

**MOLECULAR BEAM EPITAXY GROWTH AND SCANNING
TUNNELING MICROSCOPY STUDY OF CaFe_2As_2 FILMS ON
 SrTiO_3 SUBSTRATE
AND
INVESTIGATION ON THE REPORTED SUPERCONDUCTIVITY
IN INTERCALATED BLACK PHOSPHORUS**

A Dissertation Presented to
the Faculty of the Department of Physics
University of Houston

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

By
Hanming Yuan

May 2019

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Hanming Yuan

Prof. Paul C. W. Chu
Department of Physics and T_CSUH

Prof. Wei-Kan Chu
Department of Physics and T_CSUH

Prof. Zhifeng Ren
Department of Physics and T_CSUH

Prof. Chin-Sen Ting
Department of Physics and T_CSUH

Prof. John C. Wolfe
Department of Electrical and Computer
Engineering and T_CSUH

Dean, College of Natural Sciences and
Mathematics

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Abstract

CaFe₂As₂ (Ca122) has attracted lots of interest recently due to the discovery of the interface-enhanced superconductivity in this system. Although molecular beam epitaxy (MBE) growth of epitaxial thin film of Ca122 was reported, no detailed study of the growth mode and surface reconstructions were conducted *in-situ* during the growth. Therefore, we decided to use our newly purchased MBE – LT-STM combined system to explore this new material system. We have successfully obtained epitaxial CaFe₂As₂ films grown on SrTiO₃ substrate by choosing a Ca : Fe flux ratio of 1 : 1. No impurity peaks were detected from X-ray measurements. The growth mode of Ca122 films was observed to be island like instead of a layer-by-layer growth mode. In addition, a $\sqrt{2} \times \sqrt{2}$ surface reconstruction was observed. Interestingly, by drastically decreasing the Ca : Fe flux ratio, we discovered that the resulting films were epitaxially grown Fe dominated films covered by thin layers of surface reconstructed Ca122 whose quality was significant better than pure Fe grown on SrTiO₃ substrate. The growth mode of the Fe dominated films was quasi-2D film like, whereas the pure Fe on SrTiO₃ had 3D isolated islands growth mode. The surface reconstructed Ca122 was essential in improving the Fe film quality. A model was proposed to explain the discovery.

On a separate work, we decided to conduct a systematic investigation of the reported superconductivity in intercalated black phosphorus (BP) which we questioned. We have reproduced the superconducting transition at 3.8 K in Li- and Na-intercalated BP crystals that consist of minute amounts of free Sn (reduced from the residual non-superconducting Sn compounds by Li or Na) when prepared by the vapor transport

technique but not in BP crystals that are free of Sn when prepared by the high-pressure technique. The superconducting transition takes place at the same temperature as pure Sn and the field effect on the transition is similar to that on Sn. The magnetic anisotropy of the superconducting state in the Li- and Na-intercalated BP is rather small. We have therefore concluded that the superconducting transition reported by Zhang *et al.* is associated with the Sn but not intrinsic to the intercalated BP.

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Chapter 1 Molecular Beam Epitaxy (MBE) Growth and Low Temperature Scanning Tunneling Microscopy (LT-STM) Study of CaFe_2As_2 Films on SrTiO_3 Substrate

1.1 Motivation

CaFe_2As_2 can form two distinct phases at ambient pressure. The P1 phase is tetragonal ($c = 11.55 \text{ \AA}$) and paramagnetic at room temperature (RT), and it will convert into a collapsed-tetragonal and non-magnetic phase below 100 K. Whereas the P2 phase is tetragonal ($c = 11.7 \text{ \AA}$) and paramagnetic at RT, and it will convert into orthorhombic and antiferromagnetic phase below 170 K [1, 2]. P1 phase is obtained by quenching the crystal ingot from 850 °C. P2 phase can be obtained through a natural furnace-cool. P1 and P2 phases are interconvertible. P1 (P2) phase can be converted to P2 (P1) phase by 350 °C (850 °C) annealing for more than 24 h, respectively. None of the two pure phases shows superconductivity down to 2 K at ambient pressure. The temperature dependence of resistivity and magnetization of P1 and P2 phase and the conversion conditions are shown in Figure 1.1.

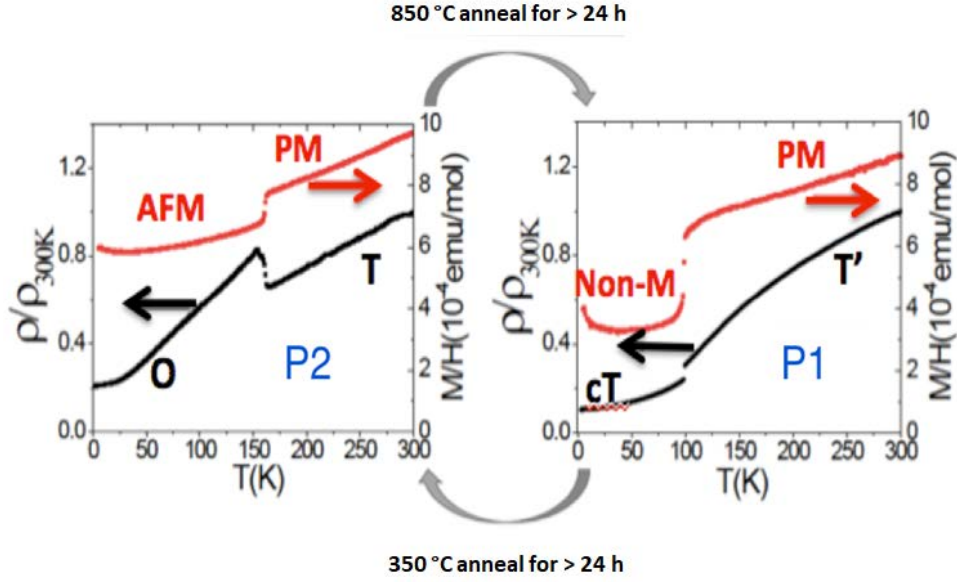


Figure 1.1. The temperature dependence of resistivity and magnetization of CaFe_2As_2 with P1 and P2 phase.

Recent work by Zhao *et al.* [3] has found that by annealing P1 phase at 350 °C for a proper time ($\sim 4 \text{ h} < t < 18 \text{ h}$) where the two phases coexist, superconductivity arises around 25 K. Furthermore, from detailed X-ray diffraction profile analyses, superconductivity is believed to be generated by the mesoscopically stacked layers of the P1 and P2 phases. The deduced interface density correlates well with the superconducting volume measured. Therefore, the discovered superconductivity in undoped CaFe_2As_2 is believed to be interface-enhanced superconductivity, consistent with the recent theoretical prediction of T_c enhancement by antiferromagnetic/metal interfaces [4]. The discovery of the interface-enhanced superconductivity in CaFe_2As_2 has attracted lots of attention.

Since most of the studies were focusing on the three-dimensional (3D) bulk CaFe_2As_2 , we would like to study this material in its two dimensional (2D) state. Although MBE growth of epitaxial thin film of CaFe_2As_2 was reported [5], no detailed investigation

of the growth mechanism and surface reconstructions were conducted *in-situ* during the growth. Therefore, the goal of this work is to use the MBE-STM combined system to systematically study growth mechanism and surface reconstructions of CaFe_2As_2 epitaxial thin films *in-situ*.

1.2 Introduction of MBE and LT-STM System

Molecular Beam Epitaxy (MBE) is a unique technique for growing epitaxial thin films of semiconductors, metals, or insulators. This technique was developed in the late 1960s at Bell Telephone Laboratories by J.R. Arthur and Alfred Y. Cho [6]. In MBE, thin films crystalize through interactions between beams of thermal-energy molecules or atoms and a substrate surface maintained at certain temperature in an ultra-high vacuum environment. The ultra-high vacuum (UHV) together with the precise control of the beam flux makes it possible of producing extreme high-quality thin films with an atomically flat and clean surface. Reflection high energy electron diffraction (RHEED) is the most commonly used technique for MBE *in-situ* characterization of the deposition process. RHEED is sensitive and related to the reciprocal lattice of the surface layers, and information such as surface lattice reconstructions, in-plane lattice constants, and growth mode could be revealed from RHEED images. However, information obtained by RHEED is an average over the surface, local structures such as defects, terrace edges and screw dislocations are hard to study. No lattice constant perpendicular to the substrate plane could be obtained from RHEED. Moreover, real-space models are not uniquely determined

Scanning tunneling microscopy (STM) was invented by G. Binnig and H. Rohrer in 1981 and implemented by G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel [7]. STM is a real-space probe which has been proven to be extremely powerful to reveal surface morphology and electronic properties at the atomic scale. The most significant feature of STM is its local study of the material, ranging from fixed at a specific atom to scanning an area of a few hundreds of nanometers of the material surface.

The combination of MBE and STM under UHV condition, one of the best combinations, can realize unique functions which could not be realized by separate systems. MBE could provide clean and smooth surface of thin films which could be *in-situ* transferred to the STM chamber without any damage of the as-grown surface. The combined STM could provide information on surface morphology, in-plane and out of plane lattice constant of the growth front. This would greatly help the growers to make corresponding modifications of the growth parameters to achieve the best quality of the film. Of course, the combined STM could also reveal the intrinsic electrical properties of the as-grown films at local areas of interest [8, 9].

1.2.1 Theory of MBE System

The schematic drawing of a typical MBE chamber is shown in Figure 1.2. As shown in the figure, source material is loaded in a crucible and is heated up by the filament around the crucible in the effusion cell located at the bottom of the chamber. The higher the effusion cell temperature, the more the material evaporates out. Turbo molecular pump and/or ion pump are used to pump the chamber to UHV. During the growth, cryo panel is usually filled with liquid nitrogen (LN_2) working as an extra cryo pump to further maintain the vacuum of the chamber. The UHV environment guarantees that the evaporated energetic molecules/atoms can form a unidirectional flow with mean free path long enough to reach the substrate without being scattered by the residual gas molecules in the chamber and that minimal residual impurities are incorporated in the growing thin film. All effusion cells are designed to focus to a same point in the center of the chamber where the substrate is located during the growth. The substrate is chosen to have matching crystal structure and lattice constant with the target material. A heating element above the substrate is used to maintain the substrate at an elevated temperature for the incoming molecular beams to crystalize at the substrate surface.

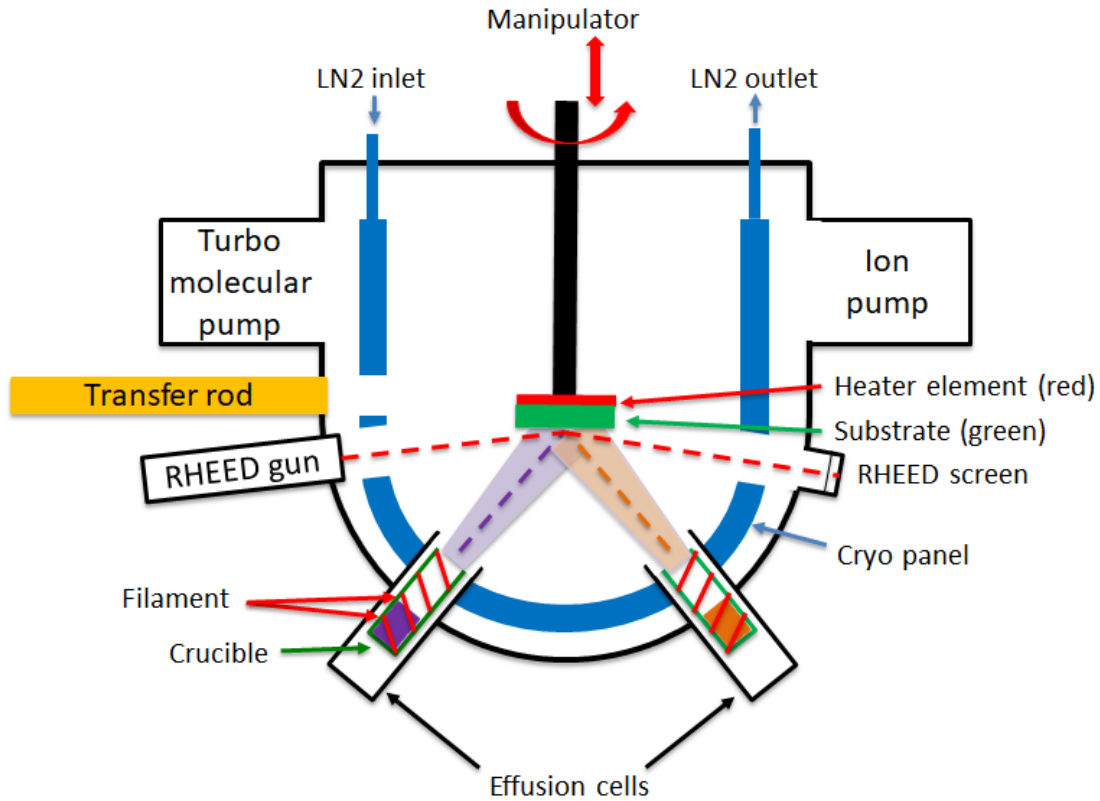


Figure 1.2. Schematic drawing showing the main components of a typical MBE chamber.

To grow the target material with precise stoichiometry, a well-known ‘Three temperature’ rule is often applied. Take epitaxial growth of GaAs as an example. Ga is an element with relatively low vapor pressure (LVP). Ga vapor is composed of single Ga atoms. Its vapor pressure is $\sim 10^{-4}$ Torr at 900 °C. Whereas As is an element with high vapor pressure (HVP) whose beam is mainly composed of As₄ and As₂ molecules. Its VP is already $\sim 10^{-4}$ Torr even at 230 °C. These fundamental properties make it possible to produce absolutely perfect stoichiometric GaAs by applying the ‘three-temperature’ rule: LVP material (Ga) effusion cell temperature > substrate temperature > HVP material (As) effusion cell temperature. In practice, based on the ‘three-temperature’ rule, the Ga effusion cell temperature, the substrate temperature, and the As effusion cell temperature are chosen

to be 800 °C, 600 °C, and 240 °C, respectively. According to the vapor pressure curve of the three elements, As/Ga flux ratio is roughly 15 at the temperatures chosen above. This means that the number of As molecules arriving at the substrate per unit area per unit time is 15 times larger than that of the Ga atoms. If they were to react completely, the stoichiometry would be totally different from the 1:1. However, what is magic is that the substrate temperature (600 °C) is much lower than the Ga (effusion cell) temperature (800 °C). At this substrate temperature, the vapor pressure of Ga is very low, indicating that Ga atoms will all stay (adsorbed) on the substrate surface instead of being desorbed as long as they land on the substrate. On the contrary, the vapor pressure of As at the 600 °C substrate temperature is far higher than atmospheric pressure, indicating that As molecules will immediately desorb from the substrate surface if they do not react with Ga to form GaAs. Therefore, the As rich ‘three-temperature’ rule can guarantee on one hand that all Ga atoms will react with As to form the thermally stable GaAs phase and thus no Ga cluster or droplet will form. On the other hand, it also guarantees that the redundant (unreacted) As can all desorb from the surface and thus form the perfect 1:1 stoichiometric GaAs.

The real time monitoring of MBE growth is done by RHEED. As shown in Figure 1.4, the high energy (4-50 keV) electrons emitted from the RHEED electron gun incident onto the substrate (sample surface) at an incident angle less than 4°. It is then reflected by the sample surface and reach the RHEED screen. By analyzing the RHEED diffraction pattern and its intensity, one can accurately know the sample surface flatness, quality of the crystallization, and the crystal structure. The small incident angle guarantees that the electron will travel in the material very far but only in the parallel direction. In other words,

electrons will not penetrate deep into the bulk but only probe the surface layers. RHEED screen is usually a phosphorus screen to pick up electrons that diffract and interfere constructively with each other by atoms from the sample surface. In momentum space (k -space), consider the following case: two atoms are hit by waves with momentum $\mathbf{k}$ and the scattered wave has momentum $\mathbf{k}'$. Laue formulation tells that electrons will have constructive interference if the difference between the scattered wave vector $\mathbf{k}'$ and incident wave vector $\mathbf{k}$ equals one of the reciprocal lattice vectors. Namely, $\mathbf{G} = \mathbf{k}' - \mathbf{k}$, where $\mathbf{G}$ is the reciprocal lattice vector. Assuming the scattering process is elastic where no energy transfer is allowed from the electrons to the sample, all the scattered wave vectors $\mathbf{k}'$ lie on the surface of a sphere of constant energy with radius being equal to the length of the incident wave vector $\mathbf{k}$, the so-called Ewald sphere. By constructing and placing an Ewald sphere in the reciprocal lattice of the sample, one can easily figure out under what circumstances the constructive interference will happen. Figure 1.3 shows the relationship between the Ewald sphere and the reciprocal lattice. Each dot in Figure 1.3 represents a reciprocal lattice point. In Figure 1.3 (a), the radius of the Ewald sphere is so small that it is impossible for any $\mathbf{k}' - \mathbf{k}$ to be equal to $\mathbf{G}$. According to de Broglie, a beam of particles with mass m and moment $\mathbf{p}$ possess undulatory properties characterized by a wavelength

$$\lambda = \frac{h}{p}, \quad (1)$$

where h is the Planck's constant. The energy of particles is

$$E = \frac{p^2}{2m}. \quad (2)$$

Insert Equation (2) into (1), one can obtain

$$\lambda = \frac{h}{\sqrt{2mE}}. \quad (3)$$

Note that

$$k = \frac{2\pi}{\lambda}. \quad (4)$$

Inserting Equation (3) into (4), one obtains the magnitude of the wave vector $\mathbf{k}$ is

$$k = \frac{2\pi\sqrt{2mE}}{h}. \quad (5)$$

One can see from Equation (5) that the magnitude of wave vector $\mathbf{k}$ is proportional to the square root of the energy E of the beam. Note that k is the radius of the Ewald sphere. Therefore, the higher the energy of the electron beam, the larger the radius of the Ewald sphere. To avoid the problem demonstrated in Figure 1.3 (a), RHEED measurements use high energy electron beams (4 - 50 keV) to make sure the Ewald sphere is large enough.

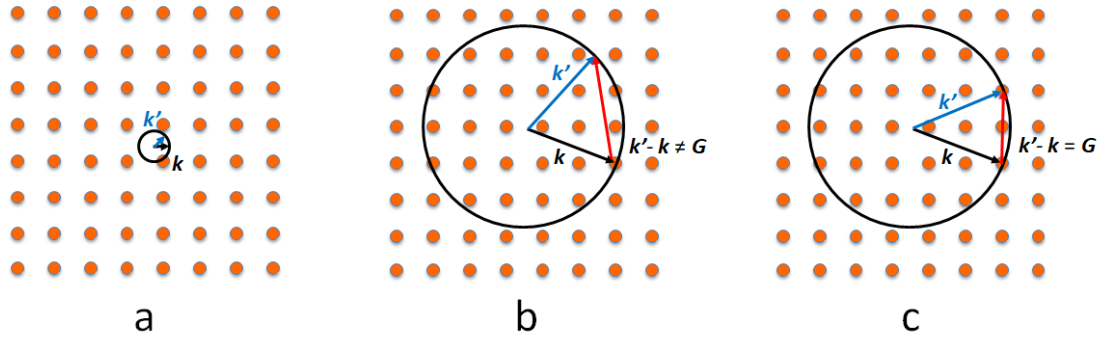


Figure 1.3. Schematic drawing of Ewald sphere in reciprocal lattice (top view). (a) Radius of Ewald sphere (energy of the incident electron beam) is too small such that no difference vector $\mathbf{k}' - \mathbf{k}$ would equal to any of the reciprocal lattice vector $\mathbf{G}$. (b) The radius of Ewald sphere is large enough, but difference vector of the chosen $\mathbf{k}$ and $\mathbf{k}'$ does not equal any $\mathbf{G}$, thus will not generate a bright spot on RHEED screen. (c) The difference vector of the chosen of $\mathbf{k}$ and $\mathbf{k}'$ equals to $\mathbf{G}$, thus will cause a bright spot on the RHEED screen due to constructive interference.

