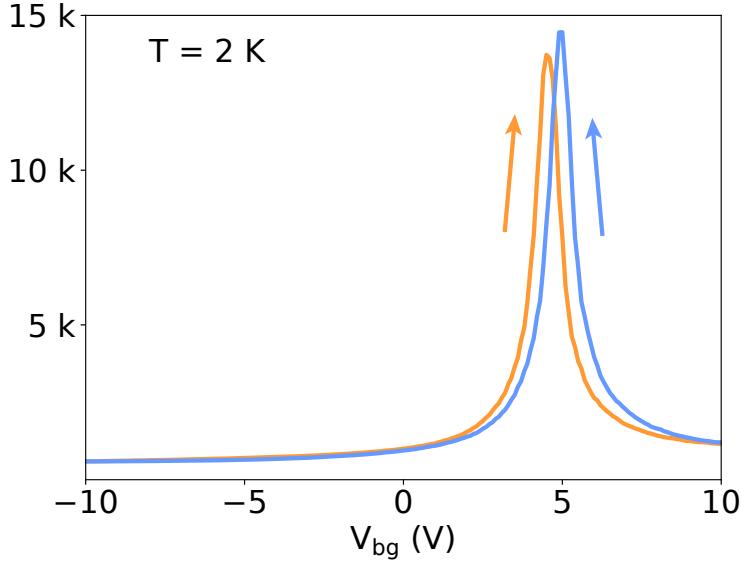


Figure 48: Graphene resistance as a function of backgate voltage. The resistance shows a maximum when the chemical potential reaches the CNP. The positions of the CNP are different for forward and backward sweeps. The arrows indicate the directions of sweeping. Measured at $T = 2$ K.

Another effect of LAO/STO substrate is the hysteresis behavior under backgate sweeping. The position of CNP on V_{bg} shifts after each backgate voltage sweep. Although STO is not ferroelectric material, the dipole moment induced by displacement of oxygen atoms would result in ferroelectric-like hysteresis behavior [66]. Similar hysteresis behavior has been reported elsewhere [67]. The position of CNP has been a widely used indication for the quality of graphene on other substrates like SiO_2 or hBN. Graphene doping level is directly related to the contaminant on substrates as dopant, and therefore high quality graphene on these substrates have CNP very close to $V_{bg} = 0$ V. For graphene on LAO/STO however, the position of CNP is usually at the positive side, even when the quality of graphene is comparable or better than those on SiO_2 substrates.

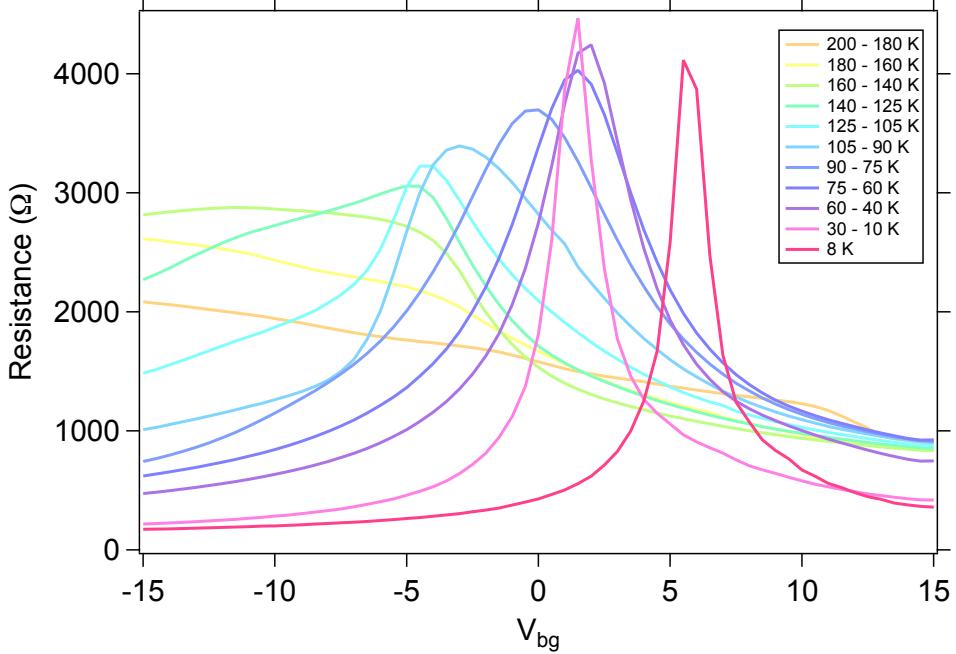


Figure 49: Resistance as a function of V_{bg} sweep at different temperatures. The width of the CNP clearly shows the change of dielectric constant of STO as a function of temperature.

2. Carrier densities and mobilities

The carrier density and mobility of graphene can be measured from Hall effect, using equation I.7. From Figure 50 it can be seen that the high dielectric constant of STO at low temperature enables graphene gating to up to $1 \times 10^{13} \text{ cm}^{-2}$ on the hole side (not shown in the Figure). On the electron side, due to the 2DEG electron gas induced by the high backgate voltage, the gating effect on graphene is shielded, and the carrier density usually saturates at about $n = 1 \times 10^{12} \text{ cm}^{-2}$. Close to the CNP the carrier density and mobility are not well defined due to the existence of electron-hole puddles. Although it was believed that the high dielectric constant of STO can shield off the scattering effect charge impurity and improve the graphene mobility, the existence of surface dipole reduces the shielding effect [66]. In spite of this, the Hyflon transfer method followed by contact AFM cleaning leaves the graphene on LAO/STO with high quality. The mobility of graphene reach 30,000

$\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, higher than most of the graphene on SiO_2 substrates.

