

Van der Waals Epitaxy of Hexagonal FeSe on Passivated Si(111) Surfaces

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In loving memory of my father

Khimlal Dahal

September 17, 1942

to

October 18, 2023

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Abstract

The discovery of high-temperature superconductivity with T_c 's of about 60 to 70 K in one unit-cell-thick FeSe films on SrTiO₃ (STO) and related oxide substrates has generated a lot of interest in the condensed matter physics community. These findings suggest entirely new strategies for controlling superconductivity via interface engineering. Little is understood, however, about why oxide substrates are so special in boosting the superconducting T_c . To advance our understanding regarding the role of the substrate, it is essential to explore a variety of other substrates. Silicon is a particularly important materials platform because it has been -and still is- the main driver of technological innovation. The synthesis of superconducting FeSe thin films on a Si substrate would thus be a first step towards integrating unconventional superconductors into existing silicon technology. Unfortunately, FeSe deposition onto the Si(001) or Si(111) substrate produces unwanted Fe silicides. In this thesis, we developed a method to passivate the Si(111) substrate, which facilitates the van der Waals epitaxy of FeSe thin films. The films are primarily hexagonal, though tetragonal films can also be stabilized, depending on the growth parameters. The purpose of this work is to explore the initial stages of growth and the structure and electronic properties of these ultrathin films.

Thin films were grown with molecular beam epitaxy and studied with electron diffraction, photoemission, and scanning tunneling microscopy/spectroscopy (STM/STS). The films adopt the NiAs structure and appear to be metallic at room temperature. Films that are only one unit cell thick are particularly interesting as

they exhibit new superstructures at low temperature that are tentatively attributed to a charge density wave instability. The latter would be in direct competition with the antiferromagnetic (or ‘altermagnetic’) ground state, a scenario that is often encountered in unconventional superconductors. Hexagonal FeSe thin films may thus become an interesting testbed for understanding superconductivity in Fe-based superconductors.

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Chapter 1

Introduction and Scope

1.1 Metal Chalcogenides

The Group VI-A elements of the Periodic Table or ‘chalcogens’ (O, S, Se, and Te) contain four electrons in their outer p -shell. Their chemical reaction with transition metal atoms produces a wide variety of metal chalcogenides. The simplest ones are binary compounds such as MX and MX_2 where M is the metal and X is the chalcogen atom. They exhibit an interesting variety of polymorphic crystal structures that are associated with the stacking sequence of the polarizable chalcogen atoms (particularly S, Se, and Te). These materials are of great interest because of their unique chemical, electronic, and optical properties ([Bhimanapati et al. \(2015\)](#)), with applications in semiconductors, electronics, photocatalysis, solar cells, photodetectors, photovoltaics, energy materials, etc. ([Gao et al. \(2013\)](#), [Gao et al. \(2012\)](#), [Puthussery et al. \(2011\)](#), [Lai et al. \(2010\)](#), [Arachchige and Brock \(2007\)](#), [Kershaw et al. \(2013\)](#)).

The crystal structure of the S, Se, and Te compounds is usually derived from a closed-packed arrangement of the chalcogen atoms where the metal ions occupy the octahedral or tetrahedral holes in this structure. For instance, hexagonal MX compounds, such as FeSe , CrTe , and MnSb , crystallize the so-called NiAs structure. This is a hexagonal close-packed (hcp) arrangement of chalcogen atoms where the

metal atoms occupy the octahedral holes of the hcp structure. These structures tend to be metal deficient or ‘sub-stoichiometric’, meaning that metal vacancies are easily accommodated. Interestingly, vacancies only appear in every other metal layer, implying an alternating stacking order of complete metal layers and metal-deficient layers with chalcogen layers in between. In extreme cases, vacancy layers are completely vacant, resulting in a layered MX_2 compound or ‘van der Waals’ compound. Here, covalently-bonded MX_2 slabs are held together by weak van der Waals forces (Lévy (2012)). Van der Waals interactions are attributed to fluctuating induced dipole-dipole interactions that are about two orders of magnitude weaker than a chemical bond (Reed-Hill and Abbaschian (1992)).

Tetragonal FeSe, on the other hand, is derived from a cubic close-packed (ccp) structure of Se atoms where the Fe atoms occupy the tetrahedral holes of the ccp structure. Since there are twice as many tetrahedral holes than octahedral ones, the composition would be Fe_2Se . However, if we allow for the presence of vacant ‘Fe layers’, one obtains a layered crystal structure where FeSe slabs are separated by van der Waals gaps. This particular van der Waals compound has sparked a great deal of interest as it turned out to be an 8 K superconductor in bulk form while showing a nearly tenfold increase in T_c for a single layer slab grown epitaxially on SrTiO_3 .