In Figure 1.3 (b), the randomly selected $\mathbf{k}$ and $\mathbf{k}'$ generate a vector $\mathbf{k}' - \mathbf{k}$. However, this particular $\mathbf{k}' - \mathbf{k}$ does not equal to $\mathbf{G}$ in the reciprocal lattice, thus does not form constructive interference. The Ewald sphere drawn in Figure 1.3 (c) has the same radius as that of Figure

1.3 (b). Nevertheless, the $\mathbf{k}$ and $\mathbf{k}'$ chosen in Figure 1.3 (c) generates a difference vector $\mathbf{k}' - \mathbf{k}$ which is exactly equal to $\mathbf{G}$, thus they generate a constructive interference bright spot on the RHEED screen. Recall that RHEED only interacts with a few layers of the thin film sample due to the small incident angle. This implies that RHEED essentially sees a two-dimensional lattice in real space with zero height. In other words, the distance between atoms in the perpendicular direction is zero. Recall that the real space lattice constant $\mathbf{a}$ and the corresponding reciprocal lattice constant $\mathbf{b}$ have the following relationship:

$$\mathbf{a} \cdot \mathbf{b} = 2\pi. \quad (6)$$

From equation (6), one can easily conclude that the zero vertical lattice constant that RHEED sees in real space will correspond to an infinite long vertical lattice constant in reciprocal lattice space (k -space). Therefore, in reciprocal space, the two-dimensional array of the surface atoms turns into vertical lines, the reciprocal rods, as shown in Figure 1.4. Based on the previous analysis, it can be concluded that wherever these reciprocal rods cross the Ewald sphere, the condition for constructive interference of elastically scattered electron beams from the epitaxial film surface is satisfied. Each crossing will have a corresponding bright spot shown on the RHEED screen, as illustrate in Figure 1.4. It is straight forward to observe that the spatial separation between spots/streaks on RHEED screen is proportional to the *reciprocal lattice* constant in the direction *perpendicular* to the incident beam.

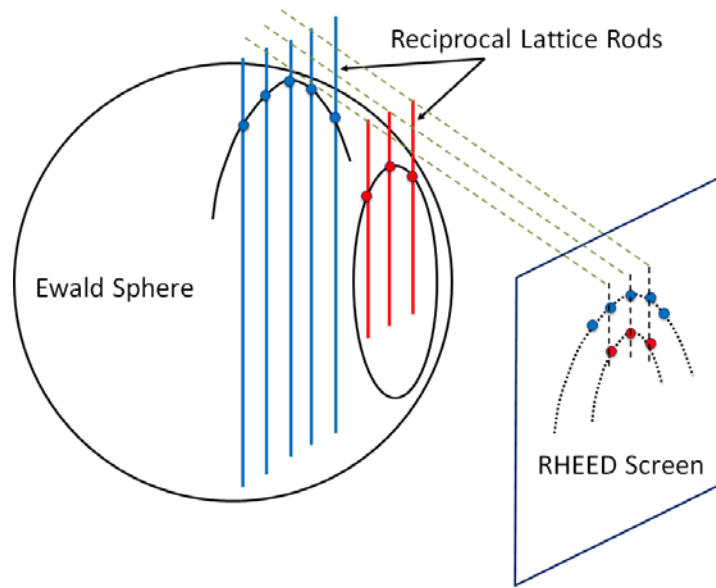


Figure 1.4. 3D schematic diagram showing the reciprocal rods crossing the Ewald sphere and the corresponding constructive interference spots on RHEED screen.

Figure 1.5 shows the well-known RHEED intensity oscillation during the formation of a complete flat monolayer of the target material on the substrate. Assuming the substrate surface is atomically flat before the growth, the 0th diffraction streak of RHEED has the highest intensity at the beginning, indicated by the red dot at the peak in Figure 1.5 (a). As the growth take place, islands with monolayer thickness start to form. Since the diffraction from different islands can not interact coherently, the intensity of the diffraction streak will decrease as shown in Figure 1.5 (b). When the total area of the islands is half of the substrate surface area, the intensity will reach the minimum value as shown in Figure 1.5 (c). However, when a complete layer of atoms is formed on the substrate surface, the intensity will reach maximum again as shown in Figure 1.5 (d). This means that the formation of a complete monolayer film correlates to one period in RHEED intensity oscillation [10]. RHEED oscillation could be used to calculate the growth rate with

monolayer accuracy. However, it is worth mentioning that the RHEED periodic intensity oscillation phenomena could only be observed for the case explained above. If the growth mode by nature is step flow mode where the surface is always smooth during the entire growth, or island growth mode where atoms tend to climb higher and higher on islands instead of forming a complete layer, RHEED oscillation would not be observable.

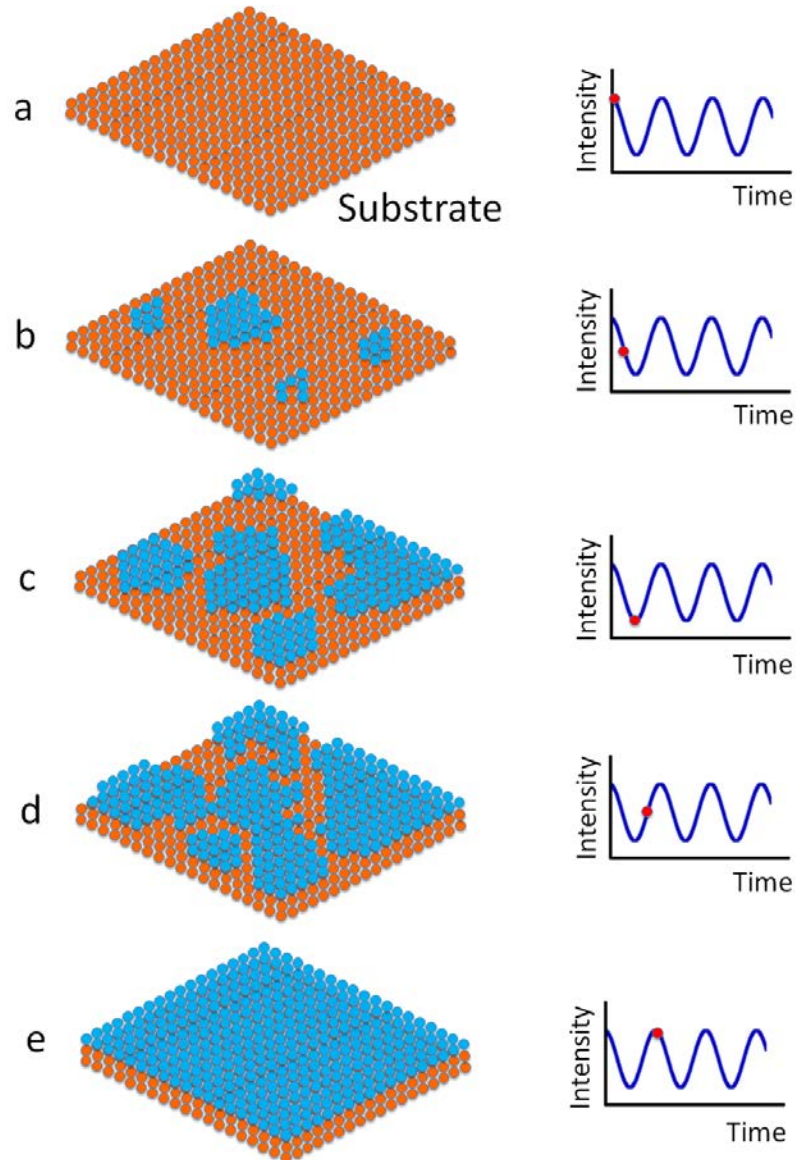


Figure 1.5. Schematic illustration of RHEED intensity oscillation. Dots in orange color represent the substrate with atomic level of flatness. The blue dots represent atoms from the source beam grown on the substrate surface.

1.2.2 Theory of STM System

The schematic drawing of main components of STM scanning head is shown in Figure 1.6. Two sets of piezo electric, coarse movement piezo and fine scanning piezo are used. The coarse piezo system moves the tip to the location of interest and the scanning piezo drives the tip attached to scan a user defined area of the sample surface. When the tip is brought close to the sample surface with a few angstroms of each, the electron wavefunctions in the tip overlap the electron wave functions in the sample surface. By applying a bias voltage (V), an electrical current (I) can flow between the tip and the sample surface even if the two are not physically contacting each other. Such phenomenon is a quantum-mechanical phenomenon called tunneling.

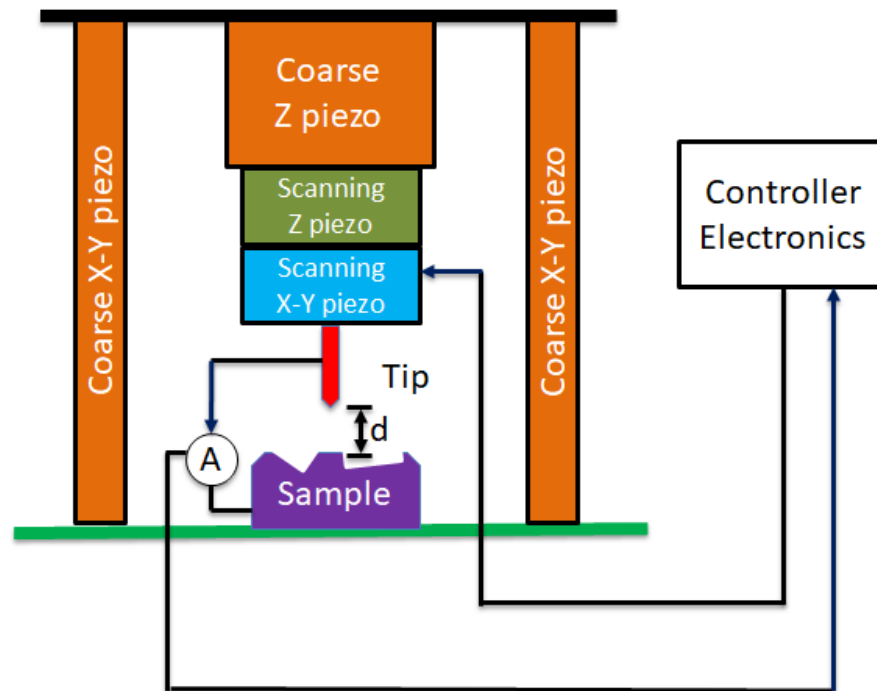


Figure 1.6. Schematic drawing showing the main components of STM scanning head. The distance between tip and sample surface at a specific location is d .

From Schrödinger's equation, it can be derived that the tunneling current between the tip and sample surface upon a biased voltage V is

$$I \propto V \rho_S(0, E_f) e^{-2\kappa d}, \quad (7)$$

where $\rho_S(0, E_f)$ is the local density of states (LDOS) of the sample, d is the distance between tip and sample surface, and κ is the decay constant. Numerical calculation shows that the decay constant κ is $\sim 1 \text{ \AA}^{-1}$, which implies the tunneling current decays about $e^2 \approx 7.4$ times per $\text{\AA}$. In other words, if the distance between the tip and sample surface changes about $1 \text{ \AA}$, the tunneling current will change about one order of magnitude. This is the reason why STM has such a high resolution of the sample surface morphology. Clearly, the vibration isolation system is of critical importance for STM to obtain the atomic resolution image.

To obtain the surface morphology of the sample, constant current mode is most commonly used, as demonstrated in Figure 1.7. In this mode, a bias voltage is applied, and a reference current is set. During the scan, the feedback loop will maintain the tunneling current as a constant at that preset reference value. At the initial position, the tip is at a distance d away from the local surface that makes the tunneling current equals to the preset value, as shown in Figure 1.7 (a). Assuming the scanning is from left to right and the tip moves to the position illustrated in Figure 1.7 (b). As can be seen, since the distance between the tip and the surface is decreased, according the Equation (7), the tunneling current will be increased and thus larger than the reference value. Therefore, the voltage applied to the z piezo will withdraw the tip from the sample surface to maintain the current as the preset value, as illustrated in Figure 1.7 (c). When the tip moves further to the right, the distance between tip and sample surface is increased and thus the tunneling current will

decrease, as illustrated in Figure 1.7 (d). In this case, the voltage applied to the z piezo will approach the tip to the sample surface to maintain the current as the preset value, as illustrated in Figure 1.7 (e). As the tip scans over the xy plane, by tracking the change in position of the tip in z direction, the sample surface morphology can be accurately represented and plotted, as shown in Figure 1.7 (f).

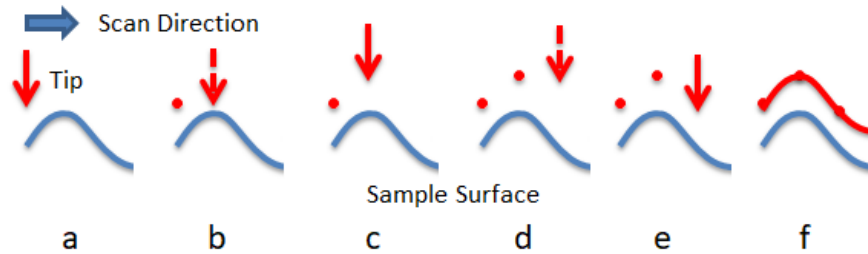


Figure 1.7. Schematic drawing illustrating the STM surface morphology scanning process under constant current mode.

The other scanning mode, constant height mode, maintains the tip at a fixed z position during the entire scan. Since the z position of the tip is fixed, as the tip scans over the xy plane, the distance between the tip and the local surface will change and thus the tunneling current will vary accordingly. By tracking and recording the value of the tunneling current during the scan, the surface morphology could be accurately represented and plotted as well. However, since the z position of the tip is fixed, if the sample has a very rough surface with somewhere being extremely high, the tip could not avoid it and could easily crash onto the local high area of the sample surface. In such case, the tip needs to be treated to be used again. This is the disadvantage of this constant height mode.

Another powerful function of STM is to obtain the spatially resolved scanning tunneling spectroscopy (STS). By considering the Metal (sample)-Insulator (vacuum)-Metal (tip) (MIM) junction, Bardeen (1960) pointed out that the tunneling current of the

MIM junction is:

$$I = \frac{4\pi e}{\hbar} \int_0^{eV} \rho_S(E_F - eV + \varepsilon) \rho_T(E_F + \varepsilon) |M|^2 d\varepsilon, \quad (8)$$

where e , V , ρ_S , ρ_T , and M are the charge of electron, bias voltage, LDOS of sample, LDOS of tip, and tunneling matrix element, respectively. Bardeen further assumed that the magnitude of the tunneling matrix element $|M|$ does not change appreciably in the interval of interest, which could be considered as a constant. Then the tunneling current could be simplified as:

$$I \propto \int_0^{eV} \rho_S(E_F - eV + \varepsilon) \rho_T(E_F + \varepsilon) d\varepsilon. \quad (9)$$

Clearly, according to the Bardeen formula, Equation (9), the tunneling current is determined by the convolution of the LDOS of both sample and tip. In other words, the LDOS of sample ρ_S and the LDOS of tip ρ_T contribute equally in determining the tunneling current. Usually, the goal in an STS measurement is to obtain the DOS of the *sample*. Therefore, this requires a non-superconducting tip with a constant DOS, or a free-electron metal tip. In practice, the tip is usually made of W or Pt-Ir alloy whose DOS ρ_T could be treated as a constant. With such tips, Equation (9) could be further simplified as:

$$I \propto \int_0^{eV} \rho_S(E_F - eV + \varepsilon) d\varepsilon. \quad (10)$$

By taking the derivative of Equation (10) with respect to the bias voltage V , one obtains

$$\frac{dI}{dV} \propto \rho_S(E_F - eV). \quad (11)$$

Thus, with a free-electron metal tip, the derivative of the tunneling current is proportional to the DOS of the sample at bias voltage V . By scanning the entire voltage, one can obtain the relationship of the sample DOS as a function of energy and thus obtain the information of the occupied states and empty states of the sample [11].

1.2.3 Actual MBE – LT-STM Combined System

The schematic drawing of the system, the laboratory floor plan, and the picture of the real system are shown in Figure 1.8, 1.9, and 1.10, respectively.

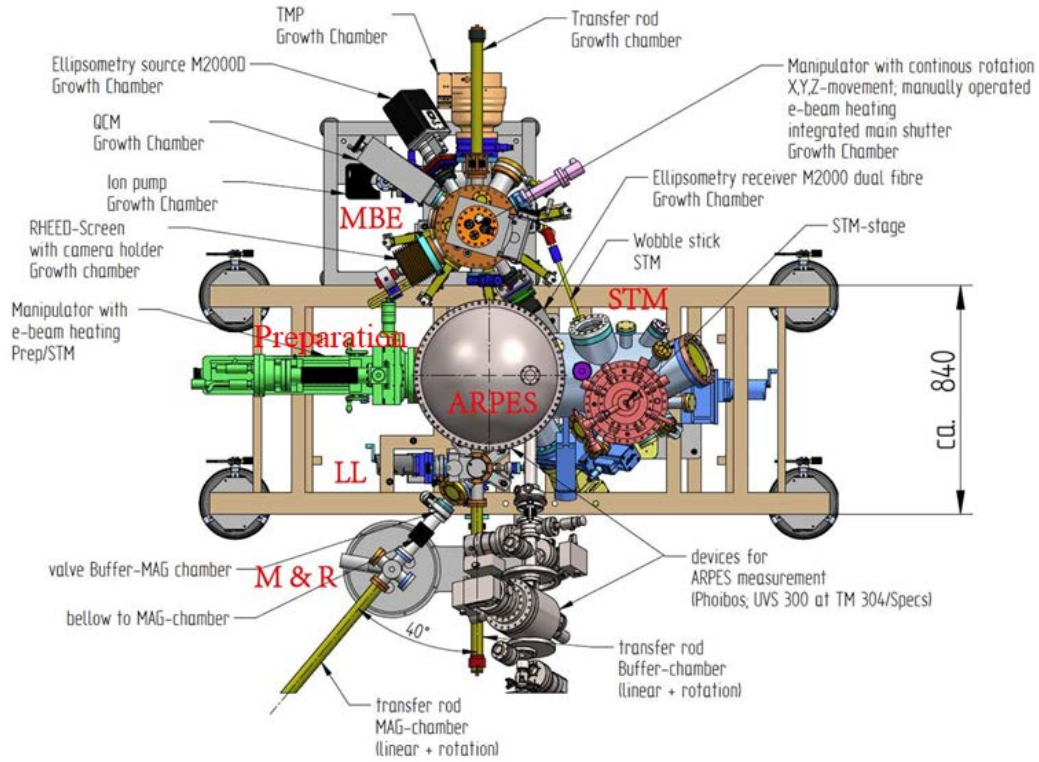


Figure 1.8. Schematic drawing of our combined MBE – LT-STM system from CreaTec company with the main components.

STM scanning is extremely sensitive to noise. To obtain high quality atomic resolution image of samples, several techniques are commonly used, such as internal spring system with Eddy current damping in the scanning unit as well as air dampers to float the system. In addition to these two techniques, to further reduce the vibrations/noise as much as possible, the system was settled in a laboratory with vibration-free pads, as shown in Figure

1.9. Ideally, if the vibration-free pad is not physically coupled to the outside area, the vibrations generated outside the pad will not propagate into the pad. Similarly, vibrations generated inside the pad will not propagate to the areas outside the pad. In University of Houston Science Center room 140 E, where the main system is, there is one vibration-free pad, denoted by the area enclosed in the red dashed rectangle. The MBE – LT-STM system was arranged inside the vibration-free pad, whereas the electronic racks are kept outside the pad. This guarantees that the noise generated by the cooling fans of the electronic racks will not propagate into the pad to affect the scanning. Likewise, a water chiller for providing necessary chilled water to the system and a helium compressor for the superconducting magnet, which can generate significant amount of vibrations, are placed inside a vibration-free pad denoted by the area enclosed in the red dashed rectangle in another room (140 G). In this case, the vibrations generated by the two equipment will stay inside the pad and would not propagate to the outside area to affect the scanning. The table with STM scanning control computers are arranged outside room 140 E so that no one need to stay inside room 140 E during the scan. With all these efforts, noise is significantly reduced.

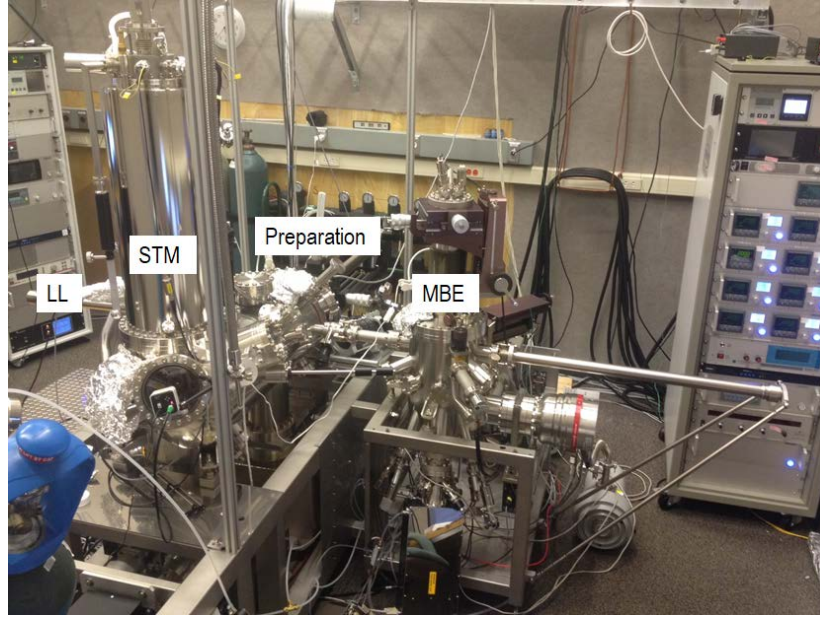


Figure 1.10. Picture of the actual MBE – LT-STM system.