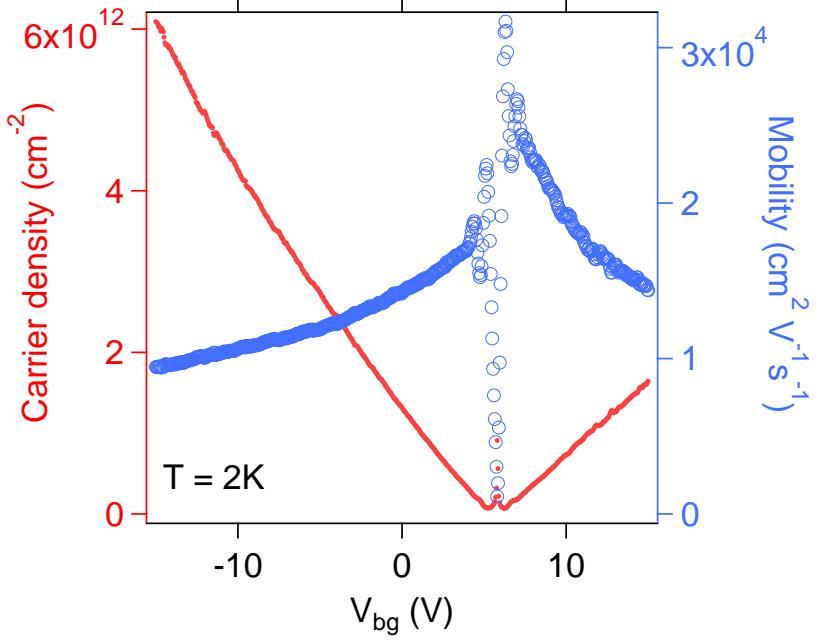


Figure 50: Carrier density and mobility of graphene measured from Hall effect. The high dielectric constant makes it possible for the backgate to tune the graphene to a high carrier density on the hole side. However, the tuning effect saturate on the electron side due to the shielding of 2DEG induced on the interface. The carrier density is not well defined close to the CNP, due to the existence of electron-hole puddles. The quality of graphene is higher than most of the CVD graphene transferred on SiO_2 , and the mobility can reach $30,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.

3. Quantum Hall effect

As discussed in Section I.C.2.b, single layer graphene has unique half integer filling factor with degeneracy $N = 4$ from spin and valley pseudo-spin. The Hall conductance is

$$\sigma_{xy} = \pm 4 \left(n + \frac{1}{2} \right) \frac{e^2}{h}.$$

in quantum Hall regime. The longitudinal resistance is suppressed except when the Fermi energy is transiting between Landau levels, and the localized states start to be filled. Figure 51 demonstrate the longitudinal and transverse resistance of graphene device in a magnetic field of $B = 5$ T. The blue line is the Hall resistance that shows quantum Hall effect plateaus, with the filling factor ν marked by the numbers. The red line is the longitudinal resistance, that shows non-zero resistance at the transition energy between Landau levels.

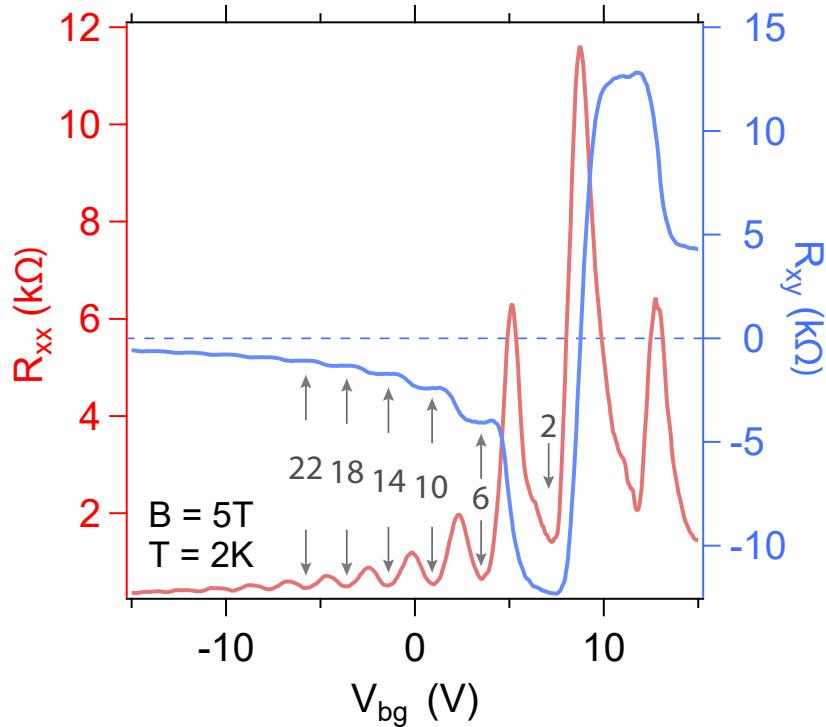


Figure 51: Integer quantum Hall effect of single layer graphene.

B. GRAPHENE P-N JUNCTION EDGE-STATE ENGINEERING

In this section, the experiment of using c-AFM to dope the graphene into p - n junction to reversibly engineer the edge state mixing is discussed.