1.2 Superconductivity in Tetragonal FeSe

The discovery of high-temperature superconductivity in copper-based oxide compounds or ‘cuprates’ in 1986 is among the greatest scientific discoveries of the 20th century (Bednorz and Müller (1986)). The more recent discovery of high-temperature superconductivity in iron-based compounds (Kamihara et al. (2006)) is also highly significant, especially because Fe is a magnetic element and thus believed to be incompatible with superconductivity. The superconducting T_c of 55 K in $\text{Sm}[\text{O}_{1-x}\text{F}_x]\text{FeAs}$ reported by Zhi-An et al. (Zhi-An et al. (2008)) held the record for Fe-based superconductivity until 2012, and was only surpassed by those

of the copper-based compounds (under atmospheric pressure conditions), the highest of which was reached in the Hg-Ba-Ca-Cu-O compound (~ 134 K) (Schilling et al. (1993)). The story became even more fascinating in 2012 when researchers discovered that the superconducting gap (2Δ) of a single unit-cell thick epitaxial FeSe film on the SrTiO₃(001) substrate is about 20 meV (Qing-Yan et al. (2012)), as shown in Figure 1.1(a). This generated a lot of interest and enthusiasm as the authors estimated the superconducting transition temperature to be about ~ 77 K. This was indeed confirmed in other studies (Rebec et al. (2017), Peng et al. (2014)). Figure 1.2 shows the timeline showing the discovery of different superconductors, including the Fe pnictides and chalcogenides. The various symbols indicate different classes of materials (de Rijk (2021)).

Many studies have been conducted in recent years to uncover the mechanism behind this nearly tenfold increase in the superconducting T_c in the ultrathin film limit. Remarkably, STS data show that the addition of a second FeSe layer completely suppresses superconductivity, displaying semiconducting behavior instead (Figure 1.1(b)). This interesting result suggests the possibility of tuning low-dimensional superconductivity via substrate modification. Whether such high T_c can indeed be realized for other substrates remains a fascinating topic for future research.

A possible explanation for the high T_c at the FeSe/STO interface is the tensile strain of the FeSe film, which would enhance the antiferromagnetic exchange interaction in FeSe and possibly the superconducting pairing interactions (Cao et al. (2014)). This postulate was ruled out later because T_c barely changes as a function of strain (Rebec et al. (2017), Huang et al. (2016), Peng et al. (2014)). It was also suggested that the enhanced T_c might be due to the large low-temperature polarizability of STO, which would enhance the screening of the Coulomb interaction between the electrons that make up the Cooper pair. This possibility was later refuted because similar T_c 's were found in substrates with very different polarizability such as FeSe/Nb:BaTiO₃ and FeSe/TiO₂ (Rebec et al. (2017), Peng et al. (2014), Ding et al. (2016), Song et al. (2019)).

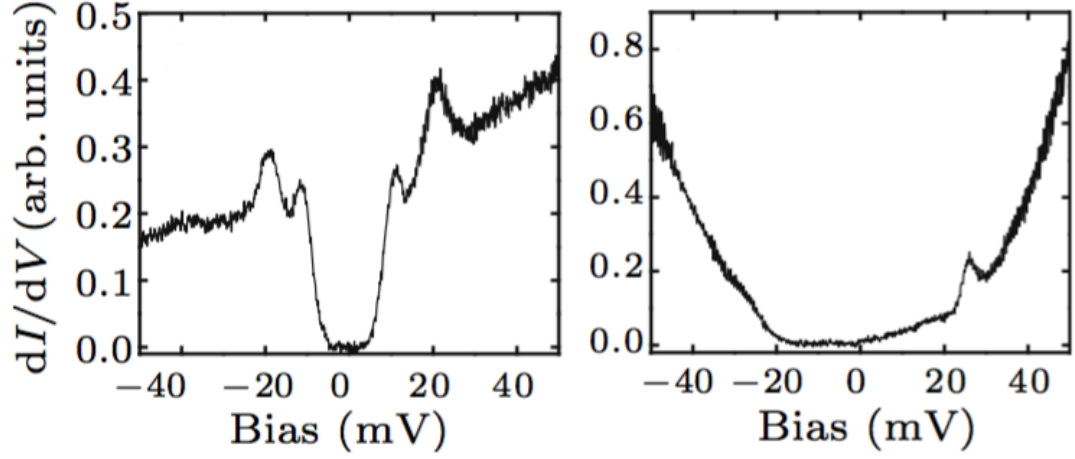


Figure 1.1: (a) Tunneling spectrum of one unit-cell-thick FeSe film grown on STO(100) at 4.2 K revealing a superconducting gap of approximately 20 meV. (b) Tunneling spectrum of a two unit-cell-thick FeSe film, indicating conventional semiconductor behavior (Qing-Yan et al. (2012)).