The combined MBE – LT-STM system was purchased from German company CreaTec in 2015. The combined system has four chambers: Load Lock (LL) chamber, Preparation (Prep) chamber, MBE chamber, and STM chamber. All the four chambers are connected in UHV environment. The base pressure of each chamber is shown in Table 1.1. Except the LL chamber, the pressure of all the other three chambers are in the range of 10^{-10} mbar, which guarantees that the sample will not degrade (oxidized) during the transfer between any of the three chambers.

Table 1.1. Pressure of each chamber of the MBE-STM combined system

Chamber	Base Pressure (mbar)	
Load Lock Chamber	2×10^{-8}	
Preparation Chamber	3×10^{-10}	
MBE Chamber	1×10^{-10}	
STM Chamber	LN ₂ Cooling	4×10^{-10}
	LHe Cooling	1×10^{-10}

The specifications of main components in each chamber is summarized in Table 1.2.

Table 1.2. Specifications of main components in each chamber

Chamber	Component		Specification
LL	Heating Lamp		Max. T: 200 °C
	Sample Storage Unit		Max. 4 Sample Holders
Prep	Manipulator	Indirect Heating	Max. T: 1100 °C
		Direct Heating	Max. T: 1200 °C
		LN ₂ Cooling	Min. T: 70 K (Continuous Pumping)
		LHe Cooling	Min. T: 15 K
	Ar Sputtering		1 keV Acceleration Voltage
MBE	Manipulator		Max. T: 1200 °C
	2 × Single Filament Effusion Cell		Max. T: 1400 °C
	2 × High Temperature Effusion Cell		Max. T: 1700 °C
	2 × Valved Cracker Cell		Effusion Zone: Max. T: 500 °C
			Cracking Zone: Max. T: 800 °C
	Electron Beam Evaporator		Max. T: 3000 K for Rod Material
	Oxygen Plasma Cracker Source (SPECS)		Max. Power: 600 W to Generate Atomic Oxygen
	RHEED Gun (Dr. GASSLER)		Electron Energy: 5 – 15 kV
LN ₂ Cryo Panel		Continuous LN ₂ flow	
STM	Cryostat		T Range: 6 – 500 K
	Scanner	Scan Range at LHe	X × Y × Z: 1.2 μm × 1.2 μm × 0.4 μm
		Max. Drift Rate	Z: 0.1 nm/h guaranteed
			XY: 0.2 nm/h guaranteed
	Vibration Isolation		Internal Spring System with
			Eddy Current Damping
			Four Air Dampers (New Port)
Sample Storage Unit		Max. 5 Sample Holders + 4 STM Tips	

The general operation procedure is described as the followings. First, cut the substrates into 2 mm $\times$ 10 mm followed by Acetone, Methanol, and Isopropyl Alcohol cleaning. Afterwards, the substrate is mounted onto a bridge style sample holder as shown in Figure 1.11 (a). Then, load the holder into load LL chamber and start pumping the LL chamber with a diaphragm pump and a turbo molecular pump. A quick degas of the sample holder and substrate by an infrared quartz lamp is then conducted in the LL chamber to quickly remove water from the sample holder. When the pressure in the LL chamber reaches the base pressure, the holder is transferred to the preparation chamber to do indirect heating by a heating filament placed above the holder to further remove water and gases adsorbed on the holder and substrate, as shown in Figure 1.11 (b). Then, direct heating/flashings of the substrate is conducted by passing DC current only through the substrate to treat it to obtain the desired surface reconstruction, as shown in Figure 1.11 (c). Next, the holder is moved to STM chamber for substrate surface morphology scan to check the quality of the treatment and to confirm the desired surface reconstruction, as shown in Figure 1.11 (d). Once confirmed, the substrate is ready for MBE growth. In the MBE chamber, the degas of effusion cells, RHEED filament, and manipulator heater at a temperature slightly higher than the actual growth temperature will be performed before each growth. Once the degas process is finished, the sample holder is then transferred into the MBE manipulator and RHEED is used to confirm the surface reconstructions, as shown in Figure 1.11 (e). Once the substrate temperature is stable, the growth starts. RHEED is used for *in-situ* characterization during the growth. Once the growth is finished, the holder is then transferred into the STM chamber to do the surface characterization including surface scanning and STS dI/dV spectrum to characterize its properties. If needed, the

holder will be transferred back to the MBE chamber to do further growth or post annealing. Sometimes, for an *ex-situ* measurement of the sample, thin layers of Si capping on the samples surface is performed in the preparation chamber under LN₂ temperature, as a protection of those air-sensitive samples preventing them from being oxidized, as shown in Figure 1.11 (f). To reuse a substrate, the substrate is immersed in 25% (v/v) HCl solution and ultrasonicated for 5 min to remove the deposited films.

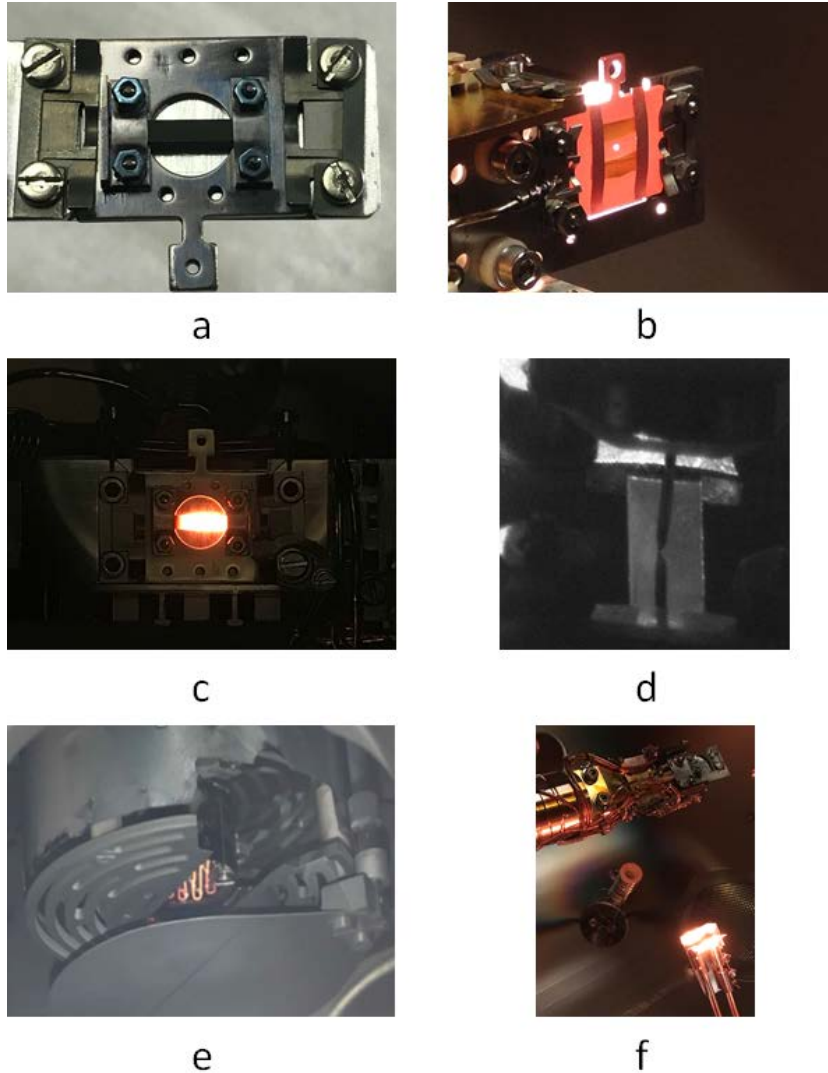


Figure 1.11. (a) A substrate mounted on the bridge style sample holder. (b) Indirect heating of sample holder by a heater mounted behind the sample holder and additional E-beam heating. The temperature of the holder in this picture is ~ 1000 °C. (c) Direct heating of substrate by passing through a DC current. The temperature of the substrate in this picture is ~ 1100 °C while the sample holder stays cool. (d) Picture taken when the STM tip is scanning over the sample surface. (e) MBE manipulator: where the sample holder is inserted during the growth. The manipulator has a heating filament mounted above the holder to heat up the holder/substrate during the growth. (f) Self-made Si capping source. A Si wafer is mounted on an electrical feedthrough inside the Prep chamber and a DC current is passed through the Si wafer. The holder/substrate is kept at LN₂ temperature. The evaporated Si atoms will land on the substrate surface as a protection layer and will have a minimum diffusion into the film since the holder/substrate is kept at LN₂ temperature.

1.3 MBE Growth and LT-STM Characterization of Superconducting Monolayer FeSe Films on SrTiO₃ Substrate as a Test of the System

In 2012, Wang *et al.* reported interface-induced high-temperature superconductivity in single-unit-cell FeSe film grown on a SrTiO₃ (STO) substrate with superconducting transition temperature (T_c) of up to 60 K [12], nearly eight times the T_c of bulk FeSe [13]. The films were grown by MBE and the superconducting property was characterized by STM and transport measurement. The significance of this work in the field of interface-induced superconductivity is self-evident. However, in terms of the growth and characterization, it is very challenging with respect to the following aspects. For growth aspect, first, an atomically flat TiO₂ terminated STO substrate is required. Second, growth of FeSe with precisely only one unit-cell (UC) is required as the second UC is no longer superconducting. From the STM characterization aspect, the noise/vibrations of the system should be extremely low to obtain the atomic resolution image of the film and to obtain the dI/dV spectrum with noticeable gap to confirm its superconducting nature. To some extent, successful growth and characterization of single-unit-cell FeSe films is performed at the limit of both MBE and STM system.

Therefore, to test the capability of our new customized MBE-STM system, we decided to grow a single-unit-cell FeSe film on STO substrate and compare our results with the published literature [12]. All STM experiments in this section were conducted at liquid Helium temperature.

1.3.1 Substrate Treatment

Conducting STO (001) substrates with 0.7% weight percent Niobium doped (Nb:STO) (100) were used through the entire experiment as undoped STO substrate is insulating and could not be used for STM scanning. Bulk STO has a cubic structure with a lattice constant of 3.905 Å.

The Nb:STO substrate was mounted onto the bridge style sample holder as shown in Figure 1.11 (a). After transferring the holder to the preparation chamber at UHV ($\sim 3 \times 10^{-10}$ mbar), indirect heating at 750 °C was performed to remove water and gases adsorbed on the holder and substrate. When the indirect heating was finished, direct heating of the substrate was performed at four steps to obtain atomically flat TiO₂ terminated surface with 2×2 reconstruction: first, the substrate was gradually heated from room temperature (RT) to 600 °C at a rate of 100 °C/min for 10-15 min by slowly increasing the DC current that passes through the substrate. Second, the substrate was further heated to 1100 °C at the same rate for 30 min. Third, the substrate temperature was decreased to 600 °C and maintained for 10 min. Finally, the substrate temperature was dropped back to RT. The substrate temperature was measured by a high-temperature pyrometer (LUXTRON, with model 10 optical fiber temperature control system).

Sample holder was then transferred to STM chamber and inserted into the STM scanning head at ~ 6 K. Figure 12 (a) and (b) shows the large-scale topography and the dI/dV spectrum of the high temperature treated STO substrate, respectively.

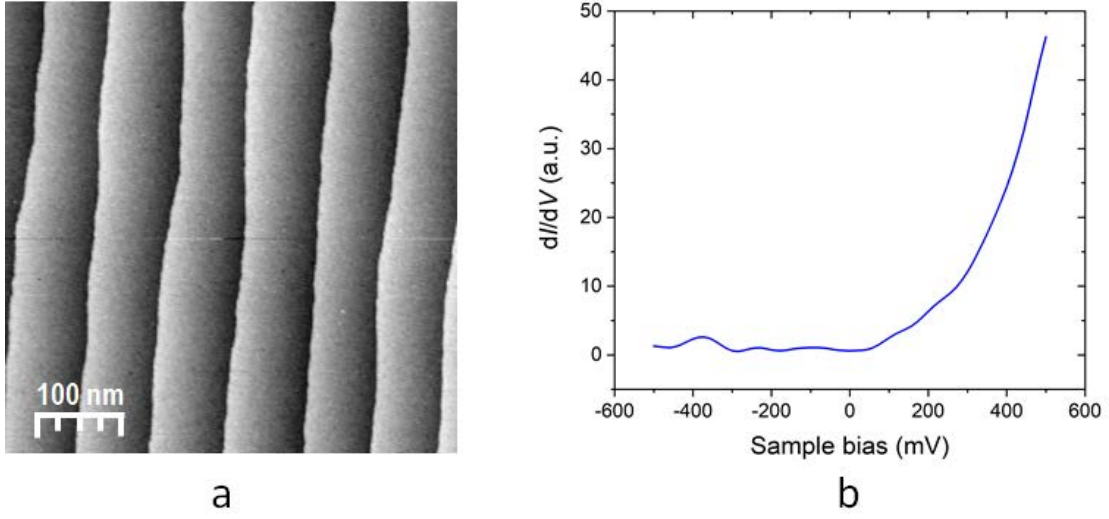


Figure 1.12. (a) STM topographic image of high temperature treated STO ($V = 3.0$ V, $I = 50$ pA, 500 nm $\times$ 500 nm). (b) Differential conductance dI/dV spectrum of high temperature treated STO. Set point was stabilized at $V = 500$ mV, $I = 50$ pA.

Clearly, the high temperature treatment results in a clean and atomically flat surface with regular straight steps. The dI/dV spectrum of the high temperature treated STO measured in our system as shown in Figure 1.12 (b) corresponds well with the literature [12]. It is worth mentioning that this spectrum is intrinsic to STO.

A zoom-in STM image taken one terrace in Figure 1.12 (a) is shown in Figure 1.13 (a). Note that Figure 1.13 (a) is the real space image. To calculate the lattice constant more precisely, one can convert the real space image to reciprocal space by performing the Fast Fourier Transform (FFT) and measure the reciprocal lattice constant. The corresponding FFT reciprocal space image is shown in Figure 1.13 (b). The reciprocal lattice constant b obtained from Figure 1.13 (b) is $\sim 0.8/\text{\AA}$. From equation (6), the lattice constant in real space, a , equals $2\pi/b$ and therefore the calculated real space lattice constant is $2\pi/(\frac{0.8}{\text{\AA}}) \sim 7.85$ $\text{\AA}$.

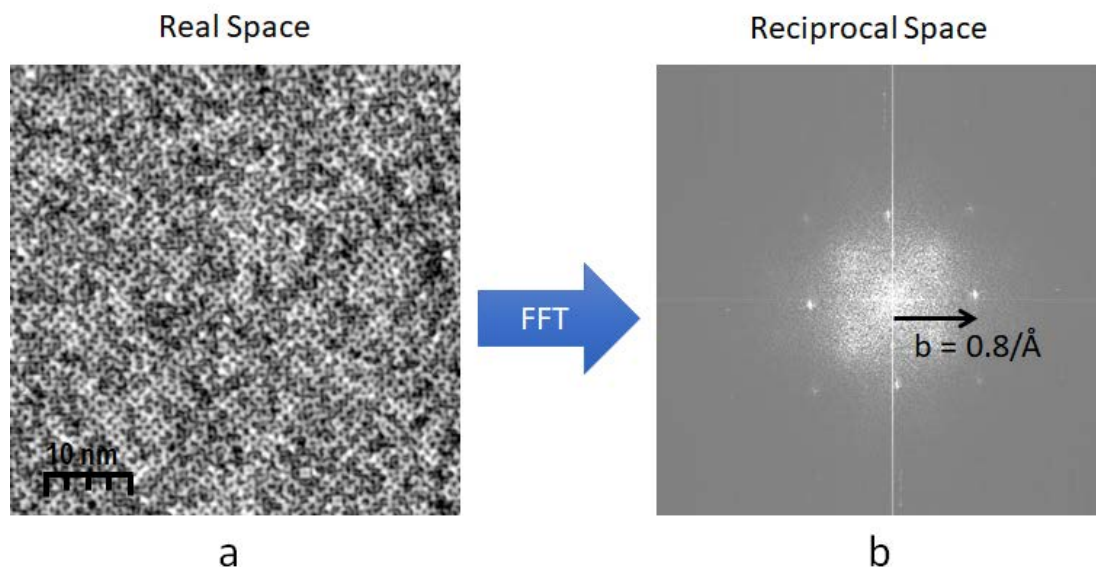


Figure 1.13. (a) Zoomed in STM topographic image taken on one terrace in Figure 1.14 (a) ($V = 0.5$ V, $I = 100$ pA, 50 nm $\times$ 50 nm). (b) FFT image of (a).

Note that 7.85 $\text{\AA}$ is almost two times 3.905 $\text{\AA}$ (original lattice constant of STO). This clearly indicates that the lattice constant of the high temperature treated STO substrate is twice as that of the untreated STO. In other words, we have obtained the desired STO substrate with 2×2 surface reconstruction. The 2×2 surface reconstruction in real space is illustrated in Figure 1.14.

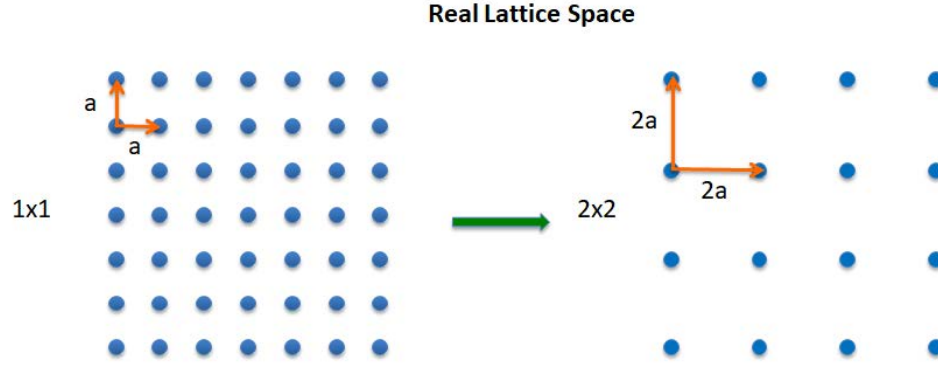


Figure 1.14. Schematic illustrations of the untreated (original) real space lattice (left) and the treated 2×2 reconstructed real space lattice (right).

Another way to verify the 2×2 surface reconstruction is by analyzing RHEED patterns. Equation (6) states that $\mathbf{a} \cdot \mathbf{b} = 2\pi$. With 2×2 surface reconstruction, the new real space surface lattice constant becomes twice as before, namely $\mathbf{a}' = 2\mathbf{a}$. Note that the new real space surface lattice constant and the new reciprocal space lattice constant also obey equation (6), namely,

$$\mathbf{a}' \cdot \mathbf{b}' = 2\pi. \quad (12)$$

From Equation (12), one can immediately obtain $\mathbf{b}' = \frac{1}{2}\mathbf{b}$. In other words, in the reciprocal space, the new surface lattice constant would be half as before, as illustrated in Figure 1.15. As explained in Section 1.2.1, the spatial separation between spots/streaks on RHEED screen is proportional to the *reciprocal lattice* constant in the direction perpendicular to the incident beam. Therefore, the RHEED spatial separation between spots/streaks of the 2×2 reconstructed STO surface would be half as that of the untreated STO.

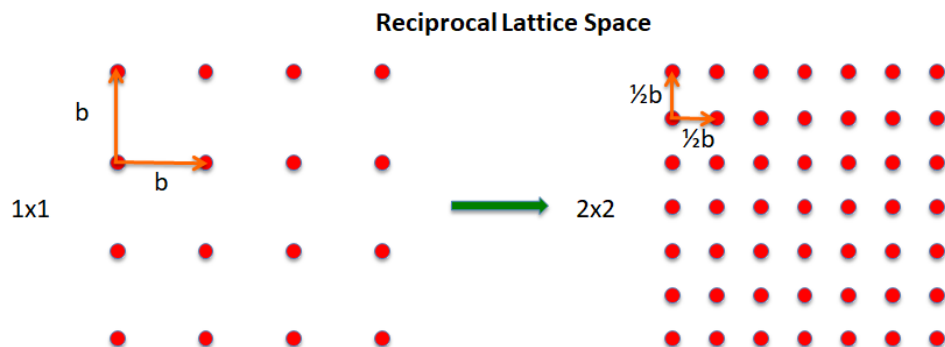


Figure 1.15. Schematic illustrations of the untreated (original) reciprocal space lattice (left) and the treated 2×2 reconstructed reciprocal space lattice (right).