1. 1D waveguide and quantum Hall edge channels

In semi-classical point of view, the electrons under high magnetic field would cycle in the 2DEG and bounce back from the edges or scattering centers. If the scattering center is far from the edge, the electrons would cycle around the scattering centers and trapped in the localized state. If the scattering centers are close to the edge, the electrons would then collide with the edge and keep moving in the same direction. Therefore, chiral edge channels are formed with back scattering being suppressed. The transport of the edge state in the quantum Hall regime can be quantified with Landauer-Büttiker formalism for 1D waveguides [68, 69].

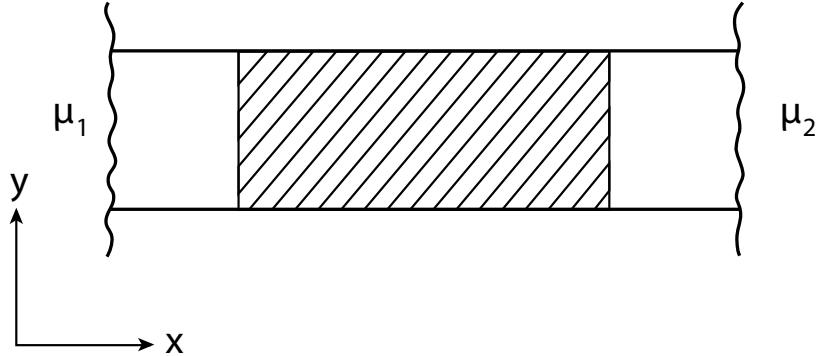


Figure 52: Conductor channel connecting two reservoirs. The chemical potential of the two reservoirs are μ_1 and μ_2 . The shaded region introduces elastic scatterings.

Consider a strip on x - y plane, as shown in Figure 52. The Hamiltonian is

$$H = \frac{1}{2m} (p_x^2 + P_y^2) + V(y)$$

x is along the direction of the strip and y is transverse to the strip. The wavefunction can be separated into the form

$$\psi_{j,k}(x, y) = e^{ikx} f_j(y),$$

k is the wave vector along the x direction, and $f_j(y)$ is the eigenfunction in y direction with energy E_j . The Fermi energy is

$$E_F = E_j + \frac{\hbar^2 k_j^2}{2m}$$

which is the sum of longitudinal and transverse energies, with $2N$ state, where N is the number of transverse energy levels E_j below E_F . μ_1 and μ_2 are the chemical potentials of the two reservoirs, with $\mu_1 > \mu_2$. Only energy between μ_1 and μ_2 contribute to the current flowing from left to right. The current in channel j is

$$I_j = \frac{dn}{dE_j} ev_j \Delta\mu,$$

with

$$v_j = \frac{1}{\hbar} \frac{dE_j}{dk}, \quad \Delta\mu = \mu_1 - \mu_2$$

and v_j being the velocity along channel j . In one dimension, density of state

$$\frac{dn}{dk} = \frac{1}{2\pi},$$

and therefore the current in channel j is

$$I_j = \frac{e}{h} \Delta\mu.$$

The current for all N channels is

$$I = N \frac{e}{h} \Delta\mu.$$

Using the voltage drop $\Delta\mu = eV$ and Ohm's law, the resistance of the conductor with N channels is

$$R = \frac{h}{e^2} \frac{1}{N}$$

which is quantized. Consider there elastic scattering that redistributing energies between the N channels, the resistance becomes [69]

$$R = \frac{h}{e^2} \frac{1}{T}$$

$T = \sum_{i,j=1\dots N} T_{ij}$, and T_{ij} is the transmission probability from channel j into channel i .

2. Edge channel mixing of graphene unipolar/bipolar junction in quantum Hall regime

In the quantum Hall regime, edge channels of graphene can be described by the Landauer-Büttiker formalism. When two adjacent regions of graphene have different carrier density and Landau level filling factors in magnetic field, the numbers or directions of channels will be different which would cause channel mixing. In Figure 53(a), the two adjacent regions have different carrier densities, and therefore the filling factors and number of edge channels for the two regions are different. The edge currents flow in the same direction (unipolar), but part of the current would be reflected into the interface of the two regions. In Figure 53(b), the two regions have opposite carrier types, and the directions of edge currents are the opposite (bipolar). The edge channels would mix on the interface. In both cases, the longitudinal resistance is non-trivial as a result of channel mixing.

For the unipolar case, as shown in Figure 54, assume the current is sourced from the left and $\mu_L > \mu_R$. Filling factors $|\nu_1| > |\nu_2|$ and the currents are flowing clock-wise (same as Figure 53(a)). The chemical potential of the four voltage leads are μ_A, μ_B, μ_C and μ_D . I_1 to I_8 are the currents flowing between the current and voltage leads:

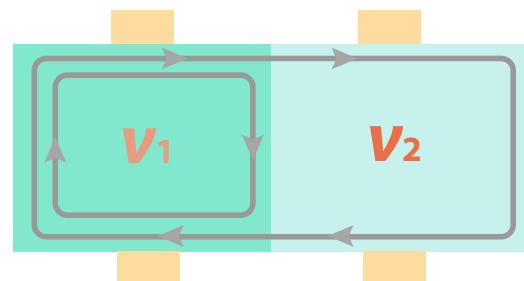
$$\begin{aligned} I_1 &= \frac{e}{h}\mu_L|\nu_1|, & I_2 &= \frac{e}{h}\mu_A|\nu_1|, \\ I_3 &= I_2 - I_M, & I_4 &= \frac{e}{h}\mu_B|\nu_2| \\ I_5 &= \frac{e}{h}\mu_C|\nu_1|, & I_6 &= I_M + I_7 \\ I_7 &= \frac{e}{h}\mu_D|\nu_2|, & I_8 &= \frac{e}{h}\mu_R|\nu_2| \end{aligned} \tag{III.1}$$

The region on the left hand side has more channels, and therefore the excessive current is reflected into the interface and $I_M = \frac{e}{h}\mu_L(|\nu_1| - |\nu_2|)$. The net currents flowing into and out of the four voltages leads are zero, i.e.