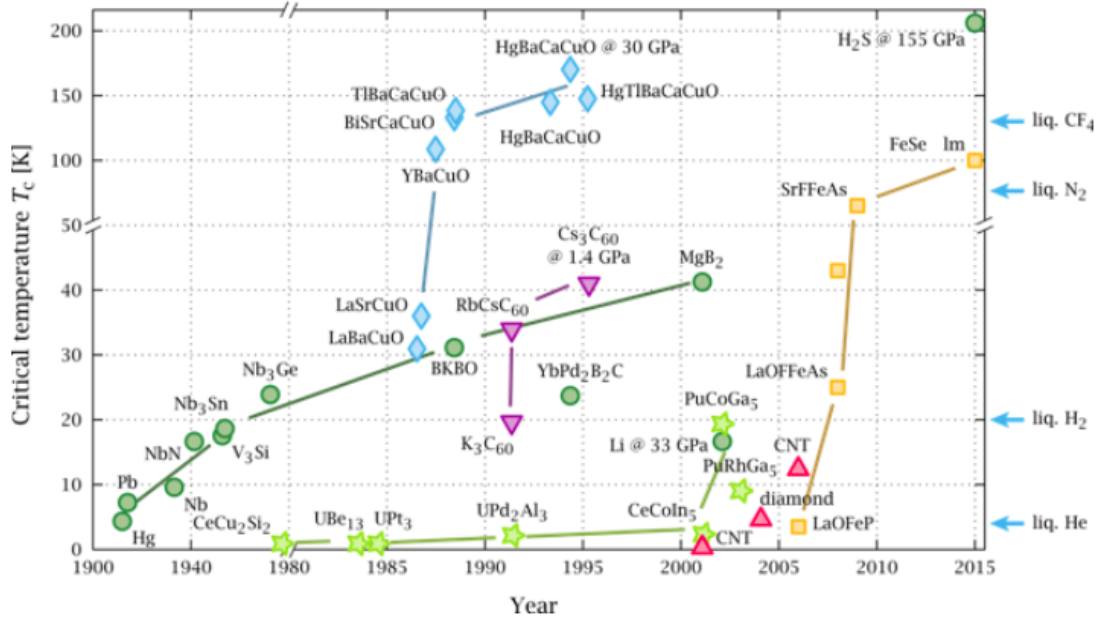


Figure 1.2: Timeline showing the discovery of different superconductors. Green circles are for the metallic superconductors, the blue rhombus denotes the cuprates, and the yellow squares represent the iron-based superconductors (de Rijk (2021)).

A possibly important lead for understanding high T_c superconductivity in one UC thick FeSe/STO is obtained from the angle-resolved photo-emission spectroscopy (ARPES) measurements reported in Ref. (Lee et al. (2014)). Here, the superconducting gap was reported to be 13 meV, which closed at around ~ 58 K. The salient finding is the observation of ‘replica bands’, shown in Figure 1.3(a) at ~ 100 meV below the main band and on top of a broad hole band. The replica for the hole band is also seen. The authors (Lee et al. (2014)) believe that the bands are due to intrinsic electron-phonon coupling. These bosonic modes are associated with the high-energy phonon band near 100 meV in the SrTiO₃ substrate (Lee et al. (2014)). Because the replica band follows precisely the same dispersion as the main band, the momentum transfer of the electron-phonon scattering must be minimal (Rademaker et al. (2016)). It was, therefore, suggested that the scattering between the optical phonons of the STO substrate and electrons in the FeSe thin film is forward-focused. This localized scattering can enhance electron pairing without disrupting their momentum significantly, providing a boost to the pairing interaction. The coupling from the phonons in STO with forward scattering stabilizes the pairing symmetry and raises T_c . As for pairing symmetry, the STS indicates a hard superconducting (U-shaped) gap, suggesting an s-wave pairing. The other significant finding is that the ARPES spectra and band structures for the thicker films (2 and 30 UC FeSe) resemble those of bulk FeSe (Rebec et al. (2017), Nakayama et al. (2014)). Importantly, the replica bands are only observed in one unit-cell-thick FeSe films, as shown in Figure 1.3.

Two interfacial effects are considered to play a role in the high T_c . One is the coupling between the FeSe electrons and STO phonons, and the other is electron transfer from the Nb-doped (n-type) STO substrate to the FeSe monolayer. Zhou et al. studied FeSe on MgO and found that Fe substitution in the interfacial MgO layer induces a charge transfer from the substrate to the films and increases the T_c of the monolayer FeSe film (Zhou et al. (2018)). An STM study by Tang et al. found that potassium absorption can induce superconducting gaps in 2 unit-cell-thick of FeSe on STO (Tang et al. (2015)).