The RHEED patterns of the high temperature treated STO substrate is shown in Figure 1.16. In addition to the streaks of the 1×1 lattice indicated by the green arrows, additional streaks lying in the center of each pair of the 1×1 streaks were observed, as indicated by the orange arrows. Since the spatial separations between the RHEED streaks of the high temperature treated STO is half as that of the untreated (1×1) STO, we concluded that we have obtained the desired STO substrate with 2×2 surface reconstruction.

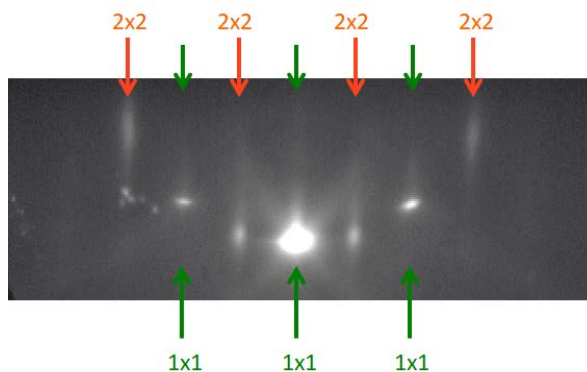


Figure 1.16. RHEED pattern of high temperature treated STO substrate with 2×2 surface reconstruction.

1.3.2 MBE Growth and STM Analysis

To grow the FeSe film with precise 1:1 stoichiometry, ‘Three temperature’ rule was applied. Therefore, the LVP material (Fe) effusion cell temperature > substrate temperature > HVP material (Se) effusion cell temperature. The growth rate is determined by the Fe cell temperature rather than Se cell temperature. Before each growth, the STO substrates were all treated at 1100 °C in the prep chamber under UHV condition and verified to have the 2×2 surface reconstruction by both STM and RHEED, as illustrated in Figures 1.12 (a), 1.13 (a), and 1.16.

The growth parameters for the first attempt were chosen as:

Fe cell: 1150 °C, Se cell: 145 °C, substrate: 650 °C, growth time: 40 min.

Figure 1.17 shows the topography of the film resulting from the growth parameters above.

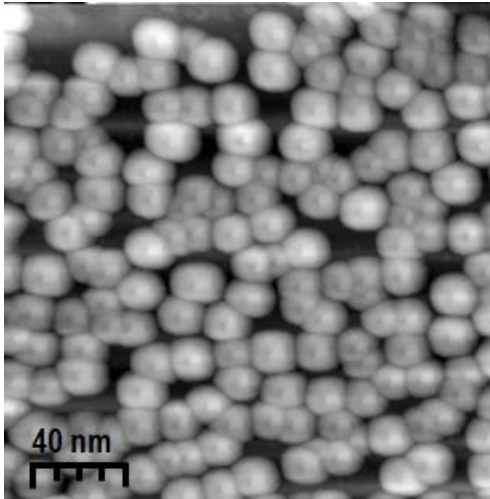


Figure 1.17. STM topographic image of the film from the first attempt ($V = 3.5$ V, $I = 50$ pA, $200 \text{ nm} \times 200 \text{ nm}$).

It is clear to see from the Figure 1.17 that Fe clusters were the dominant formation instead of FeSe film. There are two possibilities, either Se was not rich enough (Se cell temperature

was not high enough) so that the unreacted Fe atoms formed the clusters, or the substrate temperature was too high such that Se can barely land on the substrate to react with Fe. At the time, we chose to believe the former case as the deposition rate of Se at 145 °C measured by quartz crystal microbalance (QCM) was twice smaller than that of Fe at 1150 °C measured by QCM. Therefore, we decided to further increase Se cell temperature to 175 °C while keeping other parameters unchanged.

The growth parameters for the second attempt were chosen as:

Fe cell: 1150 °C, Se cell: 175 °C, substrate: 650 °C, growth time: 40 min.

The deposition rate of Se measured by QCM at 175 °C was one order of magnitude higher than that at 145 °C. Figure 1.18 (a) and (b) show the topographies of the film resulting from the growth parameters above at two different locations.

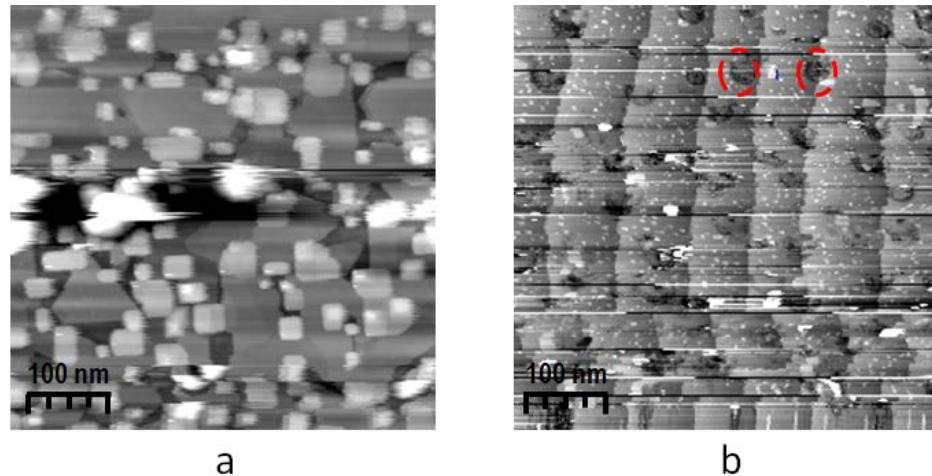


Figure 1.18. (a) and (b) STM topographic images of the film from the second attempt ((a) $V = 3.5$ V, $I = 10$ pA, 500 nm $\times$ 500 nm, (b) $V = 3.5$ V, $I = 100$ pA, 500 nm $\times$ 500 nm) at two different locations. Red dashed circles in (b) indicate holes on the substrate.

Figure 1.18 (a) clearly shows that more films were formed than the previous case which indicates that the increase of Se cell temperature indeed helped. However, multiple

holes were observed on the STO surface as indicated by the red dashed circles in Figure 1.18 (b). These holes could not be caused by the STM tip crashing into the sample as we were sure that the tip did not crash into the sample. Thanks to the comments by Dr. Yanfeng Lyu based on her previous experience, Se could react with STO substrate to ‘etch’ it resulting in the formation of the holes if the substrate temperature is too high. Combining with the fact the high substrate temperature could also result in Fe clusters, we decided to drop the substrate temperature by 200 °C.

The growth parameters for the third attempt were chosen as:

Fe cell: 1200 °C, Se cell: 195 °C, substrate: 450 °C, growth time: 40 min.

Meanwhile, Fe cell temperature was increased by 50 °C aiming to have higher deposition rate. Se cell temperature was increased by 20 °C accordingly to maintain the same Fe : Se deposition ratio as that measured by QCM in attempt two. Figure 1.19 (a) shows the topography of the film resulting from the growth parameters. Clearly, no holes were observed on the substrate surface which implies that the previous substrate temperature was indeed too high. Furthermore, compared to previous results, the substrate at this time was covered by complete film instead of scattered small-sized islands (films). Figure 1.19 (b) shows the atomic resolution image of the film. The lattice constant extracted from Figure 1.19 (b) was $\sim 3.76 \text{ \AA}$ which is almost same as the in-plane lattice constant of bulk FeSe ($3.765 \text{ \AA}$). This evidence strongly suggested the film obtained from the third attempt was FeSe film. However, it is impossible to tell how many UC of FeSe were grown as STM can only detect the most top layer.

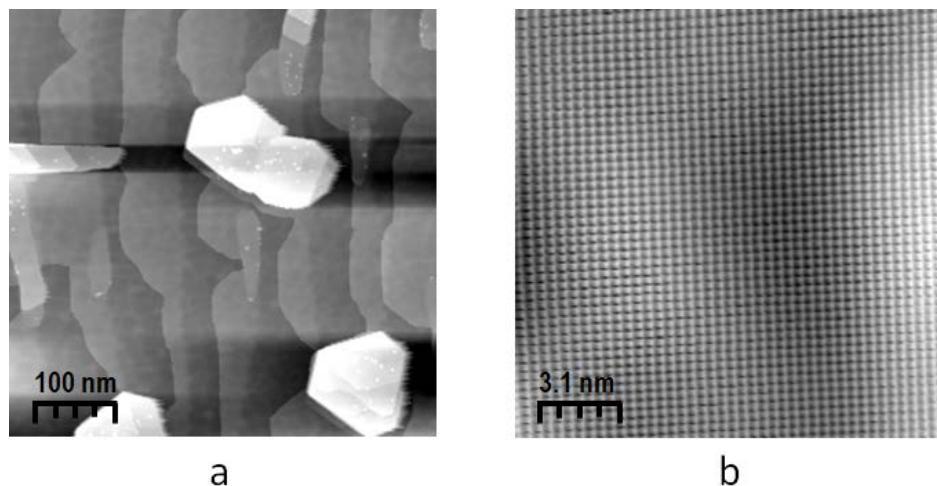


Figure 1.19. (a) STM topographic images of the film from the third attempt ($V = 3.5$ V, $I = 10$ pA, 500 nm $\times$ 500 nm). (b) Atomic resolution image ($V = 0.1$ V, $I = 300$ pA, 15.6 nm $\times$ 15.6 nm).

Since the task is to grow single-unit-cell FeSe film, we decided to decrease the growth time to 15 min while keeping other parameters unchanged to obtain thinner films.

The growth parameters for the fourth attempt were chosen as:

Fe cell: 1200 $^{\circ}\text{C}$, Se cell: 195 $^{\circ}\text{C}$, substrate: 450 $^{\circ}\text{C}$, growth time: 15 min.

The quality of the film this time was much better than before. In Figure 1.20 (a), the red dashed lines represent the terrace edges of the high temperature treated STO substrate. Areas between two neighbouring dashed lines are the terraces of the treated STO substrate. Obviously, area A and B are on the same terrace. To judge whether exposed area B is STO or FeSe film, we can perform dI/dV spectrum on area B to compare if the spectrum is the same as that of STO or FeSe.

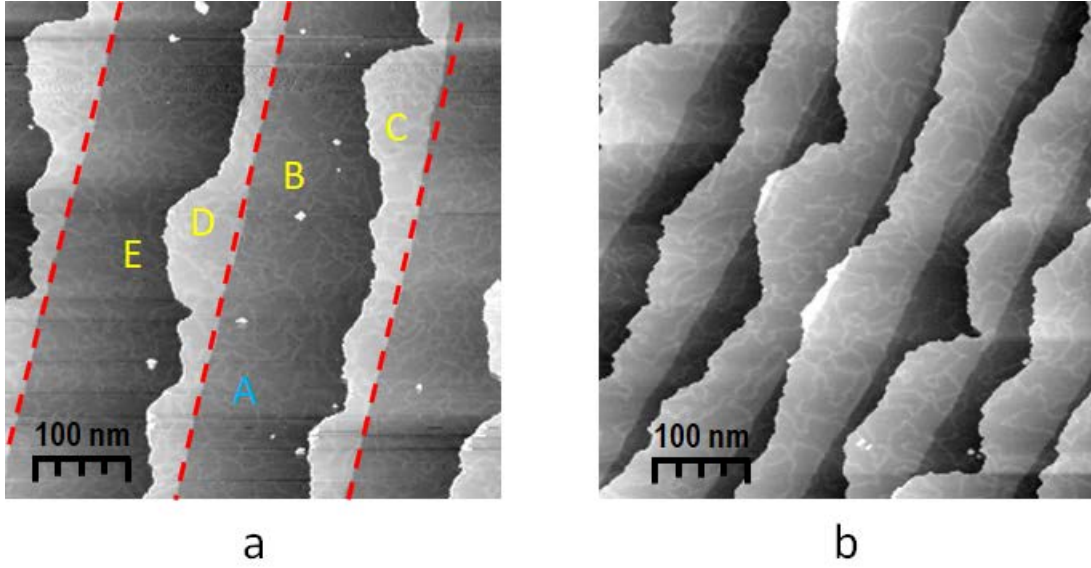


Figure 1.20. (a) and (b) STM topographic images of the film from the fourth attempt ((a) $V = 3.5$ V, $I = 100$ pA, 500 nm $\times$ 500 nm, (b) $V = 3.5$ V, $I = 10$ pA, 500 nm $\times$ 500 nm) at two different locations. Red dashed lines in (a) represent the terrace edges of the high temperature treated STO substrate.

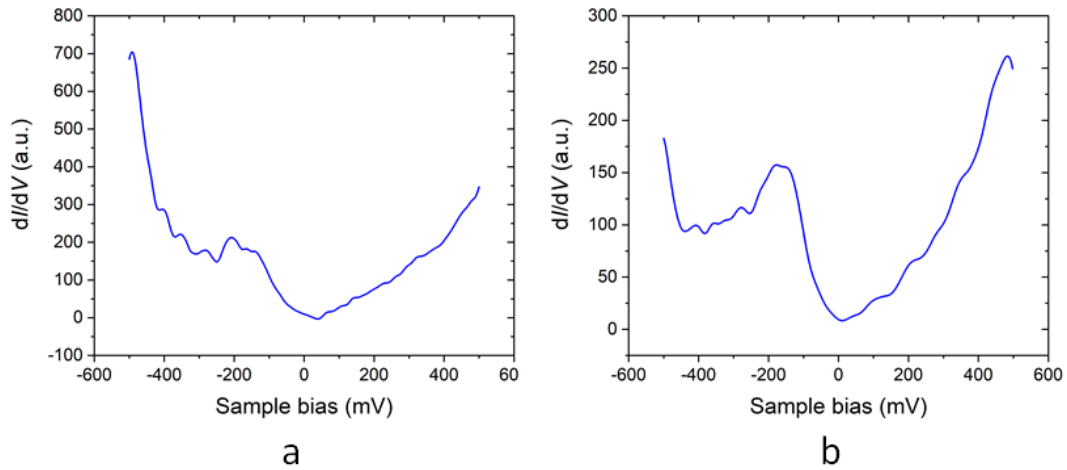


Figure 1.21. Differential conductance dI/dV spectra of (a) area B, (b) area C in Figure 1.22 (a). Set point was stabilized at $V = 500$ mV, $I = 200$ pA.

Figure 1.21 (a) and (b) show the dI/dV spectrum of area B and C in Figure 1.20 (a), respectively. It is clear that they have similar signature as that of multi-unit-cells FeSe [14] and quite different from that of STO shown in Figure 1.12 (b). Therefore, both area B and

C are FeSe. But the FeSe on area C is one UC higher than that of on area B, because the measured lateral height difference between B and C is very close to the c lattice constant of bulk FeSe. In fact, the FeSe on area B and E have the same number of UC, say n , but E is one terrace lower than B. Similarly, FeSe on D and C also have the same number of UC, but they are one UC higher than E and B, respectively, and thus they have $n + 1$ UC of FeSe. It is worth mentioning that the ‘strings’-- random lines in area B, C, D, and E are special characters of FeSe due to the in plane stress and do not belong to STO substrate. This is another way to tell if an area is FeSe or STO. It is worth mentioning that at this moment, it is still impossible to figure out the number of UC of FeSe on area B since STM can not probe the FeSe layers underneath the most top layer. So far, we have obtain good quality FeSe films, but there are two issues remaining unsolved: 1) the number of UC of the FeSe films is unknown, and 2) the films were not superconducting yet. In order to solve the first problem, we need to figure out the growth time which will result in a film that has a little less than one complete UC. In such case, there will be some small areas of uncovered STO substrate underneath the FeSe film, which can be distinguished by the dI/dV spectrum. Once we obtain the growth time for one UC, we can calculate the number of layers for a given amount of time. Previous experience from Dr. Yanfeng Lyu tells that in order to have the best quality of films, films should be grown at a temperature slightly below the point at which the film will start decomposing. In addition, for single-unit-cell FeSe film, it is critical to anneal the film to the point it starts decomposing where superconductivity will emerge. Therefore, the next goal is to see at what temperature will FeSe film start decomposing macroscopically in our system.

In the fifth attempt, we post annealed the FeSe film obtained from the fourth growth

to figure out at what temperature will FeSe film start decomposing. The film was annealed at different temperature progressively: 450 °C, 470 °C, 490 °C, 510 °C, 550 °C, and 580 °C. The sample was annealed for one hour at each temperature. Once the annealing was finished, the sample was transferred in-situ to the STM chamber for STM scanning. It was then moved back to the MBE chamber for further annealing if the previous annealing temperature was not high enough. The results of the post annealing at different temperature are shown in Figure 1.22. For the annealing temperature below 510 °C (in our system), the sample barely decomposed and the spectra were the same as the non-superconducting multi-unit-cells FeSe, indicating the annealing temperature was not high enough. For 550 °C anneal, a trace of a small superconducting gap can be found from its dI/dV spectrum. When the annealing temperature was further increased to 580 °C, the film decomposed drastically that only 1 UC out of 3 (before annealing) survived, and the remaining last 1 UC even started decomposing and the STO substrate underneath was exposed. The dI/dV spectrum of the 580 °C annealed sample in Figure 1.22 (f) shows a superconducting gap around 15 mV. Up to now, superconductivity in FeSe was achieved by post annealing a 3 UC FeSe films at 580 °C for 1 h. We estimated from the fourth growth that 15 min deposition would approximately grow 3 UC of FeSe film. Therefore, we decided to grow only 5 min for the next one to verify our estimation.

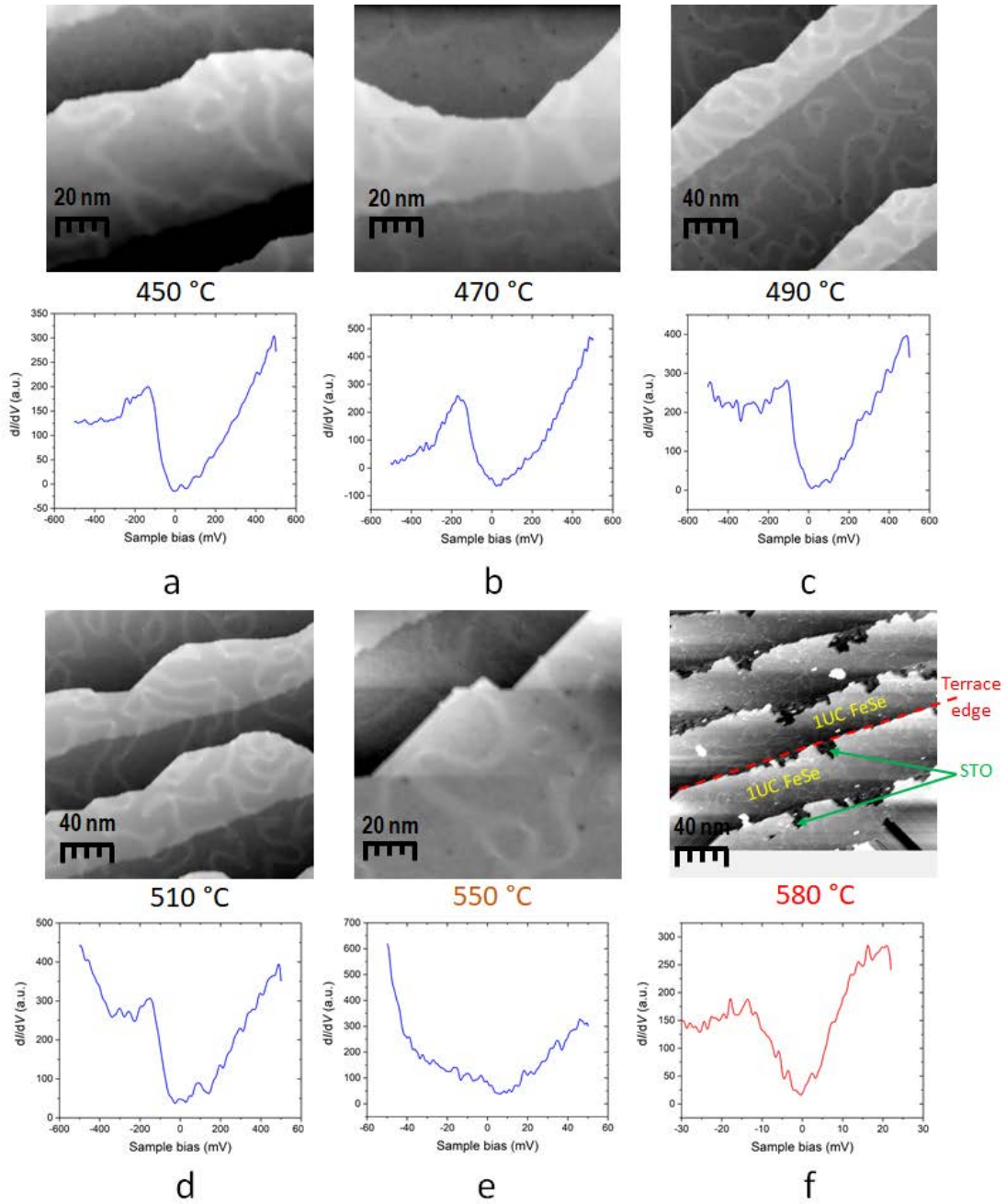


Figure 1.22. STM topographic images (upper, $V = 2.5$ V, $I = 10$ pA) and differential conductance dI/dV spectra (lower, set point was stabilized at $V = 500$ mV for (a-d), 50 mV for (e), and 30 mV for (f), $I = 200$ pA) of sample from the 4th growth post annealed for 1h at (a) 450 °C, (b) 470 °C, (c) 490 °C, (d) 510 °C, (e) 550 °C, and (f) 580 °C.