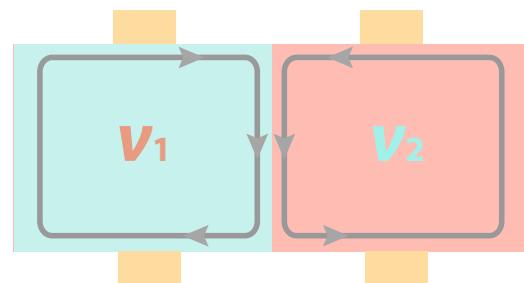
$$I_1 = I_2, \quad I_3 = I_4, \quad I_5 = I_6, \quad I_7 = I_8$$

and therefore the chemical potentials of the four leads are

$$\mu_A = \mu_B = \mu_L, \quad \mu_C = \mu_L + \frac{|\nu_2|}{|\nu_1|}(\mu_L - \mu_R), \quad \mu_D = \mu_R. \tag{III.2}$$



(a)



(b)

Figure 53: (a) Two regions with the same carrier type but the region on the left hand side has more edge channels than the right hand side. The currents are flowing in the same directions but part of the current would be reflected on the interface of the two regions. (b) Two regions with different carrier types. The currents flow in opposite directions in the two regions, and would mix on the interface of the two regions.

From equation III.1 and III.2, the total current from left to right is

$$I = I_1 - I_5 = \frac{e}{h}(\mu_L - \mu_R)|\nu_1|,$$

and the longitudinal resistances are

$$\begin{aligned} R_{AB} &= \frac{\mu_A - \mu_B}{eI} = 0, \\ R_{CD} &= \frac{\mu_C - \mu_D}{eI} = \frac{h}{e^2} \left(\frac{1}{|\nu_2|} - \frac{1}{|\nu_1|} \right). \end{aligned} \quad (\text{III.3})$$

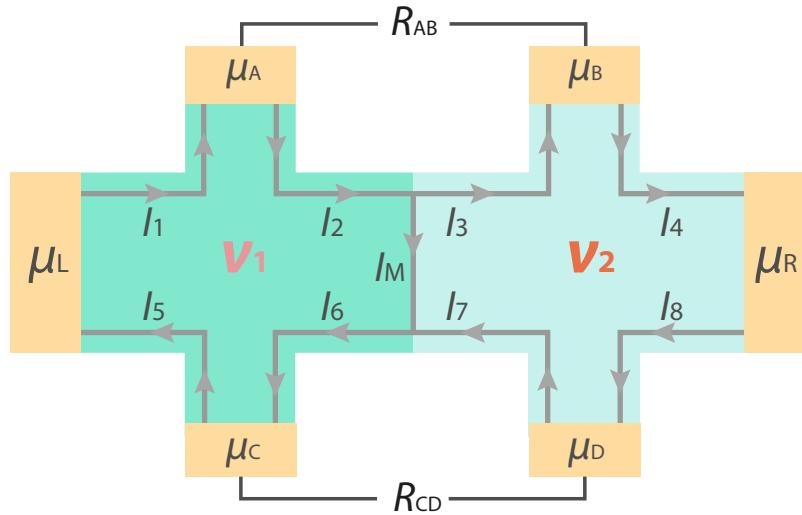


Figure 54: Edge currents of the unipolar junction.

For the bipolar case, as shown in Figure 55, again assume that the chemical potentials $\mu_L > \mu_R$. The two regions have different carrier type and the currents are flowing in the opposite directions. The channels are mixed at the interface, and therefore I_M is equal to

the sum of currents from each side, and then redistributed into edge channels on the bottom. Therefore the edge currents are

$$\begin{aligned}
I_1 &= \frac{e}{h} \mu_L |\nu_1|, & I_2 &= \frac{e}{h} \mu_A |\nu_1|, \\
I_3 &= \frac{e}{h} \mu_B |\nu_2|, & I_4 &= \frac{e}{h} \mu_R |\nu_2| \\
I_5 &= \frac{e}{h} \mu_C |\nu_1|, & I_6 &= \frac{|\nu_1|}{|\nu_1| + |\nu_2|} \cdot I_M \\
I_7 &= \frac{|\nu_2|}{|\nu_1| + |\nu_2|} \cdot I_M, & I_8 &= \frac{e}{h} \mu_D |\nu_2|,
\end{aligned} \tag{III.4}$$

with $I_M = I_2 + I_3$. The net currents flowing into and out of the four voltage leads are zero, i.e.

$$I_1 = I_2, \quad I_3 = I_4, \quad I_5 = I_6, \quad I_7 = I_8$$

and therefore the chemical potentials of the four leads are

$$\mu_A = \mu_L, \quad \mu_B = \mu_R, \quad \mu_C = \mu_D = \frac{\mu_L |\nu_1| + \mu_R |\nu_2|}{|\nu_1| + |\nu_2|}. \tag{III.5}$$