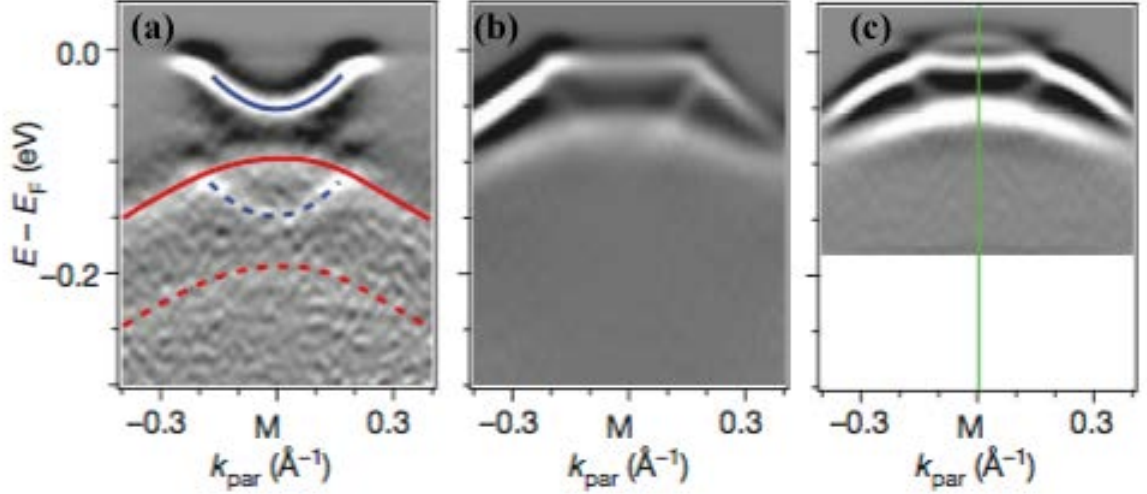


Figure 1.3: ARPES spectrum of a (a) 1 UC thick (left) film, (b) 2 UC thick film (center), and (c) 30 UC thick film (right). The solid line indicates the main band, and the dashed line indicates the replica band on the one unit-cell-thick (UC) spectrum. Replica bands are not observed for 2 UC and 30 UC thick films (Lee et al. (2014)).

Figure 1.4 (Rebec et al. (2017)) is a plot of the T_c versus the superconducting gap size for iron-based superconductors. These two have a linear relationship, as shown in Figure 1.4. The takeaway from the plot is the clear subset of the superconductors into three groups. The bulk and multilayer FeSe along with 1-4 layer FeSe/SiC (Song et al. (2011)), and FeSe_(1-x)Te_x (Noji et al. (2010)) have low T_c similar to that of bulk FeSe. There is no noticeable charge transfer or other substrate effect. The middle group reveals higher T_c due to potassium doping or gating. The third group contains single monolayer FeSe films on titanate substrates where the replica bands are seen. The Fermi surfaces between these groups and the electron-doped systems in the second group are similar, but the superconductivity is further enhanced in the latter. It is evident that superconductivity can be raised by charge doping or via electron-phonon coupling involving the substrate, which increases T_c to about 70 K. Thus, the enhanced superconductivity is due to the additive effect of charge doping and substrate selection. Recently, it has been reported that the high superconducting transition temperature in FeSe/SrTiO₃ is the combination of the intrinsic pairing

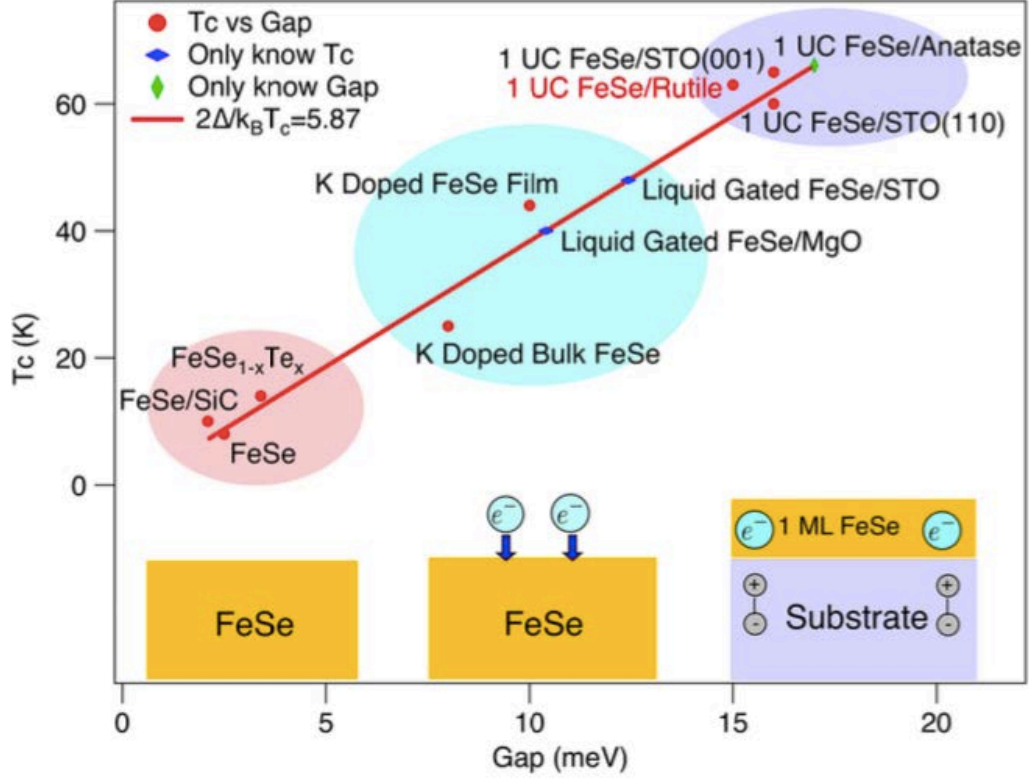


Figure 1.4: Plot of T_c and maximum superconducting gap of bulk FeSe, FeSe compounds, doped FeSe films, and 1 ML FeSe film on different substrates. The red line is the linear fit. FeSe is divided into three categories: i) (left) no effect of charge transfer or substrate, ii) (middle) effect of external charge transfer but not of substrate, iii) (right) effect of substrate-induced charge transfer and electron-phonon coupling (Rebec et al. (2017)).

mechanism in the FeSe and the coupling between the FeSe electrons and SrTiO_3 phonons (Song et al. (2019), Rademaker et al. (2021)).