As mentioned earlier, the best growth temperature would be slightly below decomposing temperature. Based on the post annealing experiment, we know that the sample barely

decomposed at 550 °C and decomposed violently at 580 °C. Therefore, we decided to choose a safe value for the substrate temperature: 560 °C.

The growth parameters for the sixth attempt were chosen as:

Fe cell: 1200 °C, Se cell: 195 °C, substrate: 560 °C, growth time: 5 min.

Figure 1.23 shows the STM topographic image of the resulted film. The 5-minute growth resulted in a $\sim 80\%$ coverage of 1 UC FeSe film, in good agreement with our estimation. The areas in black in Figure 1.23 are the uncovered STO substrate ($\sim 20\%$ of the total area), whereas the areas in grey are the single-unit-cell FeSe film grown on STO substrate ($\sim 80\%$ of the total area). However, the sample was not superconducting yet.

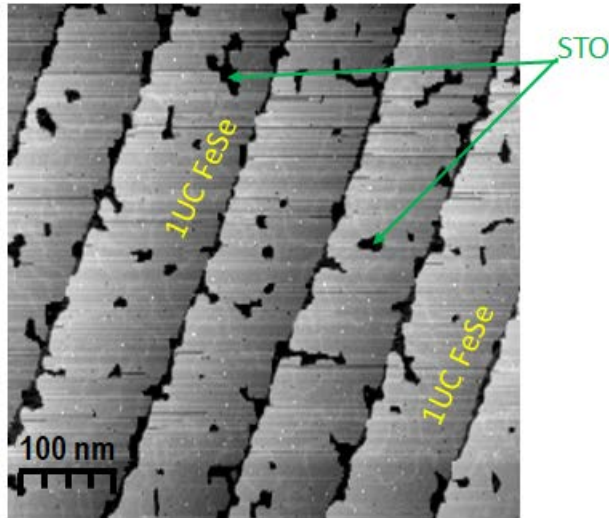


Figure 1.23. STM topographic image of the film from the sixth attempt ($V = 3.5$ V, $I = 100$ pA, $500\text{ nm} \times 500\text{ nm}$).

Since the sample was not superconducting, further annealing was required. We decided to move this sample back to MBE chamber to grow 2 min more to achieve a 100% coverage of single-unit-cell FeSe then followed by a 30 min post annealing at the growth temperature.

The growth parameters for the seventh (last) attempt were chosen as:

Fe cell: 1200 °C, Se cell: 195 °C, substrate: 560 °C, growth time: additional 2 min, annealing time: 3 minutes, annealing temperature: 560 °C.

The atomic resolution image of the post annealed single-unit-cell FeSe film is shown in Figure 1.24 (a). Figure 1.24 (b) shows the corresponding differential conductance dI/dV spectrum and a superconducting gap with 15 mV is clearly observed. We have successfully achieved the single-unit-cell superconducting FeSe film.

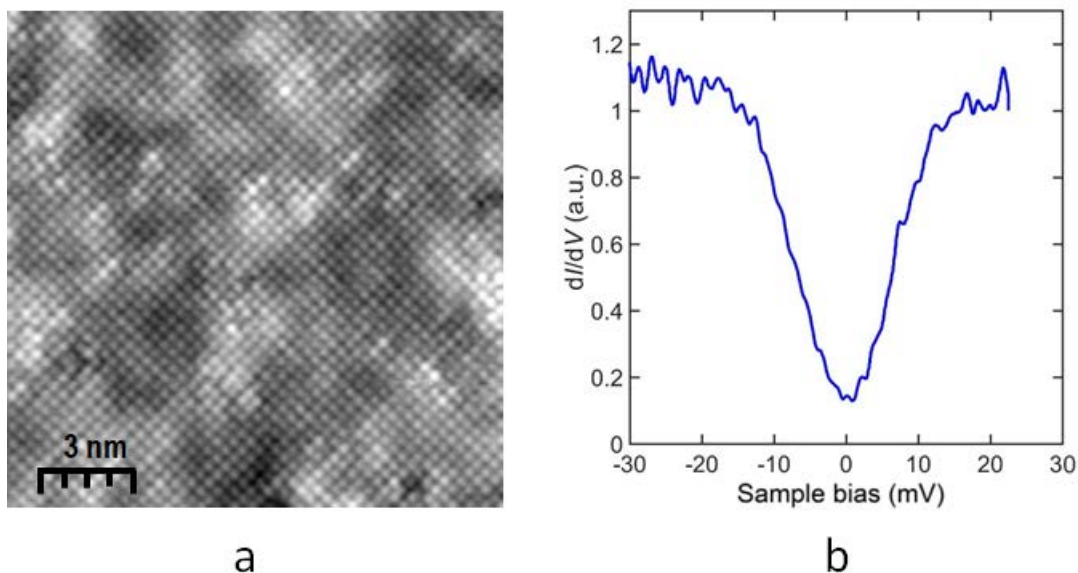


Figure 1.24. (a) Atomic resolution image of 1 UC superconducting FeSe film ($V = 0.1$ V, $I = 200$ pA, 14.8 nm $\times$ 14.8 nm). (b) Differential conductance dI/dV spectrum revealing a superconducting gap ~ 15 mV. Set point was stabilized at $V = 30$ mV, $I = 200$ pA.

In addition to the successful growth of superconducting single-unit-cell FeSe film, we observed and report for the first time the step-flow growth mode of FeSe film on STO substrate. STM topographic images of multi-unit-cells FeSe in Figure 1.20 (a) and (b) show clearly that the growth of FeSe started from the terrace edges and expanded (flow) outward, in contrast to the random nucleation mode. The step-flow growth of FeSe is schematically illustrated in Figure 1.25.

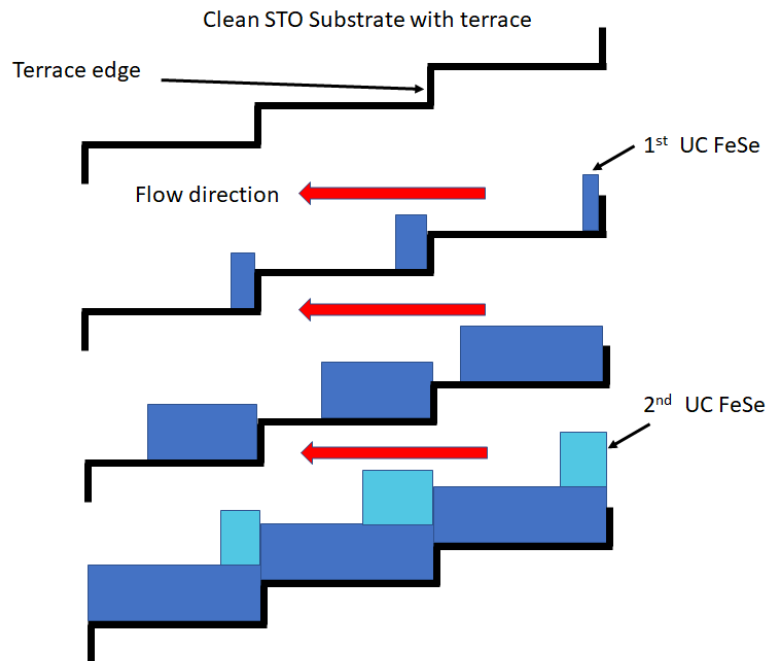


Figure 1.25. Schematic illustration of the step-flow growth mode of FeSe on STO substrate. Darker blue rectangles represent the 1st UC FeSe, and the lighter blue rectangles represent the 2nd UC FeSe.

Step-flow growth usually occurred at very high substrate temperature when the surface diffusion length of adatoms exceeded the average terrace width. Adatoms in this case migrate to the step edge where it has the lowest energy to be the most stable crystallization site. The formerly grown crystals (at the substrate terrace edge) will form new edges (some distance away from the terrace edge). The later incoming adatoms would also migrate to the newly formed step edges where they find most stable for crystallization. Therefore, the steps start to ‘flow’ as the crystal grows. It is straight forward to see that under the step-flow growth mode, the film surface will always be smooth. It is worth mentioning that RHEED oscillations were never detected during the growth of thicker (multi-unit cells) FeSe films. Recall that RHEED oscillations happen when the surface roughness increases

and decreases periodically as explained in section 1.2.1. Therefore, a near constant RHEED intensity implies that the surface of the substrate during the growth is always smooth. The observation of no RHEED oscillation supports the step-flow growth mode of FeSe on STO we observed.

1.3.3 Conclusion

As a conclusion for this section, by growing the single-unit-cell FeSe on STO substrate, we demonstrated that our MBE - LT STM system purchased from CreaTec has the ability of achieving the growth of high quality 1 UC to multi-unit cells epitaxial films, obtaining high quality atomic resolution images, and detecting the superconducting gap from dI/dV spectrum. The system meets our expectations and is ready to explore exciting new science. In addition, we observed for the first time the step-flow growth mode of FeSe on STO substrate.

1.4 MBE Growth and LT-STM Study of CaFe_2As_2 Films and CaFe_2As_2 Assisted Fe Films on SrTiO_3 Substrate

1.4.1 CaFe_2As_2 Films

1.4.1.1 Method

The crystal structure of CaFe_2As_2 (Ca122) is shown in Figure 1.26. SrTiO_3 (STO) substrate has a cubic structure with lattice constant being 3.905 Å, whose lattice mismatch with Ca122 (3.887 Å) is ~ 0.46%, in an acceptable range [4]. In order to do STM scanning, conducting substrate must be used. In this research, conducting STO (100) substrates with 0.7% weight percent Niobium doped (Nb:STO) were used through the entire experiment. All substrates were treated at 1100 °C using the same procedure as described in Section 1.3.1.

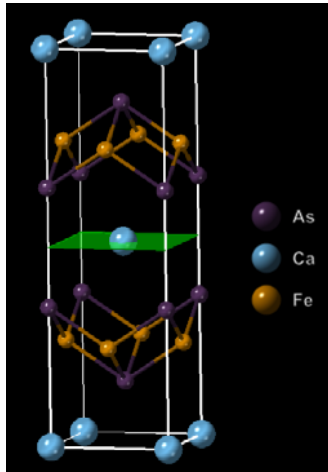


Figure 1.26. Crystal structure of CaFe_2As_2 with one complete unit-cell (UC).

Ca, Fe, and As were loaded in single filament effusion cell, high temperature

effusion cell, and cracker cell, respectively. The flux of each source was measured beforehand with continuous flow of LN₂ passing through the cryo panel. The Fe : Ca flux ratio at various temperature is shown in Table 1.3.

Table 1.3 Fe : Ca flux ratio at various temperature

Fe (°C) \ Ca (°C)	1100	1120	1140	1160	1180	1200
410	0.36	0.52	0.75	1.09	1.57	2.26
400	0.52	0.75	1.08	1.57	2.26	3.25
380	1.03	1.49	2.15	3.10	4.48	6.43
370	1.39	2.01	2.91	4.20	6.05	8.70
360	1.97	2.85	4.12	5.95	8.58	12.33

Electron energy was set to 11.5 kV for RHEED measurement for the entire experiment.

STM measurement was conducted at liquid nitrogen temperature for the entire experiment.

1.4.1.2 Results and Discussion

Based on the results reported by Hatano *et al.* [4], in order to grow Ca122 film with the best quality, the flux ratio of Fe : Ca was chosen to be 1 : 1 in this study. Even though the stoichiometric Fe : Ca ratio is 2 : 1, Hatano *et al.* found that the 2 : 1 ratio will result in films with impurities possibly due to the high vapor pressure of Ca, which can cause desorption of Ca from thin films at high substrate temperature.

The growth parameters for the first attempt were chosen as:

Fe cell: 1140 °C, Ca cell: 400 °C, As cell: both zones at 250 °C, substrate: 650 °C, growth time: 7 h.

According to Table 1.3, the selected parameters corresponded to Fe : Ca ratio being 1.08 : 1. Figure 1.27 shows the X-ray diffraction spectrum of the film grown in the first attempt. Clearly, (002), (004), (008), and (0010) peaks of Ca122 were observed. The (006) peak of Ca122 was immersed in the (200) peak of STO substrate, and thus it was not distinguishable from the substrate. No impurity peaks were detected. Figure 1.28 shows the rocking curve of the film's (008) peak with full-width-half-maximum (FWHM) $\sim 0.8^\circ$. The FWHM of the rocking curves of the film's (002), (004), and (0010) peaks were 0.7° , 1° , and 0.8° , respectively. From the X-ray diffraction spectrum results, we therefore concluded that with Fe : Ca ratio chosen as $\sim 1 : 1$, we have obtained epitaxial Ca122 films grown on STO substrate.

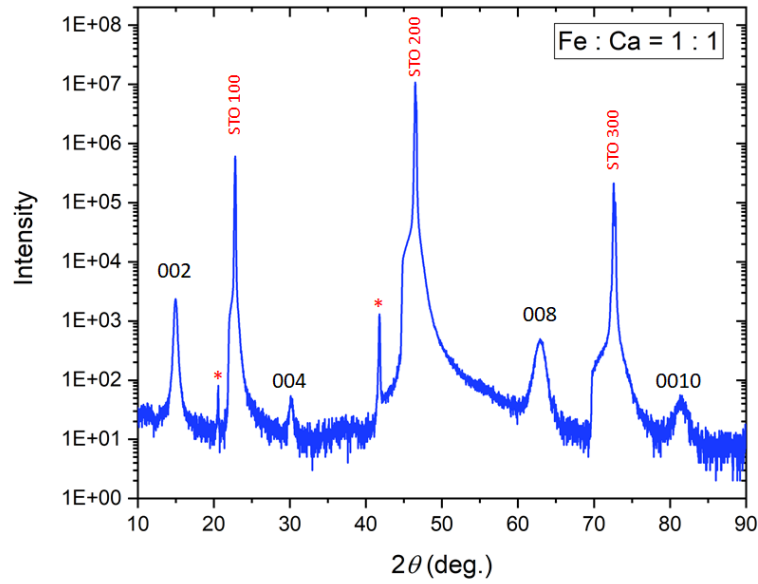


Figure 1.27. X-ray diffraction spectrum of Ca122 film grown in the first attempt. * indicates the corresponding K_{β} peaks of the STO substrate. Growth parameters were chosen as: Fe cell: 1140 °C, Ca cell: 400 °C, As cell: both zones at 250 °C, substrate: 650 °C, growth time: 7 h.

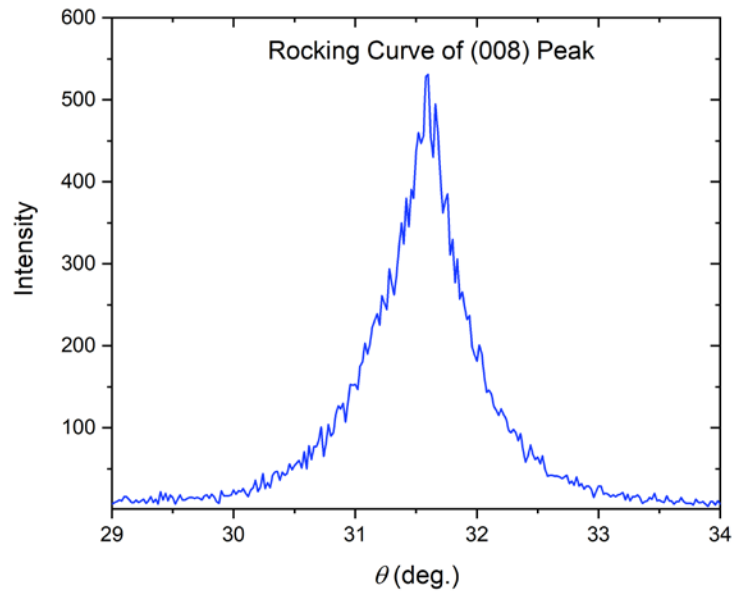


Figure 1.28. Rocking curve of film's (008) peak. FWHM $\sim 0.8^{\circ}$.

To investigate the growth mode and possible surface reconstruction, we decided to grow thinner films ~ 2 UC of Ca122. To do that, we decreased the deposition rate while still keeping the Fe : Ca ratio as $\sim 1 : 1$ by dropping Fe cell temperature from 1140 °C to 1100 °C. Growth time was also decreased to 2 h. From Table 1.3, the corresponding Ca cell temperature should be at 380 °C.

The growth parameters for the second attempt were chosen as:

Fe cell: 1100 °C, Ca cell: 380 °C, As cell: both zones at 230 °C, substrate: 650 °C, growth time: 2 h.

The evolution of RHEED pattern with electron beams incident along STO [100] direction during the growth is shown in Figure 1.29. As can be seen, RHEED streaks of the Ca122 film formed in the first 5 min. The intensity reached minimum at 30 min and maximum again at 1 h. The intensity slightly decreased from 1 h to 2 h without any more oscillations. This implies that the formation of the first complete layer of half UC Ca122 film took ~ 1 h. Afterwards, the growth tended to be island growth mode instead of layer-by-layer mode. As a result, the film surface became rougher and rougher, leading to the absence of further RHEED oscillations. The spatial separation of RHEED streaks did not have noticeable change with respect to that of the treated STO substrate, indicating that the lattice constant of the film was close to that of the STO substrate. However, data of RHEED with incident beam along STO [100] direction is insufficient to tell if there was surface reconstruction or not. To explore surface reconstruction, data of RHEED with incident beam along STO [110] direction, namely a rotation of the substrate by 45° is required, as explained in Figure 1.30.