From equation III.4 and III.5, the total current from left to right is

$$I = I_1 - I_5 = \frac{e}{h} \cdot \frac{|\nu_1||\nu_2|}{|\nu_1| + |\nu_2|} \cdot (\mu_L - \mu_R),$$

and the longitudinal resistances are

$$\begin{aligned}
R_{AB} &= \frac{\mu_A - \mu_B}{eI} = \frac{h}{e^2} \left(\frac{1}{|\nu_1|} + \frac{1}{|\nu_2|} \right), \\
R_{CD} &= \frac{\mu_C - \mu_D}{eI} = 0.
\end{aligned} \tag{III.6}$$

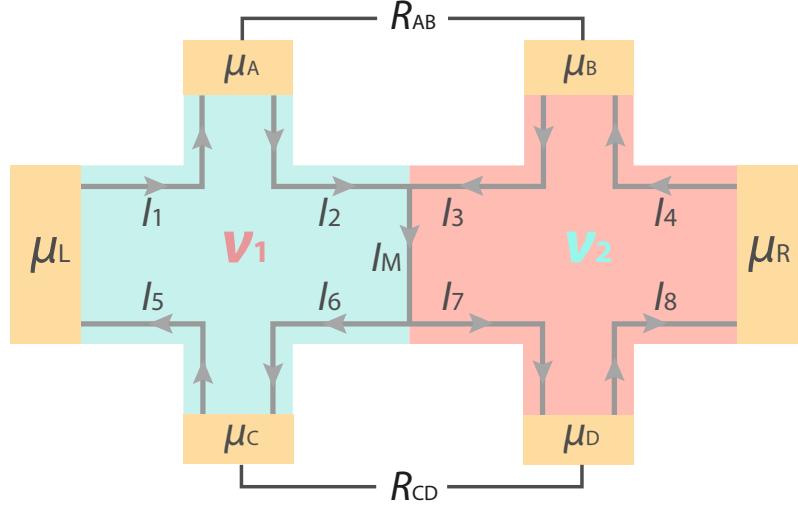


Figure 55: Edge currents of the bipolar junction.

3. Graphene doping using c-AFM

There have been efforts to locally control the CNP of graphene on silicon or hBN substrates using AFM [70] or STM [71]. However, those doping techniques are either non-reversible, or can only be performed in ultra-high vacuum and low temperature, which limits the applications. In this work, we demonstrate how local control over the metal-insulator transition in LAO/STO can be used to reversibly pattern interacting edge channels in a proximal graphene layer under ambient conditions. The CNP of graphene can be locally shifted by c-AFM tip with positive bias voltage. Therefore, c-AFM writing can be used to selectively dope graphene regions and engineer edge state mixing in quantum Hall regime.

4. Measurement of graphene *p-n* junction

C. GRAPHENE BAND STRUCTURE ENGINEERING WITH SUPERLATTICE

IV. MAGNETO-OPTICAL KERR EFFECT ON LAO/STO INTERFACE

A. MAGNETISM ON LAO/STO INTERFACE

B. MFM MEASUREMENT

C. KERR-ROTATION OPTICS SETUP

D. RESULTS

V. OUTLOOK

VI. CONCLUSIONS

BIBLIOGRAPHY

- [1] S Geller and VB Bala. Crystallographic studies of perovskite-like compounds. ii. rare earth alluminates. *Acta crystallographica*, 9(12):1019–1025, 1956.
- [2] Joseph A Sulpizio, Shahal Ilani, Patrick Irvin, and Jeremy Levy. Nanoscale phenomena in oxide heterostructures. *Annual Review of Materials Research*, 44:117–149, 2014.
- [3] K Alex Müller and H Burkard. SrTiO₃: An intrinsic quantum paraelectric below 4 K. *Physical Review B*, 19(7):3593, 1979.
- [4] T Sakudo and H Unoki. Dielectric properties of SrTiO₃ at low temperatures. *Physical review letters*, 26(14):851, 1971.
- [5] A Ohtomo and HY Hwang. A high-mobility electron gas at the LaAlO₃/SrTiO₃ heterointerface. *Nature*, 427(6973):423, 2004.
- [6] Naoyuki Nakagawa, Harold Y Hwang, and David A Muller. Why some interfaces cannot be sharp. *Nature materials*, 5(3):204, 2006.
- [7] Alexey Kalabukhov, Robert Gunnarsson, Johan Börjesson, Eva Olsson, Tord Claeson, and Dag Winkler. Effect of oxygen vacancies in the SrTiO₃ substrate on the electrical properties of the LaAlO₃/ SrTiO₃ interface. *Physical Review B*, 75(12):121404, 2007.
- [8] PR Willmott, SA Pauli, R Herger, CM Schlepütz, D Martoccia, BD Patterson, B Delley, R Clarke, D Kumah, C Cionca, et al. Structural basis for the conducting interface between LaAlO₃ and SrTiO₃. *Physical Review Letters*, 99(15):155502, 2007.
- [9] H Lee, N Campbell, J Lee, TJ Asel, TR Paudel, H Zhou, JW Lee, B Noesges, J Seo, B Park, et al. Direct observation of a two-dimensional hole gas at oxide interfaces. *Nature materials*, 17(3):231, 2018.
- [10] JF Schooley, WR Hosler, E Ambler, JH Becker, Marvin L Cohen, and CS Koonce. Dependence of the superconducting transition temperature on carrier concentration in semiconducting SrTi O₃. *Physical Review Letters*, 14(9):305, 1965.
- [11] Stefan Thiel, German Hammerl, A Schmehl, CW Schneider, and Jochen Mannhart. Tunable quasi-two-dimensional electron gases in oxide heterostructures. *Science*, 313(5795):1942–1945, 2006.