The Fermi surface of Fe-based superconductors consists of a hole pocket centered at the Γ -point and an electron pocket centered at the M-point of the Brillouin zone. The pairing symmetry is believed to be an extended s-wave, which may be mediated by phonons and/or antiferromagnetic fluctuations (Sadovskii (2008), Hirschfeld et al. (2011)). On the other hand, the FeSe monolayer on STO has no hole-pockets, and there is no consensus yet regarding its pairing symmetry. (Rademaker et al. (2016), Wang et al. (2016)).

1.3 Hexagonal FeSe

All the FeSe films with the enhanced superconducting temperature discussed above have a tetragonal crystal structure. These films, referred to as β -FeSe, are grown at a relatively high substrate temperature of around 450 °C. When the substrate temperature is low, around 300-350 °C, hexagonal FeSe films, labeled α -FeSe, are obtained (Tan et al. (2017)). These hexagonal FeSe films are found to be non-superconducting. The crystal structure of PbO-type tetragonal (Tan et al. (2017)) and NiAs-type hexagonal FeSe (Zhou et al. (2019)) is shown in Figure 1.5. The small and large spheres are Fe and Se atoms, respectively, for hexagonal FeSe.

Recently, Hong et al. grew hexagonal and tetragonal phases of FeSe on two different reconstructed STO surfaces, namely the 2×1 and $(\sqrt{13} \times \sqrt{13})\text{-R}33.7^\circ$ reconstructions, respectively (Hong et al. (2024)). Also, different FeSe phases were grown on bilayer graphene. The hexagonal phase is observed at a substrate temperature of about 180 °C, while the tetragonal and orthorhombic phases are obtained between 180 °C and 220 °C (Song et al. (2011)).

Figure 1.6 shows the NiAs crystal structure. As mentioned before, it consists of an hcp stacked crystal of anions (e.g., As, Se) with cations (e.g., Cr, Mn, Fe) filling the octahedral holes of the hcp sublattice. The cations are octahedrally coordinated by the anions, whereas the anions are at the center of a trigonal prism of cations. Thus, the NiAs structure is AcBcAcBc... layered where Ni occupies the c-sites. This structure would be unstable for ionic compounds because direct cation-cation repulsion along the c -axis would destabilize the NiAs structure. Typically, NiAs compounds contain polarizable anions, such as S, Se, P, As, Te, etc, in combination with divalent or trivalent transition metal cations, such as Cr, Mn, and Fe.

Many of these systems contain cation vacancies in every second cation layer. Vacancy ordering leads to non-stoichiometric phases such as Cr_3S_4 , Cr_7S_8 , Fe_7S_8 , Fe_7Se_8 , etc. In the extreme case where every second cation layer is completely vacant, we obtain a layered van der Waals material (e.g., CrSe_2).

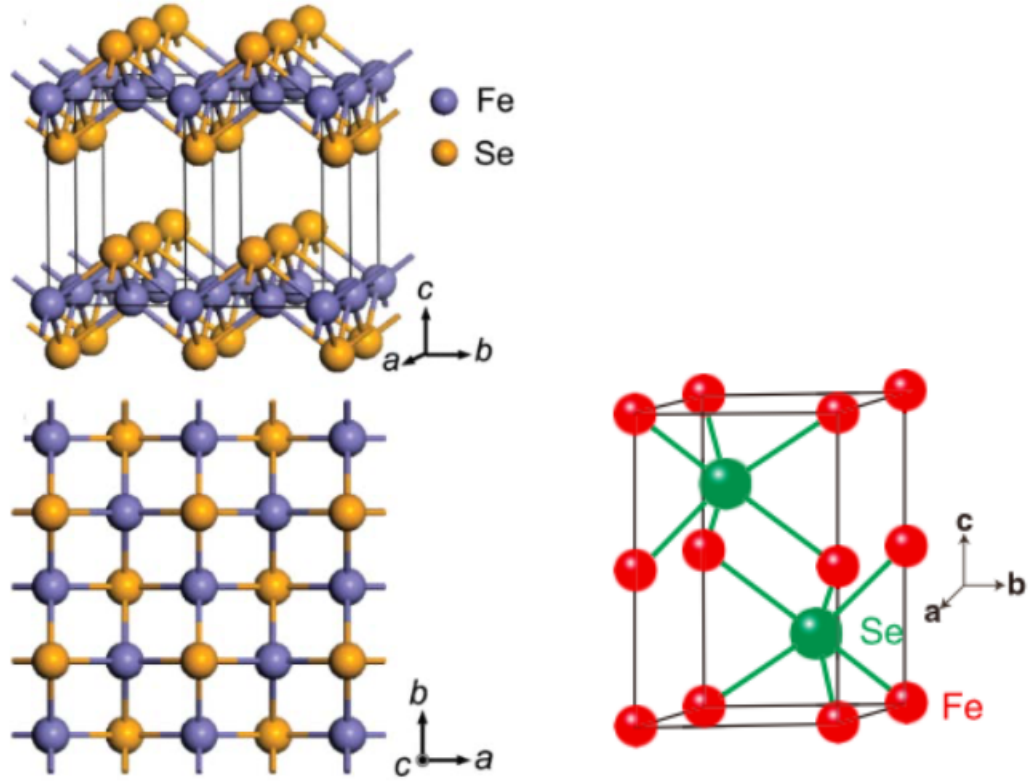


Figure 1.5: Crystal Structure of tetragonal (left) and hexagonal (right) FeSe.