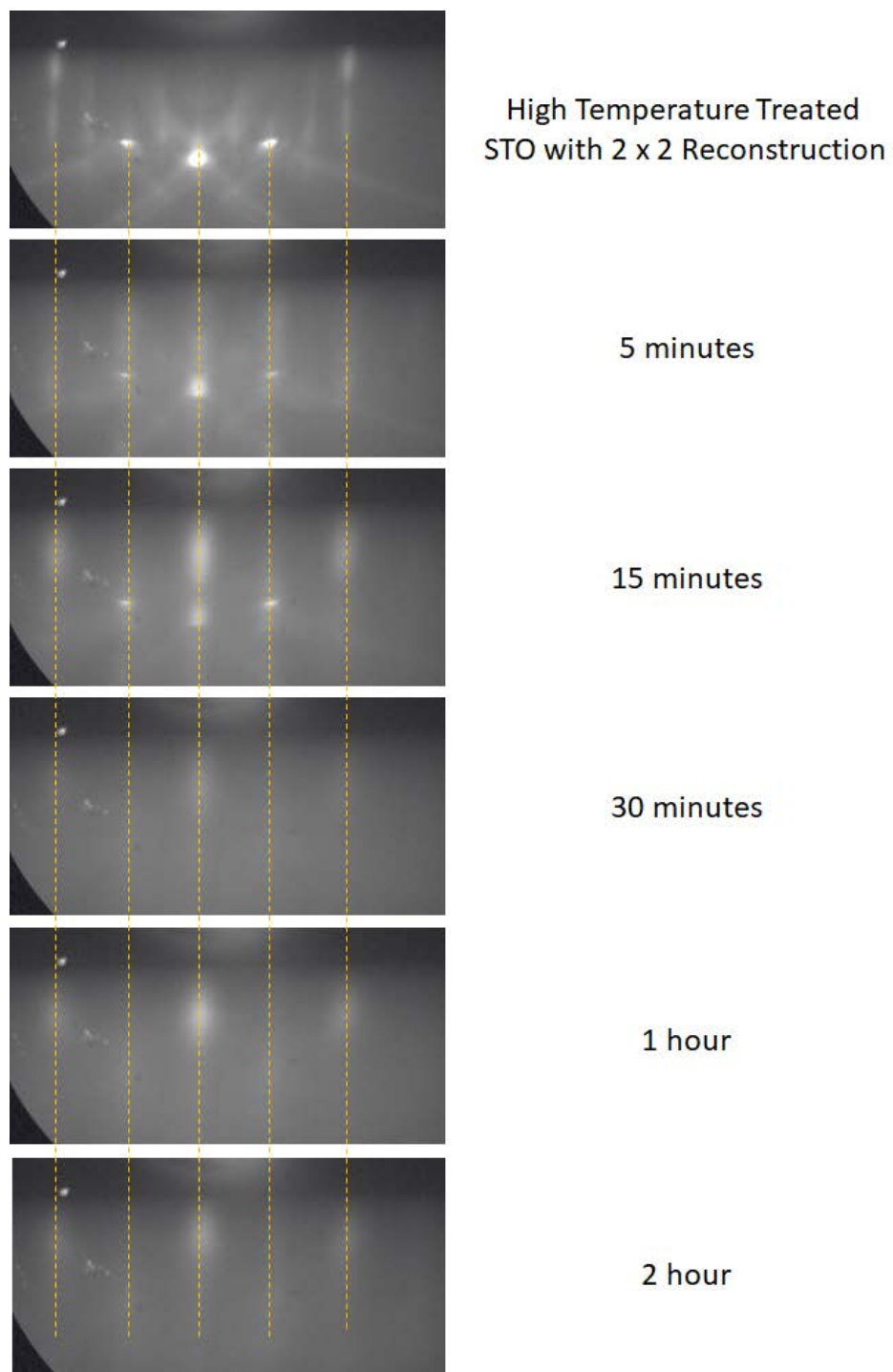


Figure 1.29. Evolution of RHEED pattern taken along STO [100] during the 2-h growth of the second attempt.

Figure 1.30 (a) shows the original (unreconstructed) reciprocal lattice. As illustrated, in this case, the reciprocal lattice constant along STO [110] direction (a 45° rotation of the substrate) should be $\sqrt{2}$ times longer than that along the STO [100] (no rotation). In other words, the RHEED streaks separation at 45° rotation should be $\sqrt{2}$ times longer than that along the STO [100] (no rotation). However, if a $\sqrt{2} \times \sqrt{2}$ surface reconstruction occurred, the situation would be different. Figure 1.30 (b) shows the corresponding $\sqrt{2} \times \sqrt{2}$ reconstructed reciprocal lattice. As illustrated, in this case, the reciprocal lattice constant along STO [110] direction (a 45° rotation of the substrate) should be $1/\sqrt{2}$ times shorter than that along the STO [100] (no rotation). In other words, the RHEED streaks separation at 45° rotation should be $1/\sqrt{2}$ times shorter than that along the STO [100] (no rotation).

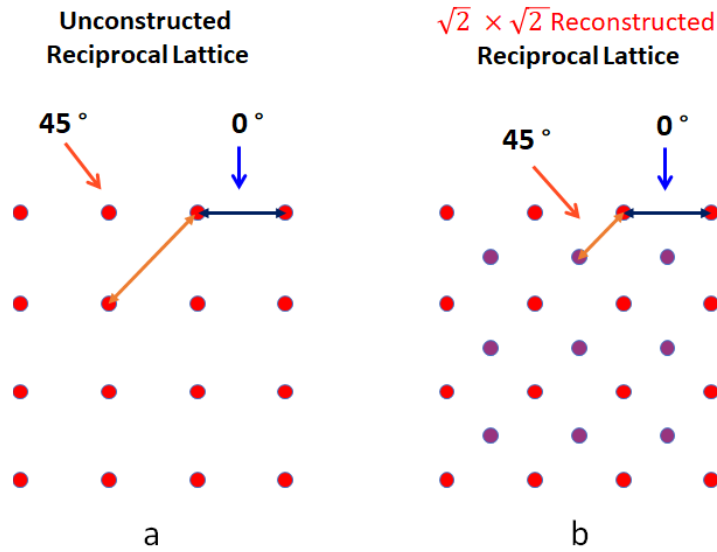


Figure 1.30. Schematic diagrams of (a) original reciprocal lattice, (b) $\sqrt{2} \times \sqrt{2}$ reconstructed reciprocal lattice. The extra purple dots in (b) is caused by the $\sqrt{2} \times \sqrt{2}$ surface reconstruction.

As explained above, by comparing the RHEED streaks separation between STO [100] direction (0°) and a 45° rotation of the substrate, one can judge whether surface

reconstruction occurred or not. Figure 1.31 shows the comparison between 0° and 45° RHEED patterns. Clearly, the 45° RHEED streaks were narrower than that of 0° and careful measurement showed that streaks of 45° rotation are indeed $1/\sqrt{2}$ times shorter than at 0° . Therefore, from RHEED measurement, we conclude that a $\sqrt{2} \times \sqrt{2}$ surface reconstruction was observed. The calculated reconstructed in-plane lattice constant is $\sim 5.55 \text{ \AA}$ and the corresponding unreconstructed in-plane lattice constant is $\sim 3.92 \text{ \AA}$.

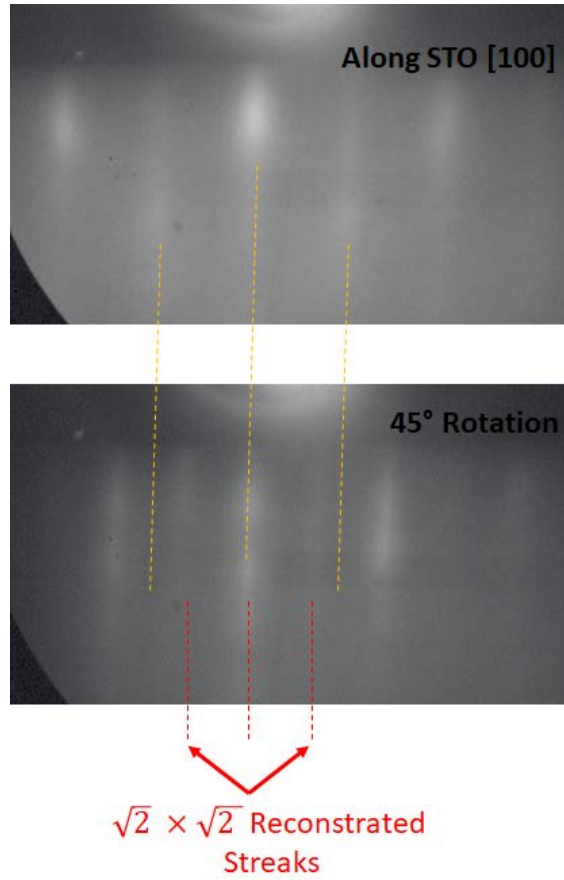


Figure 1.31. Comparison between 0° (upper, along STO [100] direction) and 45° (lower) RHEED pattern.

The STM topographic images of the Ca122 film are shown in Figure 1.32 (a) and (b). Instead of forming perfect 2D film, islands of sizes $\sim 20 \text{ nm}$ with screw dislocation were

formed. This could explain the absence of RHEED oscillations after 1-h growth as the surface was getting rougher and rougher. From the FFT of the atomic resolution images, the surface in-plane lattice constants in x and y directions were both calculated to be ~ 5.56 Å, which is $\sim \sqrt{2}$ times that of the bulk Ca122, consistent with the RHEED results, indicating a $\sqrt{2} \times \sqrt{2}$ surface reconstruction.

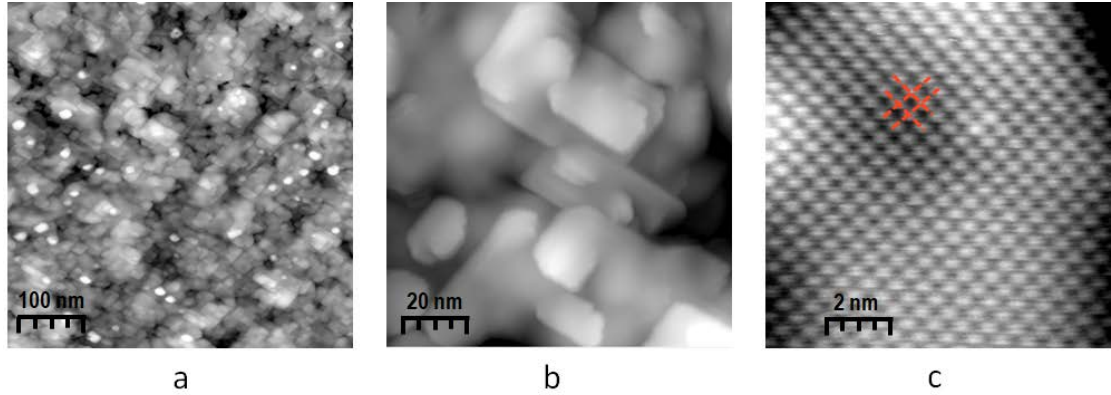


Figure 1.32. (a) and (b) STM topographic images of Ca122 film from the second attempt ((a) $V = 3.0$ V, $I = 20$ pA, 500 nm $\times$ 500 nm, (b) $V = 3.0$ V, $I = 20$ pA, 100 nm $\times$ 100 nm). (c) Atomic resolution image ($V = 0.05$ V, $I = 100$ pA, 10 nm $\times$ 10 nm).

The $\sqrt{2} \times \sqrt{2}$ surface reconstruction in real space is schematically illustrated in Figure 1.33. The light blue dots in Figure 1.33 (b) represent the missing atoms which result in the surface reconstruction. In addition, the fact that the predicted reconstructed lattice orientation is the same as the observed reconstructed lattice orientation further supports observation of the reconstruction. From charge neutrality consideration, we believe it is the Ca atoms that formed this $\sqrt{2} \times \sqrt{2}$ surface reconstruction.

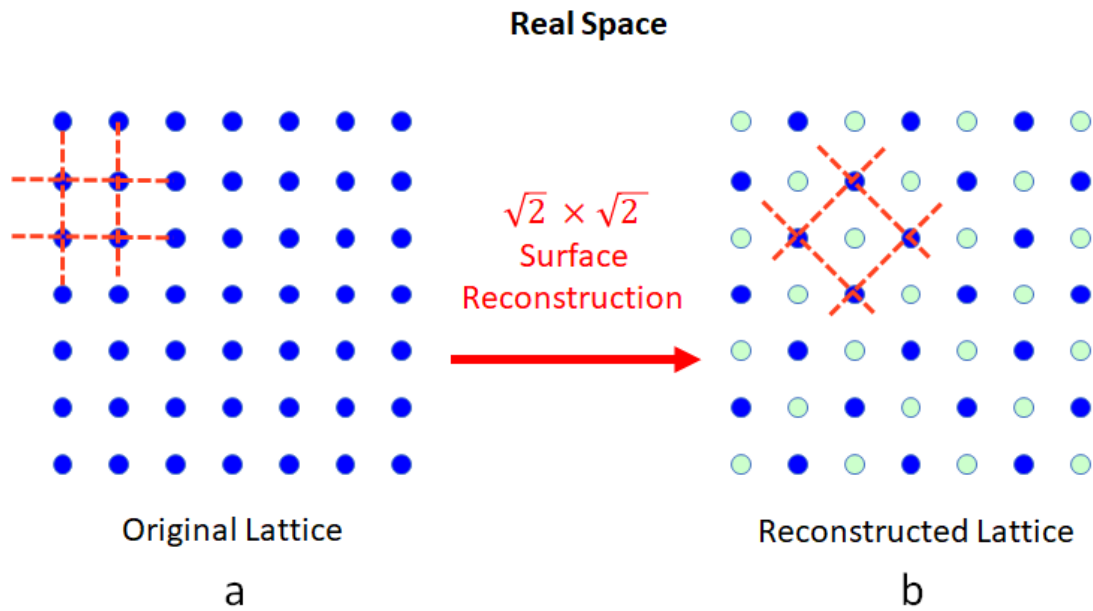


Figure 1.33. Schematic diagrams of (a) original real lattice, (b) $\sqrt{2} \times \sqrt{2}$ reconstructed real lattice. The light blue dots in (b) represent the missing atoms caused by the $\sqrt{2} \times \sqrt{2}$ surface reconstruction.

1.4.2 CaFe_2As_2 Assisted Growth of Fe Films

To explore the effect of Fe : Ca flux ratio on the growth, we decided to drastically increase the Fe : Ca flux ratio to be larger than 6 : 1.

To determine the phase of the film, we first grew thicker films for X-ray measurement.

The growth parameters for the third attempt were chosen as:

Fe cell: 1200 °C, Ca cell: 380 °C for 1 h then 370 °C for 9 h, As cell: both zones at 210 °C, substrate: 650 °C, growth time: 10 h.

According to Table 1.3, the selected parameters corresponded to Fe : Ca ratio being 8.7 : 1. Figure 1.34 shows the X-ray diffraction spectrum of the film grown in the third attempt.

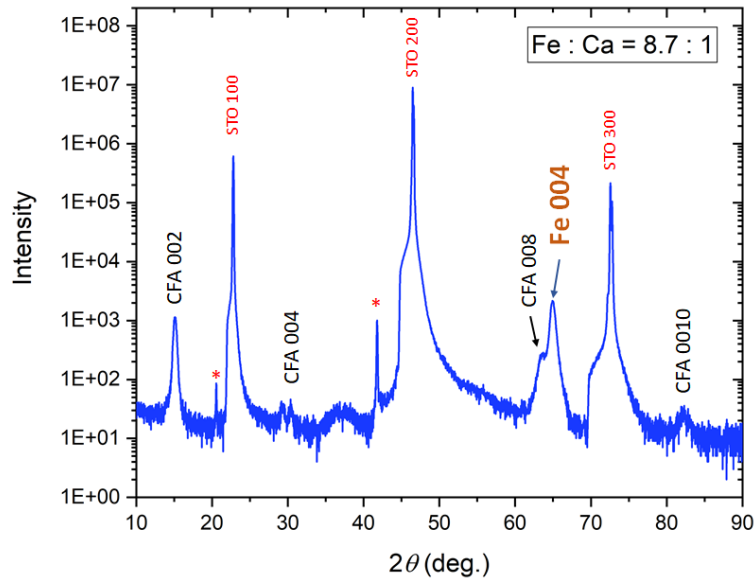


Figure 1.34. X-ray diffraction spectrum of the film grown in the third attempt. * indicates the corresponding K_{β} peaks of the STO substrate. Growth parameters were chosen as: Fe cell: 1200 °C, Ca cell: 380 °C for the 1st h and then dropped to 370 °C, As cell: both zones at 210 °C, substrate: 650 °C, growth time: 10 h.

As shown in Figure 1.34, (004) peak of Fe was detected in addition to the (002), (004), (008), and (0010) peaks of Ca₁₂Fe₂As₂O₁₀, indicating the coexistence of excessive epitaxially grown Fe in the film. Table 1.4 shows the atomic proportions of Ca, Fe, As, Sr, Ti, and O in the film measured by wavelength-dispersive spectroscopy (WDS). As the points were randomly selected across the sample, the data suggested that the sample was uniform. The calculated average atomic proportions of Ca : Fe : As was $\sim 1 : 9.38 : 2.4$. The WDS result further confirmed the excessive Fe in the film. It is worth mentioning that the epitaxially grown Fe should be the dominant phase of the film. Note that the ratio of Fe : Ca obtained from WDS measurement was very close to that obtained from the flux calibration.

Table 1.4 Atomic proportions of Ca, Fe, As, Sr, Ti, and O in the film from the 3rd attempt

	Ca (%)	Fe (%)	As (%)	Sr (%)	Ti (%)	O (%)
Point 1	0.6255	5.731	1.6369	19.468	19.195	53.343
Point 2	0.7313	6.569	1.8675	22.717	22.07	46.046
Point 3	0.6212	5.601	1.5962	19.546	19.214	53.422
Point 4	0.6288	5.647	1.4752	19.632	19.186	53.431
Point 5	0.6756	6.814	1.608	19.531	19.73	51.641
Point 6	0.6767	6.787	1.4831	21.598	21.086	48.36
Average	0.65985	6.1915	1.61115	20.41533	20.08017	51.0405

Six points were randomly selected across the sample.

The magnetization as a function of the magnetic field of the film is shown in Figure 1.35.

Clearly, a ferromagnetic hysteresis loop with coercivity ~ 310 Oe was observed, indicating that the dominant phase of the films is ferromagnetic Fe.

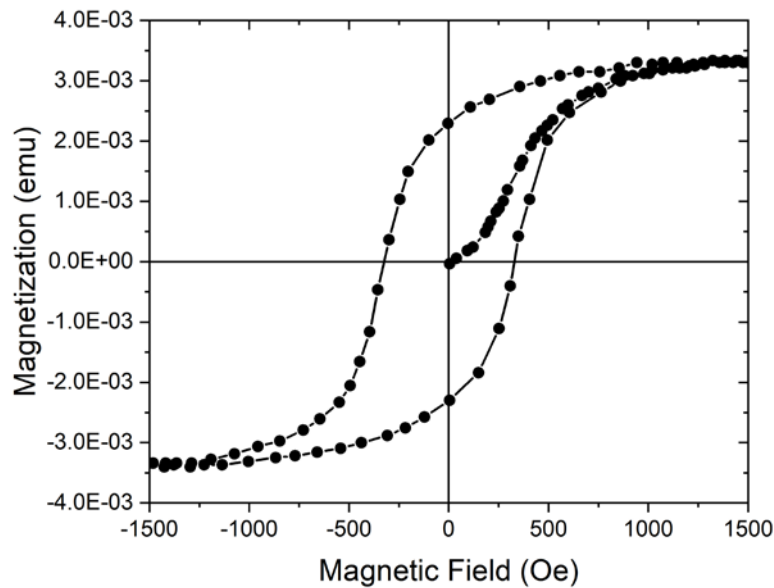


Figure 1.35. Magnetization vs. applied magnetic field curve of the film grown in the third attempt. A clear hysteresis loop with coercivity ~ 310 Oe was observed.

Since we have obtained the Fe dominated film with a certain amount of Ca122 impurities when using Fe : Ca ratio $\sim 8.7 : 1$, we decided to explore what effect of Ca122 had on the growth of epitaxial Fe film. To do that, we first grew pure Fe on STO substrate.

The growth parameters for the fourth attempt were chosen as:

Fe cell: 1200 °C, substrate: 650 °C, growth time: 3 h.

The evolution of RHEED pattern with electron beams incident along STO [100] direction during the growth is shown in Figure 1.36 (a).