- [12] Cheng Cen, S Thiel, G Hammerl, CW Schneider, KE Andersen, CS Hellberg, J Mannhart, and J Levy. Nanoscale control of an interfacial metal–insulator transition at room temperature. *Nature materials*, 7(4):298, 2008.
- [13] Feng Bi, Daniela F Bogorin, Cheng Cen, Chung Wung Bark, Jae-Wan Park, Chang-Beom Eom, and Jeremy Levy. “water-cycle” mechanism for writing and erasing nanostructures at the LaAlO₃/SrTiO₃ interface. *Applied Physics Letters*, 97(17):173110, 2010.
- [14] JF Schooley, WR Hosler, and Marvin L Cohen. Superconductivity in semiconducting srtio₃. *Physical Review Letters*, 12(17):474, 1964.
- [15] Nicolas Reyren, S Thiel, AD Caviglia, L Fitting Kourkoutis, German Hammerl, Christoph Richter, CW Schneider, Thilo Kopp, A-S Rüetschi, Didier Jaccard, et al. Superconducting interfaces between insulating oxides. *Science*, 317(5842):1196–1199, 2007.
- [16] Guanglei Cheng, Michelle Tomczyk, Shicheng Lu, Joshua P Veazey, Mengchen Huang, Patrick Irvin, Sangwoo Ryu, Hyungwoo Lee, Chang-Beom Eom, C Stephen Hellberg, et al. Electron pairing without superconductivity. *Nature*, 521(7551):196, 2015.
- [17] Alexander Brinkman, Mark Huijben, M Van Zalk, J Huijben, U Zeitler, JC Maan, Wilfred Gerard van der Wiel, GJHM Rijnders, David HA Blank, and H Hilgenkamp. Magnetic effects at the interface between non-magnetic oxides. *Nature materials*, 6(7):493, 2007.
- [18] Lu Li, Christoph Richter, Jochen Mannhart, and RC Ashoori. Coexistence of magnetic order and two-dimensional superconductivity at LaAlO₃/SrTiO₃ interfaces. *Nature physics*, 7(10):762, 2011.
- [19] Julie A Bert, Beena Kalisky, Christopher Bell, Minu Kim, Yasuyuki Hikita, Harold Y Hwang, and Kathryn A Moler. Direct imaging of the coexistence of ferromagnetism and superconductivity at the LaAlO₃/SrTiO₃ interface. *Nature physics*, 7(10):767, 2011.
- [20] J-S Lee, YW Xie, HK Sato, C Bell, Y Hikita, HY Hwang, and C-C Kao. Titanium d_{xy} ferromagnetism at the LaAlO₃/SrTiO₃ interface. *Nature materials*, 12(8):703, 2013.
- [21] Feng Bi, Mengchen Huang, Sangwoo Ryu, Hyungwoo Lee, Chung-Wung Bark, Chang-Beom Eom, Patrick Irvin, and Jeremy Levy. Room-temperature electronically-controlled ferromagnetism at the LaAlO₃/SrTiO₃ interface. *Nature communications*, 5:5019, 2014.
- [22] Kostya S Novoselov, Andre K Geim, Sergei V Morozov, DA Jiang, Y_ Zhang, Sergey V Dubonos, Irina V Grigorieva, and Alexandr A Firsov. Electric field effect in atomically thin carbon films. *science*, 306(5696):666–669, 2004.
- [23] Mark Wilson. Electrons in atomically thin carbon sheets behave like massless particles. *Physics Today*, 59(1):21, 2006.

- [24] Pierre E Allain and Jean-Noel Fuchs. Klein tunneling in graphene: optics with massless electrons. *The European Physical Journal B*, 83(3):301, 2011.
- [25] MI Katsnelson, KS Novoselov, and AK Geim. Chiral tunnelling and the klein paradox in graphene. *Nature Physics*, 2(9):620, 2006.
- [26] Andrea F Young and Philip Kim. Quantum interference and Klein tunnelling in graphene heterojunctions. *Nature Physics*, 5(3):222, 2009.
- [27] Andrei V Shytov, Mark S Rudner, and Leonid S Levitov. Klein backscattering and Fabry-Pérot interference in graphene heterojunctions. *Physical Review Letters*, 101(15):156804, 2008.
- [28] JR Williams, L DiCarlo, and CM Marcus. Quantum Hall effect in a gate-controlled pn junction of graphene. *Science*, 317(5838):638–641, 2007.
- [29] DA Abanin and LS Levitov. Quantized transport in graphene pn junctions in a magnetic field. *Science*, 317(5838):641–643, 2007.
- [30] Timm Lohmann, Klaus von Klitzing, and Jurgen H Smet. Four-terminal magneto-transport in graphene pn junctions created by spatially selective doping. *Nano letters*, 9(5):1973–1979, 2009.
- [31] F Amet, JR Williams, K Watanabe, T Taniguchi, and D Goldhaber-Gordon. Selective equilibration of spin-polarized quantum hall edge states in graphene. *Physical Review Letters*, 112(19):196601, 2014.
- [32] Christopher Gutiérrez, Daniel Walkup, Fereshte Ghahari, Cyprian Lewandowski, Joaquin F Rodriguez-Nieva, Kenji Watanabe, Takashi Taniguchi, Leonid S Levitov, Nikolai B Zhitenev, and Joseph A Stroscio. Interaction-driven quantum hall wedding cake-like structures in graphene quantum dots. *Science*, 361(6404):789–794, 2018.
- [33] Cory R Dean, L Wang, P Maher, C Forsythe, Fereshte Ghahari, Y Gao, Jyoti Katoch, M Ishigami, P Moon, M Koshino, et al. Hofstadters butterfly and the fractal quantum hall effect in moiré superlattices. *Nature*, 497(7451):598, 2013.
- [34] B Hunt, JD Sanchez-Yamagishi, AF Young, M Yankowitz, Brian J LeRoy, K Watanabe, T Taniguchi, Pilkyung Moon, M Koshino, P Jarillo-Herrero, et al. Massive dirac fermions and Hofstadter butterfly in a van der Waals heterostructure. *Science*, page 1237240, 2013.
- [35] Yuan Cao, Valla Fatemi, Ahmet Demir, Shiang Fang, Spencer L Tomarken, Jason Y Luo, Javier D Sanchez-Yamagishi, Kenji Watanabe, Takashi Taniguchi, Efthimios Kaxiras, et al. Correlated insulator behaviour at half-filling in magic-angle graphene superlattices. *Nature*, 556(7699):80, 2018.