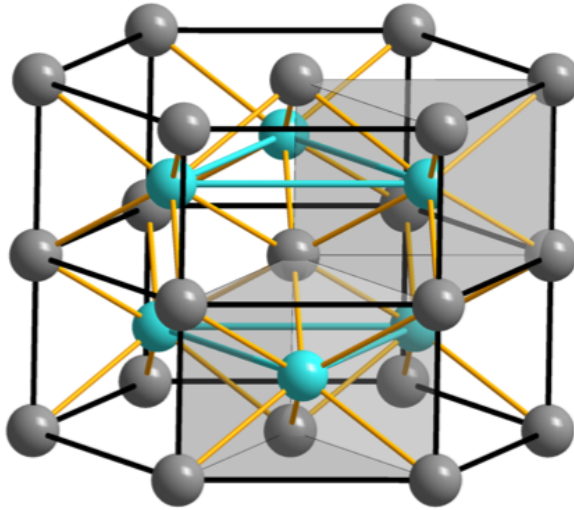


Figure 1.6: Crystal Structure of NiAs. The shaded gray are the Ni₆As trigonal prisms. The figure is taken from (Polvi et al. (2016)).

According to the bulk phase diagram of FeSe, stoichiometric FeSe does not exist. However, Fe₇Se₈ does exist. Its structure is derived from the same NiAs structure. Here, the Fe vacancies are confined to alternating layers where one of four atoms is missing. The unit cell of Fe₇Se₈ is shown in Figure 1.7 with the lattice parameters as $A = 2a = 7.21 \text{ \AA}$ and $C = 3c = 17.60 \text{ \AA}$, where a and c are the lattice parameters of hexagonal FeSe (Andresen and Leciejewicz (1964)). The Se atoms are omitted in the figure.

The main aim of our experiment is to grow hexagonal FeSe, and we are primarily interested in whether those hexagonal FeSe films are superconducting like their tetragonal counterparts. While hexagonal FeSe would likely be antiferromagnetic with antiferromagnetic coupling between ferromagnetic cation layers, Fe₇Se₈ is ferrimagnetic as the magnetic moments in alternating layers are not fully compensated (Hirone et al. (1954), Terzieff and Komarek (1978)). The question is whether this hexagonal phase would be superconducting if we could control the stoichiometry in an MBE growth experiment. The parent compounds of the Fe-based superconductors are mostly antiferromagnetic, and it is possible that antiferromagnetism and superconductivity in FeSe coexist. This makes hexagonal FeSe an interesting comparison with the superconducting tetragonal phase of FeSe. Moreover, according to recent new insights, FeSe might be classified as an altermagnet, meaning that the band structure of the normal state could be spin-polarized. It is not yet clear what implications that would have on the pairing symmetry of the superconducting phase, if present.

1.3.1 Magnetism in the FeSe system

The superconducting tetragonal phase of FeSe is paramagnetic (Grechnev et al. (2012)) and has a slight excess of Fe atoms. As mentioned above, the hexagonal FeSe phase is likely Fe-deficient and is ferrimagnetic (Mozgovykh et al. (2023), Kawaminami and Okazaki (1970)). Fe₇Se₈ has a ferrimagnetic to paramagnetic phase transition at $\sim 450 \text{ K}$, which is above the typical MBE growth temperature. There is

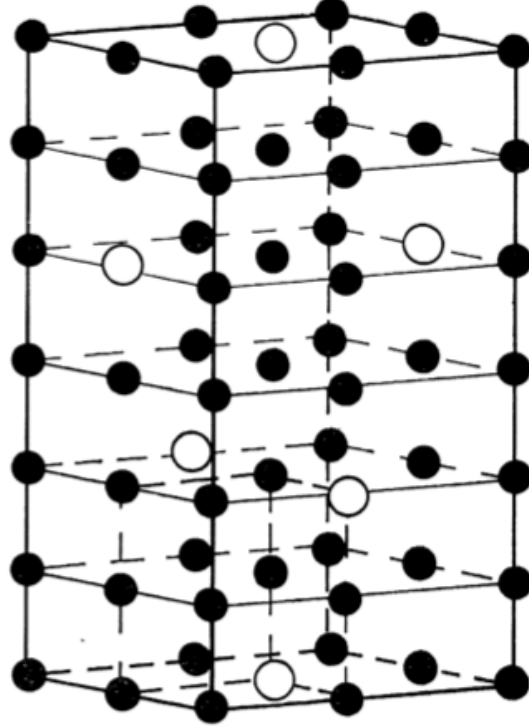


Figure 1.7: Unit cell of Fe_7Se_8 . The figure is taken from (Andresen and Leciejewicz (1964)).

another magnetic transition at $\sim 100\text{-}130\text{ K}$ (Mozgovykh et al. (2023), Kawaminami and Okazaki (1970), Kamimura (1977), Li et al. (2016)). This is attributed to the spin reorientation, where the spins rotate from the ab plane to the c -axis with decreasing temperature. Figure 1.8(a) shows the unit cell of Fe_7Se_8 , where the arrows represent the direction of magnetic moments. Figure 1.8(b) shows the magnetization curve with respect to the temperature measured with and without magnetic field. In both cases, the magnetic transition is observed at 100 K. This figure is taken from (Li et al. (2016)).