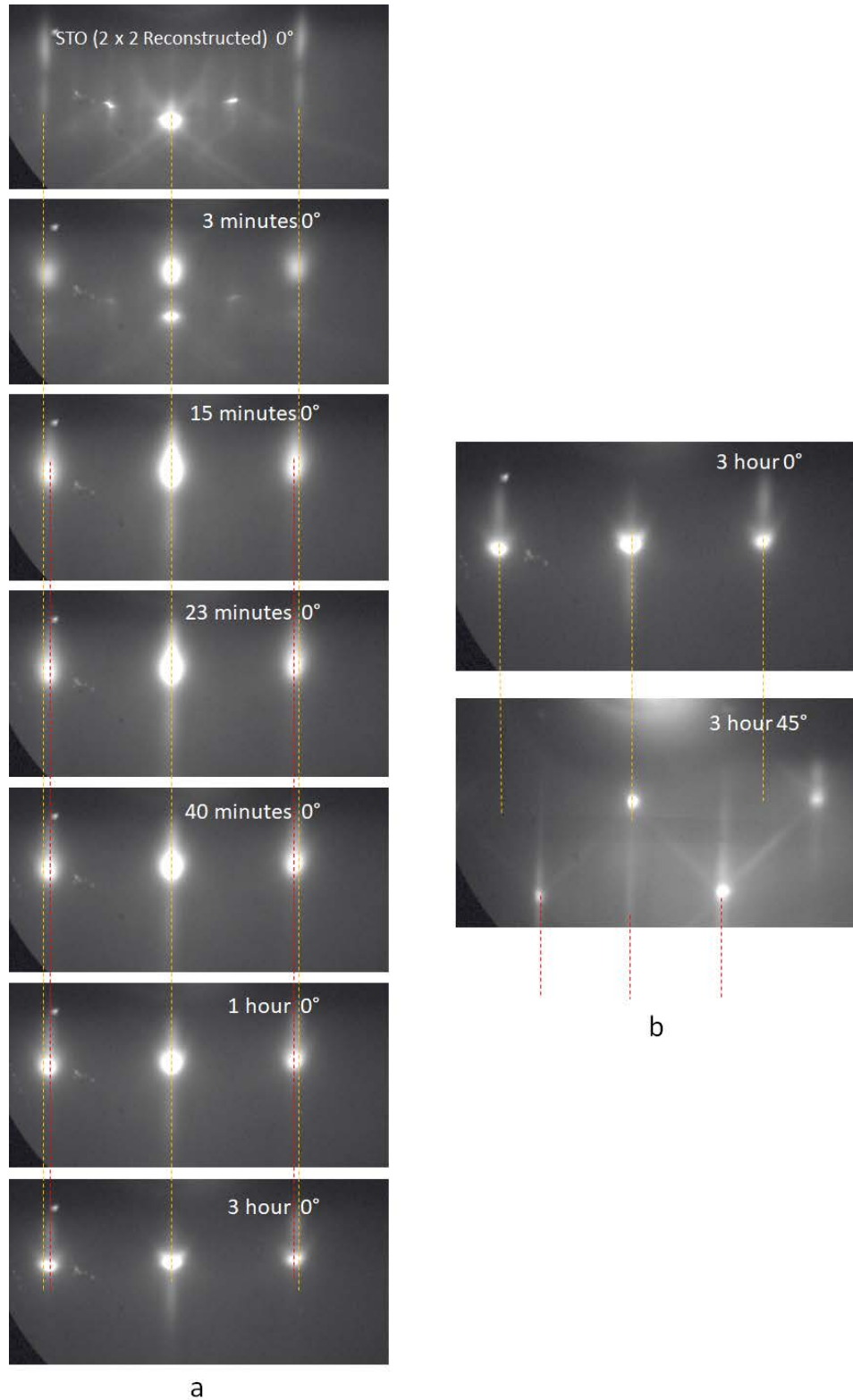


Figure 1.36. (a) Evolution of RHEED pattern taken along STO [100] during the 3-h growth of the fourth attempt. (b) Comparison between 0° (upper, along STO [100] direction) and 45° (lower) RHEED pattern.

Three RHEED spots were formed at 3 min and remained till the end of the growth. Even though weak streaks were formed at 15 min, the dots were still the dominant RHEED pattern, indicating the growth of Fe is isolated 3D island mode instead of 2D film mode. Combined with data of the 45° rotation shown in Figure 1.36 (b), the lattice constant calculated for the pure Fe sample is $\sim 2.865 \text{ \AA}$, in good agreement with the lattice constant of bcc ferromagnetic Fe ($2.866 \text{ \AA}$) [15]. No surface reconstruction was observed. It is worth mentioning that the STO UC dimension along $[110]$ was $5.52 \text{ \AA}$, and two Fe UC along the $[100]$ direction is $5.73 \text{ \AA}$. A small compressive lattice mismatch of $\sim 4 \%$ and a commensurate interface was achieved via a 45° rotation.

Figure 1.37 (a) and (b) show the topographic images of the pure Fe sample with 1-h and 3-h growth, respectively.

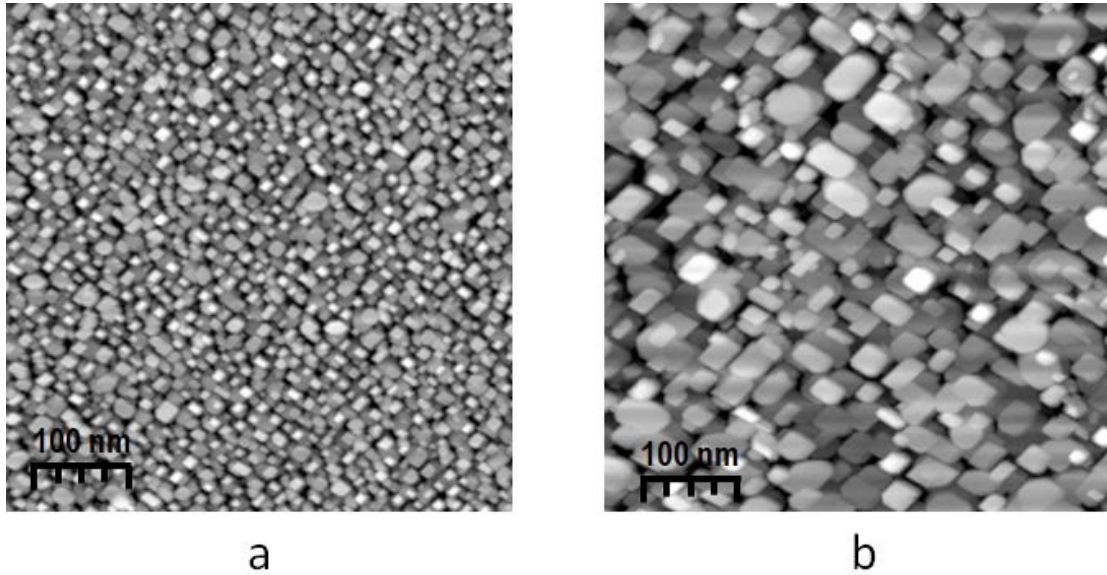


Figure 1.37. STM topographic images of the Fe sample from the fourth attempt with (a) 1-h growth, (b) 3-h growth. ($V = 3.0 \text{ V}$, $I = 20 \text{ pA}$, $500 \text{ nm} \times 500 \text{ nm}$)

3D isolated island growth was observed for both 1-h and 3-h pure Fe samples, consistent

with the RHEED observation. The average island size of the 1-h and 3-h samples are $\sim 15 \times 15 \text{ nm}^2$ and $30 \times 30 \text{ nm}^2$, respectively.

We decided to grow a thinner Fe dominated film with a certain amount of Ca122 impurities of 3 h to compare with the result of pure Fe samples.

The growth parameters for the fifth attempt were chosen as:

Fe cell: 1200 °C, Ca cell: 380 °C, As cell: both zones at 210 °C, substrate: 650 °C, growth time: 3 h, corresponding Fe : Ca ratio $\sim 8.7 : 1$.

The evolution of RHEED pattern with electron beams incident along STO (100) direction during the growth is shown in Figure 1.38. For the first 15 min, instead of immediately forming the streaks as the pure Ca122 film, formation of three spots (the same spots as that observed in Figure 1.36 (a)) was observed which corresponded to the formation of 3D Fe clusters. Note that during this period, no reconstruction was observed. After 15 min, RHEED streaks were gradually formed and the three spots were gradually faded away, indicating the growth tended to be quasi-2D like, instead of 3D island growth. Note that from 23 min, surface reconstruction streaks started forming and lasted till the end of the growth. By calculating the lattice constant, there were two possibilities: either the 2×2 surface reconstruction of Fe lattice, or a $\sqrt{2} \times \sqrt{2}$ surface reconstruction of Ca122 lattice. From the previous growth, we have confirmed that the growth of pure Fe on STO did not have surface reconstruction. Therefore, the observed surface reconstruction was believed to be the $\sqrt{2} \times \sqrt{2}$ surface reconstruction of Ca122. In other words, from 23 min onward, the surface of the Fe film was always covered by thin layers (few UC) of $\sqrt{2} \times \sqrt{2}$ surface reconstructed Ca122.

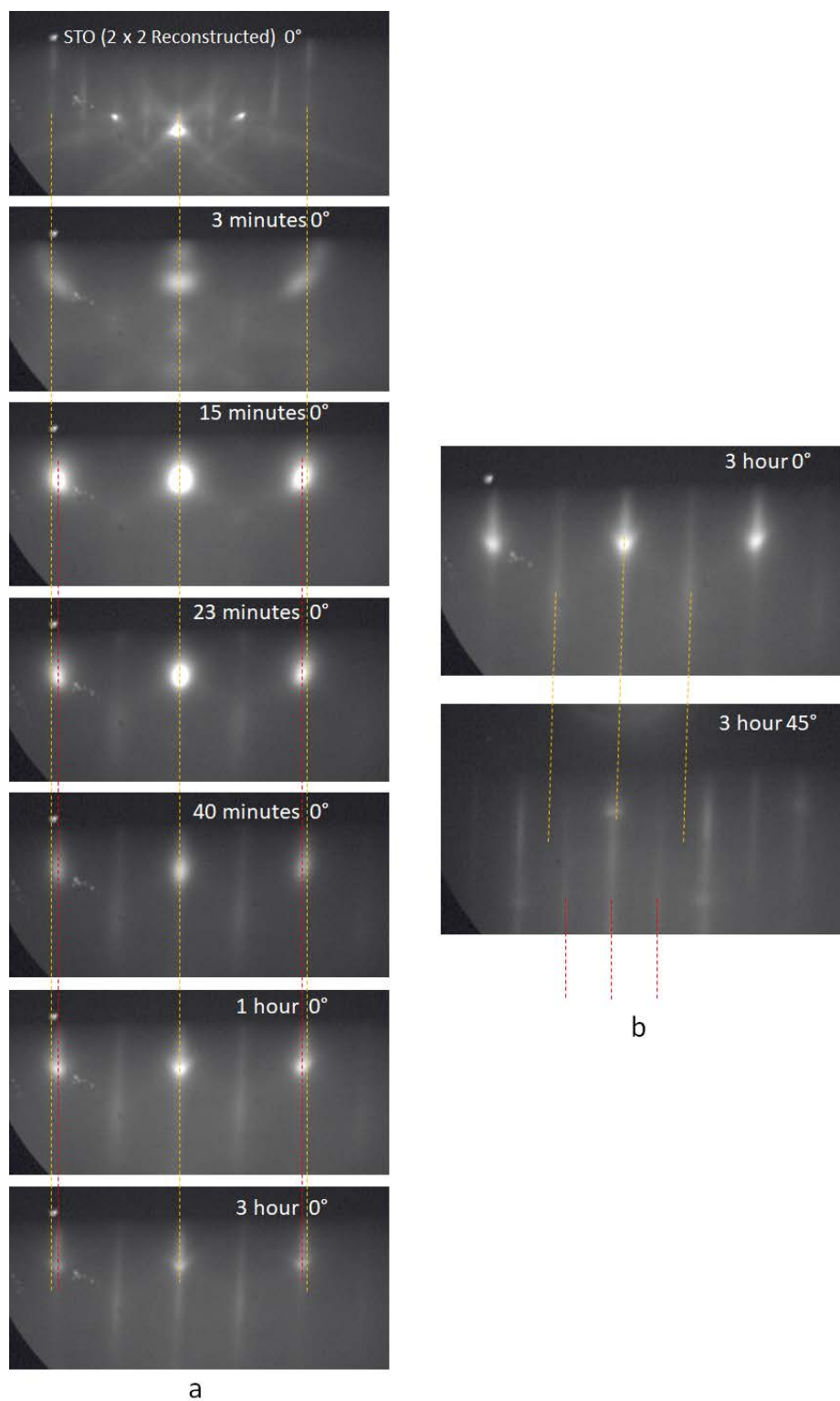


Figure 1.38. (a) Evolution of RHEED pattern taken along STO [100] during the 3-h growth of the fifth attempt. (b) Comparison between 0° (upper, along STO [100] direction) and 45° (lower) RHEED pattern.

Since the surface reconstructed Ca122 was grown on top of Fe whose 2 UC lattice constant (5.73 Å) along [100] is larger than the STO [110] lattice constant (5.52 Å), the calculated reconstructed lattice constant of the surface Ca122 is therefore ~ 5.73 Å, larger than the lattice constant calculated for the pure Ca122 grown on STO substrate directly (~ 5.56 Å). The exact coverage of the surface reconstructed Ca122 on Fe film would require the atomic resolution TEM measurement to be revealed. Figure 1.39 (a) and (b) show the topography of the Ca122/Fe sample with 1-h and 3-h growth, respectively.

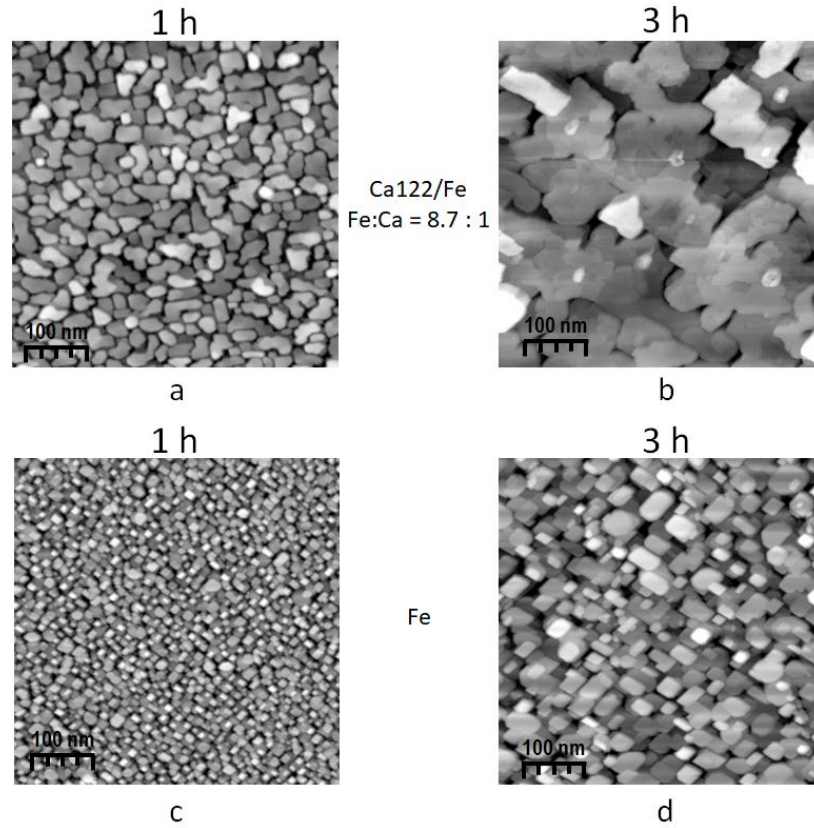


Figure 1.39. STM topographic images of the Ca122/Fe sample from the fifth attempt with (a) 1-h growth, (b) 3-h growth. ($V = 3.0$ V, $I = 20$ pA, 500 nm $\times$ 500 nm). The corresponding images for pure Fe sample with 1-h and 3-h growth are displayed in (c) and (d), respectively, for better comparison.

Clearly, with the co-existence of Ca122, the Fe film quality for both 1-hour and 3-hour

were significantly improved, and the growth of Fe tended to be quasi-2D film like, instead of 3D island growth with the absence of Ca122. The island average size was increased from $15 \times 15 \text{ nm}^2$ to $50 \times 50 \text{ nm}^2$ for 1-h growth, and $30 \times 30 \text{ nm}^2$ to $> 100 \times 100 \text{ nm}^2$ for 3-h growth.

To explain the improvement of the Fe film quality by the co-existence of surface reconstructed Ca122, we propose the following model as schematically illustrated in Figure 1.40. Initially, due to the Fe-rich flux ratio, there were not enough Ca and As to fully react with all of the Fe atoms. Therefore, for the first 15 min, isolated Fe islands were formed, as Fe atoms tended to climb along the deposited Fe islands, as illustrated in Figure 1.40 (a) and (b). In the meanwhile, Ca and As atoms were accumulated. At ~ 23 min, the accumulated Ca and As atoms started to react with the surface Fe atoms to form thin layers of $\sqrt{2} \times \sqrt{2}$ surface reconstructed Ca122 on top of Fe islands, as illustrated in Figure 1.40 (c). As supported by the fact that the reconstruction RHEED streaks occurred till the end of the growth, the thin layers of $\sqrt{2} \times \sqrt{2}$ surface reconstructed Ca122 existed through out the entire growth, and thus worked as a protection layer which suppressed the Fe atoms from climbing along the islands. As a result, the high-energy Fe atoms broke through the surface-reconstructed Ca122 layers and diffused into the film to fill the gaps, and thus formed quasi-2D epitaxial Fe films underneath, as illustrated in Figure 1.40 (d), (e), and (f). Since Ca and As atoms were continuously supplied, the broken surface-reconstructed Ca122 layers were continuously self-healed. The Fe film kept growing thicker with quasi-2D mode.

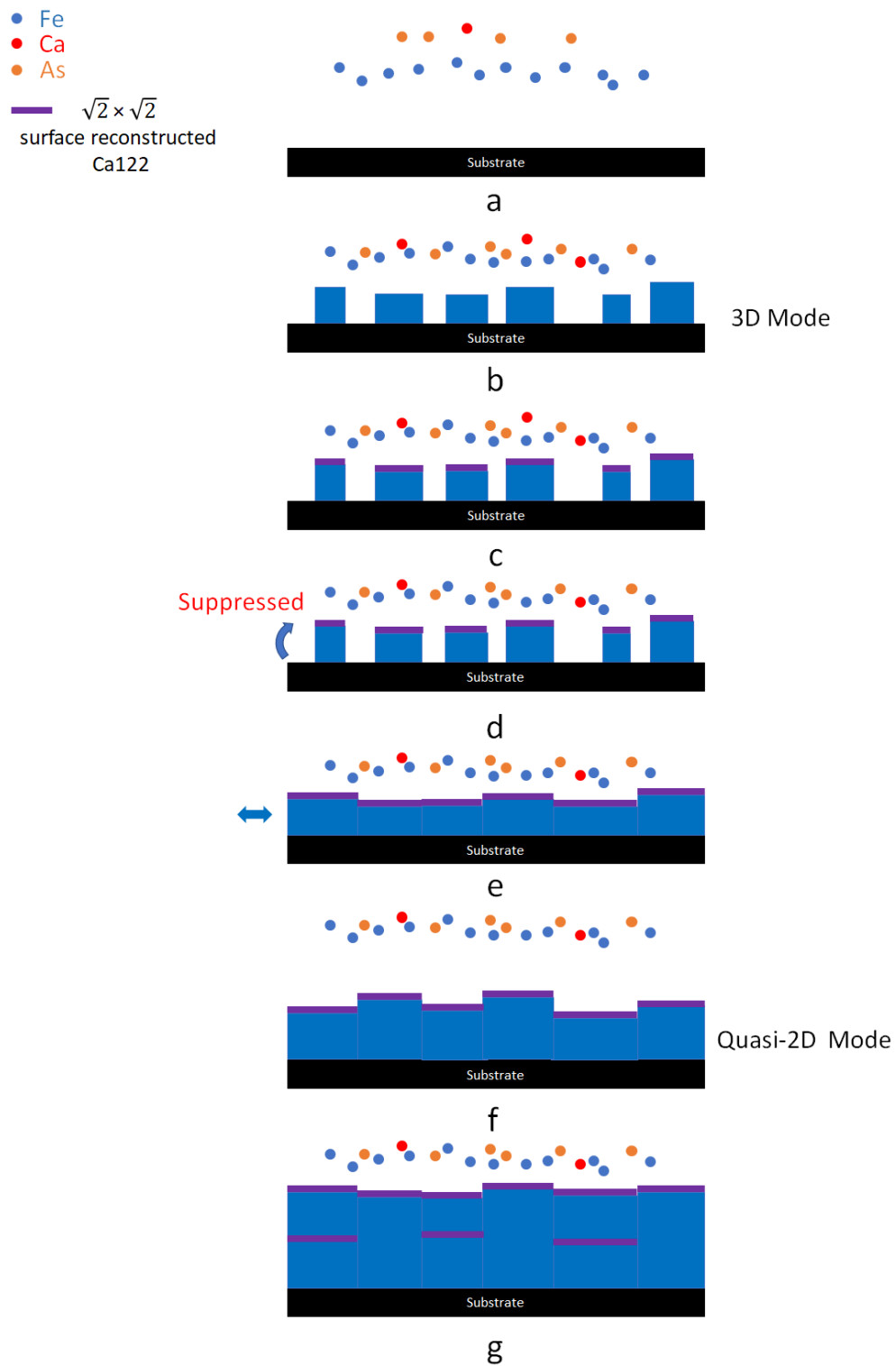


Figure 1.40. Schematic illustration of the model proposed to explain the improvement of the growth of Fe film by co-existence of $\sqrt{2} \times \sqrt{2}$ reconstructed Ca122.

Eventually, the surface-reconstructed Ca122 layers would become so thick that the high-energy Fe atoms could no longer break them. As a result, Fe atoms would then form epitaxial Fe films on top of the thick Ca122 layers, and the Fe film kept growing thicker in a quasi-2D mode, as illustrated in Figure 1.40 (g). Obviously, the top layers of the surface reconstructed Ca122 is crucial in improving the film quality and realizing the quasi 2D epitaxial growth of Fe films.