- [36] Yuan Cao, Valla Fatemi, Shiang Fang, Kenji Watanabe, Takashi Taniguchi, Efthimios Kaxiras, and Pablo Jarillo-Herrero. Unconventional superconductivity in magic-angle graphene superlattices. *Nature*, 556(7699):43, 2018.
- [37] Carlos Forsythe, Xiaodong Zhou, Kenji Watanabe, Takashi Taniguchi, Abhay Pasupathy, Pilkyung Moon, Mikito Koshino, Philip Kim, and Cory R Dean. Band structure engineering of 2d materials using patterned dielectric superlattices. *Nature nanotechnology*, page 1, 2018.
- [38] Philip Richard Wallace. The band theory of graphite. *Physical Review*, 71(9):622, 1947.
- [39] AH Castro Neto, Francisco Guinea, Nuno MR Peres, Kostya S Novoselov, and Andre K Geim. The electronic properties of graphene. *Reviews of modern physics*, 81(1):109, 2009.
- [40] Kostya S Novoselov, Andre K Geim, SVb Morozov, Da Jiang, MIc Katsnelson, IVa Grigorieva, SVb Dubonos, Firsov, and AA. Two-dimensional gas of massless Dirac fermions in graphene. *nature*, 438(7065):197, 2005.
- [41] Yuanbo Zhang, Yan-Wen Tan, Horst L Stormer, and Philip Kim. Experimental observation of the quantum Hall effect and Berry's phase in graphene. *nature*, 438(7065):201, 2005.
- [42] JP Podkaminer, JJ Patzner, BA Davidson, and CB Eom. Real-time and in situ monitoring of sputter deposition with rheed for atomic layer controlled growth. *APL Materials*, 4(8):086111, 2016.
- [43] Sukang Bae, Hyeongkeun Kim, Youngbin Lee, Xiangfan Xu, Jae-Sung Park, Yi Zheng, Jayakumar Balakrishnan, Tian Lei, Hye Ri Kim, Young Il Song, Young-Jin Kim, Kwang S. Kim, Barbaros Özyilmaz, Jong-Hyun Ahn, Byung Hee Hong, and Sumio Iijima. Roll-to-roll production of 30-inch graphene films for transparent electrodes. *Nature Nanotechnology*, 5:574 – 578, 06 2010.
- [44] Gyula Eres, Murari Regmi, Christopher M Rouleau, Jihua Chen, Ilia N Ivanov, Alexander A Puretzky, and David B Geohegan. Cooperative island growth of large-area single-crystal graphene on copper using chemical vapor deposition. *ACS nano*, 8(6):5657–5669, 2014.
- [45] Shonali Dhingra, Jen-Feng Hsu, Ivan Vlassiouk, and Brian DURso. Chemical vapor deposition of graphene on large-domain ultra-flat copper. *Carbon*, 69:188–193, 2014.
- [46] Dae Woo Kim, Yun Ho Kim, Hyeon Su Jeong, and Hee-Tae Jung. Direct visualization of large-area graphene domains and boundaries by optical birefringency. *Nature nanotechnology*, 7(1):29, 2012.
- [47] Hong Wang, Guanzhong Wang, Pengfei Bao, Shaolin Yang, Wei Zhu, Xing Xie, and Wen-Jun Zhang. Controllable synthesis of submillimeter single-crystal monolayer