The case of stoichiometric FeSe may be different from that of Fe_7Se_8 . While there are no studies on stoichiometric FeSe , its crystal and magnetic structure would likely be identical to that of CrSb , a newly discovered altermagnet (Reimers et al. (2024), Šmejkal et al. (2022)). The synthesis of stoichiometric FeSe , however, necessitates utmost control of the composition of the films, which is highly non-trivial. A slight

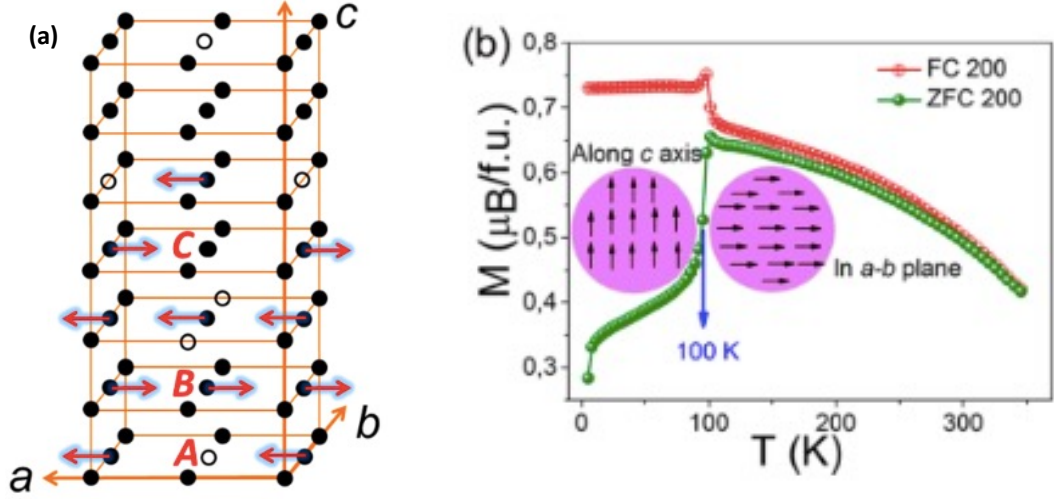


Figure 1.8: (a) Unit cell of Fe₇Se₈ superstructure. The open circles represent Fe vacancies. The arrows represent the direction of magnetic moments. Se atoms are omitted for clarity. (b) Zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves were measured under a magnetic field of 200 Oe. The arrows denote the spin-flip from the ab plane to the c axis at 100 K. The figure is taken from (Li et al. (2016)).

change in the growth condition and flux ratio of Fe and Se can produce different crystal phases with different compositions. Considering the already delicate interplay between magnetism and superconductivity, it is crucial to understand how these can be influenced by cation excess or deficiencies. This thesis outlines our first systematic attempts along this line.

1.4 Motivation

Our motivation for these studies is twofold. First, in light of the spectacular superconductive properties of one-unit-cell thick tetragonal FeSe on STO, we wonder if high-temperature superconductivity can be replicated on other non-oxide substrates. In particular, we are interested in whether the technologically important Si crystal can be used as a substrate for the growth of superconducting FeSe films. Si is used extensively in integrated circuits, microprocessors, solar cells, and various

electronic devices. If superconductivity could be obtained on silicon, it would facilitate the integration of superconducting devices with traditional silicon-based technology, and hence, the development of novel devices would be relatively cheap, fast, and efficient. It is not *a priori* clear, however, whether FeSe synthesis on Si is possible because Fe reacts very strongly with Si, forming stable silicides. In this thesis, we develop a protocol to prevent such chemical reaction from happening, and find that hexagonal FeSe can be grown on Si(111), provided that it is chemically passivated with a GaSe monolayer. The latter then serves as a template for van der Waals epitaxial growth.

Second, given the fact that hexagonal FeSe can be stabilized on Si(111), what can we learn about its low-temperature properties? The FeSe films are clearly metallic and may thus be susceptible to an electronic instability at very low temperatures. Interestingly, we find preliminary evidence for a CDW instability at low temperature. CDWs often compete with superconductivity, meaning that these two different ground states may be close in total energy. In addition, one would expect strong magnetic interactions as well. The competition between CDW ordering, superconductivity, and antiferromagnetism or altermagnetism is intriguing and makes hexagonal FeSe a very interesting testbed for exploring complex phases of matter on the Si platform.

1.5 Overview of thesis

Chapter 2 provides a comprehensive overview of the ultra-high vacuum setup utilized for the growth and characterization of the ultrathin films. We briefly outline the principles of MBE, and describe *in-situ* characterization methods such as Low Energy Electron Diffraction (LEED), Reflection High Energy Electron Diffraction (RHEED), Scanning Tunneling Microscopy and Spectroscopy (STM/STS), and X-ray Photoemission Spectroscopy (XPS). We conclude with a discussion of *ex-situ* Rutherford Backscattering Spectroscopy (RBS), which was used for the quantitative determination of the Fe deposition rate.