1.4.3 Conclusion

As a conclusion for this section, we have successfully obtained stoichiometric Ca₁Fe₂ film grown on STO substrate by choosing Ca : Fe flux ratio being 1 : 2. No impurity peaks were detected from X-ray measurements. The growth mode of Ca₁Fe₂ film was observed to be island growth mode instead of layer-by-layer growth. In addition, a $\sqrt{2} \times \sqrt{2}$ Ca surface reconstruction was observed. Interestingly, by drastically decreasing the Ca : Fe flux ratio, we discovered that the film we obtained was epitaxially-grown Fe-dominated film covered by thin layers of surface reconstructed Ca₁Fe₂, whose film quality was significantly better than pure Fe grown on STO. The growth mode of the Fe dominated film was quasi-2D film like, whereas the pure Fe on STO was a 3D isolated islands growth. The surface reconstructed Ca₁Fe₂ was essential in improving the Fe film quality. A model was proposed to explain the discovery.

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Chapter 2 Investigation on the Reported Superconductivity in Intercalated Black Phosphorus [1]

2.1 Introduction

Building on the work on graphene and a few other layered materials that followed, the two-dimensional layered black phosphorus (BP) has attracted great interest recently because of its scientific significance and device potential. Of particular interest is the tunability of its physical properties by varying the band structures by strain, electric field, number of layers, and intercalation. Superconductivity has also been predicted in an electron-doped monolayer [2] and Li-intercalated bilayer phosphorene [3]. This culminated in the recent report by Zhang *et al.* [4] of superconductivity intrinsic to the intercalated BP with a transition temperature T_c of 3.8 K, independent of the intercalant, whether an alkali or an alkaline earth element. Indeed, this is an observation of a highly unusual superconducting state that is independent of the valence, the content, and the size of the dopant, in contrast to previous understanding of known superconductors. The authors attribute this so-called universal superconductivity to the heavily doped phosphorene layers with the intercalated layers serving as charge reservoirs, similar to the modulation doping in layered high temperature superconductors. The significance of the report is self-evident, if proven.

We have therefore examined the reported results [4] carefully. The intercalant-independent T_c of BP and the apparent small superconducting volume fraction of all

samples investigated led us to the obvious question, *i.e.* could the observed superconductivity be caused by a small superconducting contamination in the samples? Given the reputation of the group, contamination introduced during sample preparation seems to be highly unlikely. However, it is rather intriguing to find that the reported T_c of 3.8 K and the field effect on the superconducting transition both appear to be similar to those for the pure Sn [5]. The magnetic anisotropy reported is also too small to be consistent with the model proposed. It is known that most of the commercially available BP crystals are prepared by transforming the red phosphorus through the chemical vapor transport technique with transport agents consisting of Sn or Sn-related compounds [6-9]. We have therefore decided to determine whether a minute amount of Sn is present in the starting BP crystals and, if yes, whether it is the culprit for the small superconducting signal detected.

2.2 Measurement and Characterization Techniques

2.2.1 X-ray Characterization

The powdered single crystals of BPs and Li (Na)-treated BPs synthesized by different methods were characterized by XRD using the Rigaku DMAX III-B diffractometer at room temperature with a Cu K ($\lambda = 0.154056$ nm) radiation source. To prepare the BP sample for X-ray measurement, the powders (small pieces) of BP (single crystals) were firmly pressed between two glass substrates. Due to the layered structural nature of BP, the pressed BP samples naturally prefer to orient along the basal plane. This explains why the intensity of $(00l)$ peaks is much higher than that of the other directions.

2.2.2 Energy-Dispersive X-ray Spectroscopy Analysis

The scanning electron microscope (SEM) images were taken by JEOL JSM 6330F. The corresponding energy dispersive X-ray spectra (EDX) mappings were executed in the same facility with the accelerating voltage of 15 V and working distance of 15 mm. Collection time was 5 min for all measurements.

2.2.3 Magnetization Measurement

The magnetic susceptibilities in this work were measured using a quantum design magnetic property measurement system (MPMS-3), which can measure magnetization

signal as precise as 10^{-8} emu. All samples were prepared and loaded in gelatin capsules in glove box with Ar gas to prevent from any possible oxidization.

2.2.4 Resistance Measurement

The resistance in this work were measured using a quantum design physical property measurement system (PPMS) with standard 4-leads method. Silver paste were used to attach platinum wire to samples.

2.3 Material Synthesis and Intercalation Methods

To determine if the Sn-contamination can be introduced from chemical vapor transport synthesis, we have started with three different BP crystal sources (BP-1, BP-2, and BP-3): BP-1 was purchased from Smart Elements Germany, from which Zhang *et al.* obtained their BP crystals; BP-2 was prepared in our lab by the standard vapor transport method at ambient pressure; and BP-3 was made in our lab by the well-known high-pressure technique [10].

2.3.1 Material Synthesis

BP-1 crystals were purchased from Smart Elements in Germany, from which Zhang *et al.* obtained their BP crystals with the same purity (99.998%).

BP-2 crystals were prepared by converting the red phosphorus to black phosphorus by sealing appropriate amounts of red phosphorus (99.999%, Aldrich, 350 mg), Sn (99.99+%, Alfa Aesar, 35 mg), and I₂ (99.8+%, Fisher Scientific, 30 mg) in an evacuated quartz tube (12.7 mm in diameter, 127 mm in length), which is then placed in a tubular furnace with a temperature of 620 °C at the center and 27 °C at the end. Crystals of sizes up to $\sim 3 \text{ mm} \times 1 \text{ mm} \times 0.5 \text{ mm}$ were harvested at the cold end of the quartz tube.

BP-3 crystals were achieved by transforming red phosphorus powder (99.99+%, Aldrich, 0.28 g) wrapped in Au-foil under 1.5 GPa at 750 °C for 30 min followed by quenching to room temperature.

2.3.2 Intercalation Methods

Two different intercalation methods were performed on these starting BP crystals: A) n-Butyllithium treatment for Li-intercalant, and B) electrochemical treatment for Li- and Na-intercalants. According to method A, the BP crystals were immersed for one week in the 1.33 M n-butyllithium (Alfa Aesar) in hexane (Aldrich) solution in a beaker covered by parafilm in an Ar atmosphere at room temperature. According to method B, a galvanostatic cell with a BP-composite electrode as a cathode and a metal anode immersed in an electrolyte is discharged to 0.01 V at a current of 2 μ A. For Li-intercalation the anode is Li-metal and the electrolyte is 1 M LiPF_6 in a 1:1 diethyl carbonate/ethylene carbonate mixed solution with Celgard polypropylene as the separator. For Na-intercalation, the anode is Na-metal and the electrolyte is 1 M NaClO_4 in a 1:1 propylene carbonate/ethylene carbonate mixed solution with glass fiber as the separator.

2.4 Results and Discussion

X-ray diffraction (XRD) results with distinct $(0\ell0)$ - peaks characteristic of nice single crystals of the starting BP-1, -2, and -3 (with weak peaks from other orientations and a trace amount of Au_2P_3 from the wrapping during synthesis), all with $b \sim 10.472 \text{ \AA}$, in agreement with published data, are shown in Figure 2.1. Energy-dispersive X-ray spectroscopy (EDS) has also been carried out on all these starting BP crystals, as shown in Figure 2.2. The results show traces of Sn and I in BP-1 and -2, but not in BP-3, as expected. Detailed magnetic measurements ($\chi_\perp$ s) with the measuring field perpendicular to the ac-plane to maximize the signal did not display any sign of superconductivity within the MPMS3 sensitivity limit of 10^{-8} emu down to 2 K in these starting BP crystals.

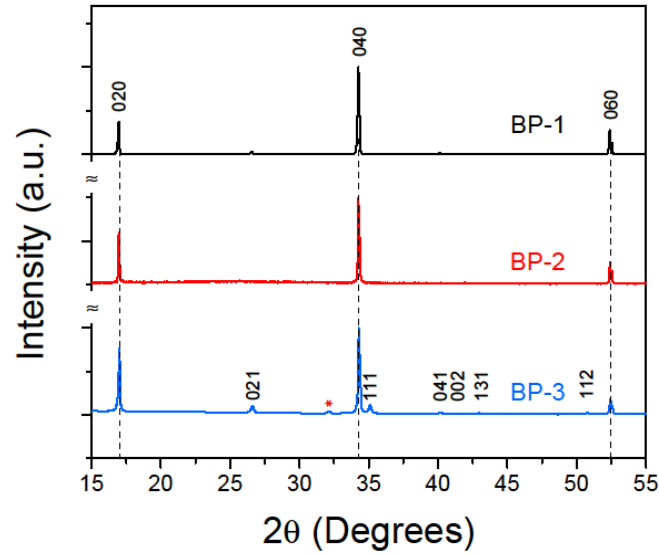


Figure 2.1. X-ray diffraction spectra of starting BP-1, -2, and -3. * indicates the known peak for Au_2P_3 .

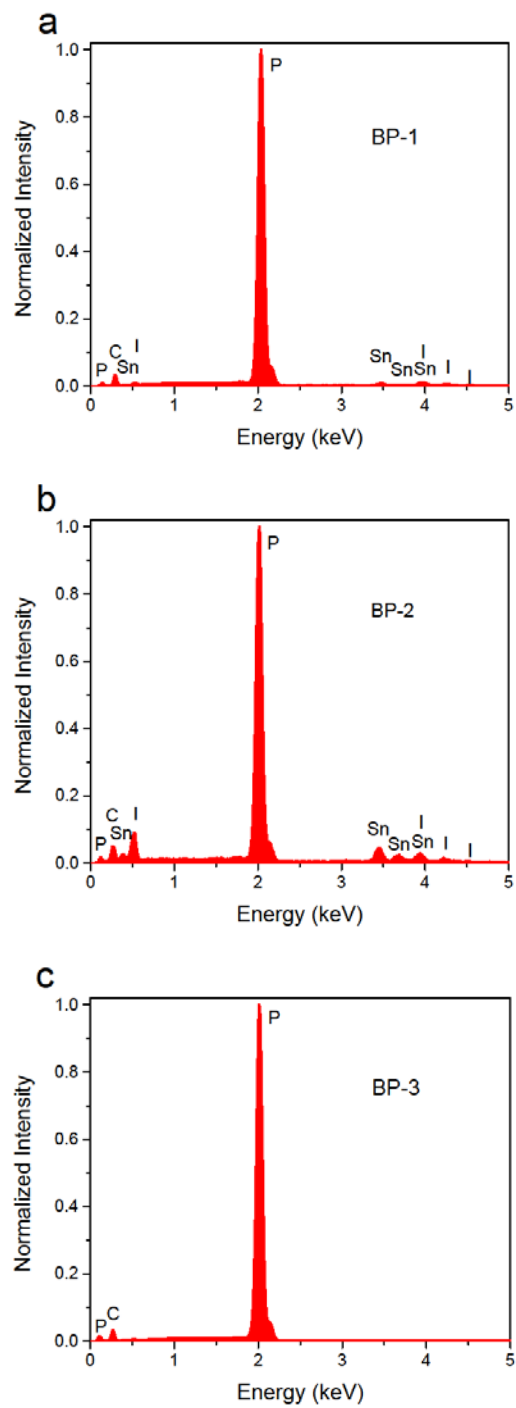


Figure 2.2. EDS analysis for starting BP crystals. (a) BP-1. (b) BP-2. (c) BP-3.

Intercalations were then performed on these starting BP crystals as explained in

Section 2.3.2. XRD of the Li- and Na-intercalated BP samples all show the same diffraction patterns within our resolution as those before intercalation, as shown in Figure 2.3. The exposure to air does not seem to affect XRD patterns, in contrast to that previously reported [4], probably due to the slight misalignment of the crystals in the previous report.

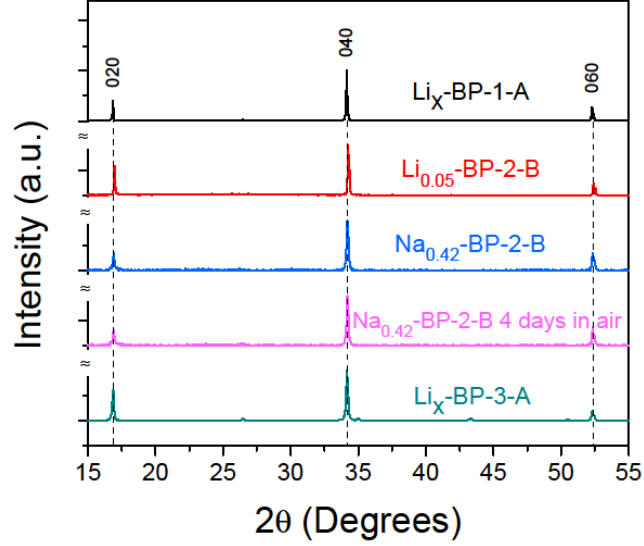


Figure 2.3. X-ray diffraction spectra of Li- or Na-intercalated BP-1, -2, and -3. The same Na-intercalated BP-2 was measured before and after exposure to air for four days.

The magnetic measurements, $\chi_{\perp}$ s, with the measuring field perpendicular to the ac-plane, show a small but distinct and sharp superconducting transition with a $T_c \sim 3.8$ K of up to $\sim 1\%$ volume fraction in the Li- and Na-intercalated BP-1 and -2 but not in the BP-3, as shown in Figure 2.4 (a) and (b), consistent with the absence of the resistive sign of superconductivity shown in Figure 2.5. In Figure 2.4 (c), an externally applied magnetic field is shown to suppress the superconducting transition progressively to below 2 K above ~ 300 Oe, suggesting a critical field of ~ 300 Oe. Similar to Zhang *et al.*, we found that the T_c is ~ 3.8 K in BP-1 and BP-2 intercalated with Li by method A or B, and Na by method

B, independent of the intercalant or the amount of intercalant. For comparison, the superconducting transition of Sn is also included in Figure 2.4 (a) and (b). The similarity between the intercalated BP-1 and -2 and Sn is evident. Field effects on the superconducting transitions of Li-intercalated BP-2-B and Sn are depicted in Figure 2.4 (c). The similarity between the two again is clear. The magnetic anisotropy is small ~ 1.3 , as shown in Figure 2.6, in contrast to that expected of the model proposed [4].

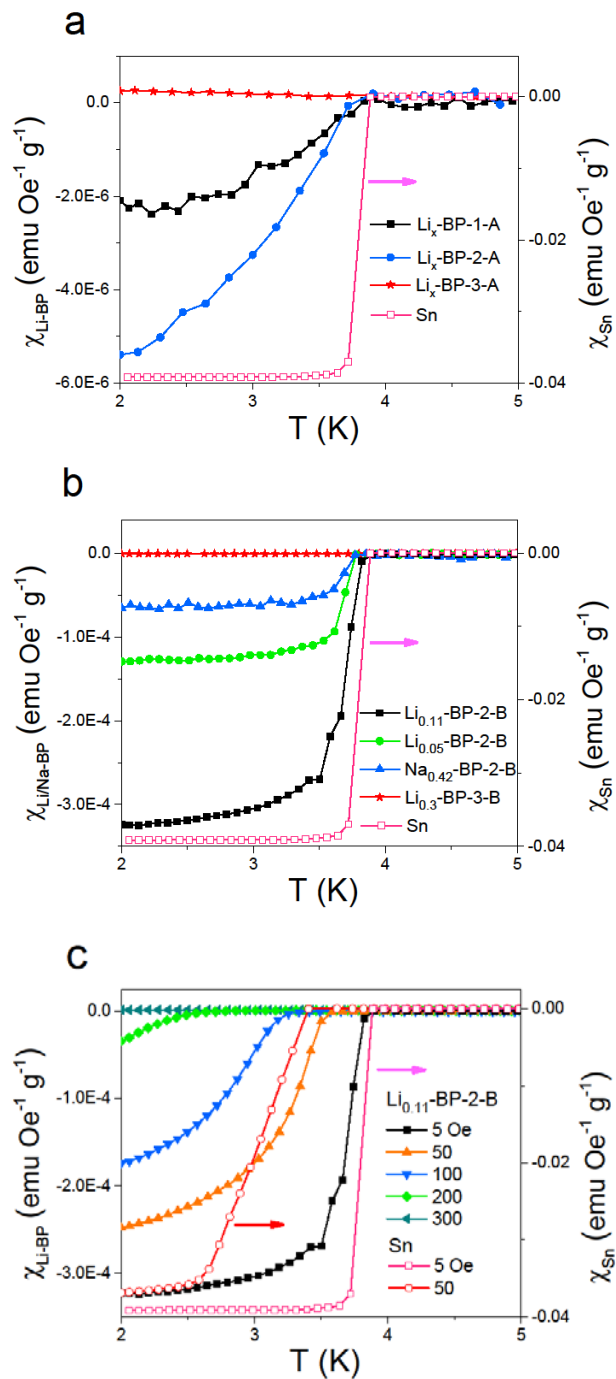


Figure 2.4. Comparison between intercalated BP and Sn. Temperature dependence of $\chi_{\perp s}$ for (a) n-Butyllithium-intercalated BP-1, -2, and -3, and Sn, and (b) Electrochemically intercalated BP-2 and -3 and Sn. (c) Field effects on lithium-intercalated BP-2 and Sn. All data shown are ZFC $\chi_{\perp s}$.

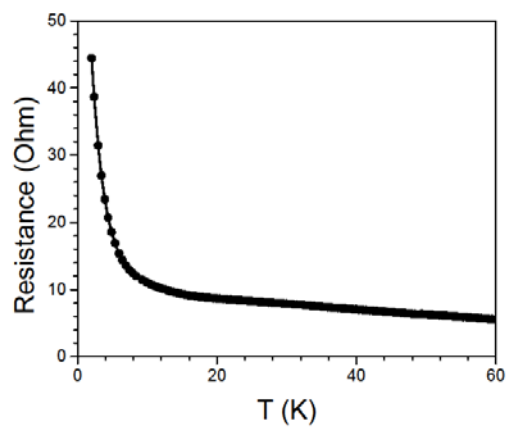


Figure 2.5. Resistance vs. temperature of lithium-intercalated BP-2.

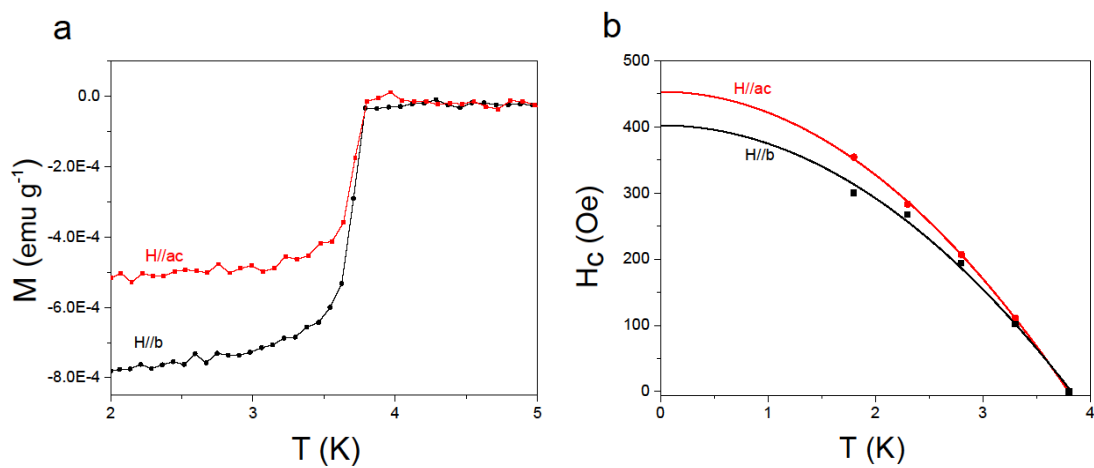


Figure 2.6. Magnetic anisotropy of Li-intercalated BP-2. (a) Parallel and perpendicular magnetization as a function of temperature at 5 Oe. ZFC curves are shown. (b) Parallel and perpendicular critical fields as a function of temperature.

2.5 Conclusion

In conclusion, we have reproduced the superconducting transition at 3.8 K in Li- and Na-intercalated BP crystals that consist of minute amounts of free Sn (reduced from the residual non-superconducting Sn compounds by Li or Na) when prepared by the vapor transport technique but not in BP crystals that are free of Sn when prepared by the high-pressure technique. The superconducting transition takes place at the same temperature as pure Sn and the field effect on the transition is similar to that on Sn. The magnetic anisotropy of the superconducting state in the Li- and Na-intercalated BP is rather small. We have therefore concluded that the superconducting transition reported by Zhang *et al.* is associated with the Sn but not intrinsic to the intercalated BP.

2.6 References

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