- graphene domains on copper foils by suppressing nucleation. *Journal of the American Chemical Society*, 134(8):3627–3630, 2012.
- [48] Joseph M Wofford, Shu Nie, Kevin F McCarty, Norman C Bartelt, and Oscar D Dubon. Graphene islands on Cu foils: the interplay between shape, orientation, and defects. *Nano letters*, 10(12):4890–4896, 2010.
- [49] Ivan Vlassiouk, Pasquale Fulvio, Harry Meyer, Nick Lavrik, Sheng Dai, Panos Datskos, and Sergei Smirnov. Large scale atmospheric pressure chemical vapor deposition of graphene. *Carbon*, 54:58–67, 2013.
- [50] Shonali Dhingra. *Quadratic coupling between a classical nanomechanical oscillator and a single spin*. PhD thesis, University of Pittsburgh, 2015.
- [51] U Hartmann. Magnetic force microscopy. *Annual review of materials science*, 29(1):53–87, 1999.
- [52] C. R. Dean, A. F. Young, I. Meric, C. Lee, L. Wang, S. Sorgenfrei, K. Watanabe, T. Taniguchi, P. Kim, K. L. Shepard, and J. Hone. Boron nitride substrates for high-quality graphene electronics. *Nature Nanotechnology*, 5:722 EP –, 08 2010.
- [53] K. S. Novoselov, A. Mishchenko, A. Carvalho, and A. H. Castro Neto. 2d materials and van der waals heterostructures. *Science*, 353(6298), 2016.
- [54] Xuesong Li, Yanwu Zhu, Weiwei Cai, Mark Borysiak, Boyang Han, David Chen, Richard D Piner, Luigi Colombo, and Rodney S Ruoff. Transfer of large-area graphene films for high-performance transparent conductive electrodes. *Nano letters*, 9(12):4359–4363, 2009.
- [55] Alfonso Reina, Hyungbin Son, Liying Jiao, Ben Fan, Mildred S Dresselhaus, ZhongFan Liu, and Jing Kong. Transferring and identification of single-and few-layer graphene on arbitrary substrates. *The Journal of Physical Chemistry C*, 112(46):17741–17744, 2008.
- [56] Alfonso Reina, Xiaoting Jia, John Ho, Daniel Nezich, Hyungbin Son, Vladimir Bulovic, Mildred S Dresselhaus, and Jing Kong. Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition. *Nano letters*, 9(1):30–35, 2008.
- [57] A Pirkle, J Chan, A Venugopal, D Hinojos, CW Magnuson, S McDonnell, L Colombo, EM Vogel, RS Ruoff, and RM Wallace. The effect of chemical residues on the physical and electrical properties of chemical vapor deposited graphene transferred to SiO₂. *Applied Physics Letters*, 99(12):122108, 2011.
- [58] Yung-Chang Lin, Chun-Chieh Lu, Chao-Huei Yeh, Chuanhong Jin, Kazu Suenaga, and Po-Wen Chiu. Graphene annealing: how clean can it be? *Nano letters*, 12(1):414–419, 2011.
- [59] Zengguang Cheng, Qiaoyu Zhou, Chenxuan Wang, Qiang Li, Chen Wang, and Ying Fang. Toward intrinsic graphene surfaces: a systematic study on thermal annealing and

- wet-chemical treatment of SiO₂-supported graphene devices. *Nano letters*, 11(2):767–771, 2011.
- [60] Vincenzo Arcella, Claudio Troglia, and Alessandro Ghielmi. Hyflon ion membranes for fuel cells. *Industrial & engineering chemistry research*, 44(20):7646–7651, 2005.
 - [61] L Merlo, A Ghielmi, L Cirillo, M Gebert, and V Arcella. Membrane electrode assemblies based on HYFLON® ion for an evolving fuel cell technology. *Separation Science and Technology*, 42(13):2891–2908, 2007.
 - [62] Liwei Zhang, So-Ryong Chae, Zachary Hendren, Jin-Soo Park, and Mark R Wiesner. Recent advances in proton exchange membranes for fuel cell applications. *Chemical Engineering Journal*, 204:87–97, 2012.
 - [63] Cecilia Mattevi, Florian Colléaux, HoKwon Kim, Yen-Hung Lin, Kyung T Park, Manish Chhowalla, and Thomas D Anthopoulos. Solution-processable organic dielectrics for graphene electronics. *Nanotechnology*, 23(34):344017, 2012.
 - [64] I Aliaj, A Sambri, V Miseikis, D Stornaiuolo, E di Gennaro, C Coletti, V Pellegrini, F Miletto Granozio, and S Roddaro. Probing charge transfer during metal-insulator transitions in graphene-LaAlO₃/SrTiO₃ systems. *APL Materials*, 6(6):066103, 2018.
 - [65] Nuno J. G. Couto, Benjamin Sacépé, and Alberto F. Morpurgo. Transport through graphene on SrTiO₃. *Phys. Rev. Lett.*, 107:225501, Nov 2011.
 - [66] Raymond Sachs, Zhisheng Lin, and Jing Shi. Ferroelectric-like SrTiO₃ surface dipoles probed by graphene. *Scientific Reports*, 4:3657 EP –, 01 2014.
 - [67] Giriraj Jnawali, Mengchen Huang, Jen-Feng Hsu, Hyungwoo Lee, Jung-Woo Lee, Patrick Irvin, Chang-Beom Eom, Brian D’Urso, and Jeremy Levy. Room-temperature quantum transport signatures in graphene/LaAlO₃/SrTiO₃ heterostructures. *Advanced Materials*, 29(9):1603488, 2017.
 - [68] M Büttiker. Four-terminal phase-coherent conductance. *Physical Review Letters*, 57(14):1761, 1986.
 - [69] Markus Büttiker. Absence of backscattering in the quantum hall effect in multiprobe conductors. *Physical Review B*, 38(14):9375, 1988.
 - [70] H Schmidt, JC Rode, C Belke, D Smirnov, and Rolf J Haug. Mixing of edge states at a bipolar graphene junction. *Physical Review B*, 88(7):075418, 2013.
 - [71] Jairo Velasco Jr, Long Ju, Dillon Wong, Salman Kahn, Juwon Lee, Hsin-Zon Tsai, Chad Germany, Sebastian Wickenburg, Jiong Lu, Takashi Taniguchi, et al. Nanoscale control of rewriteable doping patterns in pristine graphene/boron nitride heterostructures. *Nano letters*, 16(3):1620–1625, 2016.