Chapter 3 describes the growth and characterization of GaSe on Si (111). We discuss the principles of surface passivation and provide a detailed picture of how GaSe passivation of Si(111) is achieved. Finally, we describe the structure and growth of Ga₂Se₃ multilayers on Si(111).

Chapter 4 is at the heart of the dissertation and focuses on FeSe growth on a GaSe passivated Si (111) surface. The vast majority of the films consists of hexagonal FeSe, although one occasionally finds a tetragonal domain. The composition of the film is determined with XPS.

Chapter 5 provides a more in-depth discussion of the core-level and valence band spectra, and we present preliminary data of Auger electron spectroscopy data to compare hexagonal FeSe with the tetragonal phase.

Chapter 6 provides atomic resolution imaging of a low-temperature superstructure that we attribute to the formation of a CDW. Interestingly, CDW ordering seems to be in competition with another type of ordering that we tentatively ascribe to magnetism.

Finally, Chapter 7 summarizes our conclusions and provides an outlook for possible future experiments based on the findings presented in this dissertation.

Chapter 2

Experimental Methods

2.1 The need for Ultra-high Vacuum System

All experiments are performed in an ultra-high vacuum (UHV) environment with a base pressure of about 10^{-10} mbar (approximately 10^{-8} Pa) or below. Such an environment is necessary to prepare well-defined surfaces with very little contamination. The number of particles impinging on a surface is directly proportional to the pressure, and it only takes about one second to cover the sample surface with undesirable pollutants at 10^{-6} mbar. UHV also allows longer lifetimes for the sample after growth, giving ample time to carry out the experiments.

UHV systems are equipped with different pumps to obtain low pressure, which is measured by pressure gauges, and experimental apparatus to grow and characterize the samples. Several different pumps, which operate at different pressure regions, are used. First, a roughing pump achieves pressure down to 10^{-3} mbar (see Table [2.1](#) for the conversion factors of different pressure units). After that, a turbo-molecular pump is used that can pump the chamber down to 10^{-9} mbar. An ion-getter pump (also called an ion pump) is used to obtain even better pressure. Also, the chamber is equipped with a titanium sublimation pump (TSP), where Ti atoms are sublimated

Table 2.1: Conversion factors between different pressure units. Table adapted from (Chiggiato (2014)).

	Pa	bar	atm	mbar
1 Pa	1	10^{-5}	9.87×10^{-6}	7.5×10^{-3}
1 bar	10^5	1	0.987	750.06
1 mbar	10^2	10^{-3}	0.987×10^{-3}	0.75
1 atm	1.013×10^5	1.013	1	760
1 mbar	133.32	1.33×10^{-3}	1.32×10^{-3}	1

from a heated Ti filament. This creates a chemically active Ti coating that traps residual gas molecules.

Pumping alone is not enough to obtain UHV conditions. When the chamber is exposed to atmospheric pressure, water molecules stick to the walls of the chamber. This water desorbs slowly, which makes a pressure below 10^{-8} mbar difficult to achieve. The water molecules can be removed by heating the system at 150 °C, known as a bake-out. After the bake-out, the chamber pressure is typically in the 10^{-11} mbar range. The pressure can be monitored by an ionization gauge, which covers pressures from $\sim 10^{-5}$ mbar to 10^{-12} mbar. Higher pressures between $\sim 10^{-4}$ mbar to 1 atm can be measured with a Pirani gauge, which records pressure by measuring thermal conductivity. Additional analysis of individual gases can be done with a residual gas analyzer (RGA), which consists of a mass spectrometer and provides mass information on the residual gases present in the chamber. The RGA is also used to check any leaks present in the system.

Growth and characterization of the samples were performed in the UHV chamber called the ‘Growth and Analysis chamber’. The growth chamber is equipped with effusion cells for Ga, Se, and Fe deposition, and with a RHEED system to monitor the quality of the substrate and the thin films. It also has a sample manipulator for precise sample positioning with the ability to, directly and indirectly, heat the substrates used in the experiments for sample preparation and growth. The analysis chamber is equipped with XPS, LEED, and VT-STM for detailed surface characterization. In

addition, it has a sample manipulator with direct and indirect heating capabilities. The chamber schematic is shown in Figure 2.1. The sample can be transferred between the growth chamber and analysis chamber using magnetic transfer arms. In this operation, the sample remains under UHV at all times. Figure 2.2 shows the growth and analysis chamber, which is equipped with a loadlock for inserting or removing samples from the vacuum. The RHEED, LEED, STM, and XPS systems are also shown. They will be discussed in detail later. The vacuum pumps, i.e., ion pump, turbo pump, and scroll pump, are outside this picture frame.

2.2 Thin film synthesis via Molecular Beam Epitaxy

UHV systems either employ thermal evaporation (liquid source) or sublimation (solid source) to deposit atoms or molecules onto a substrate. The flux I of atoms or molecules deposited onto the sample is given by Equation (2.1)

$$I = \frac{p(T)A}{\pi L^2 \sqrt{2\pi m k_B T}} \quad (2.1)$$

where $p(T)$ is the equilibrium vapor pressure at temperature T of the deposited material, A is the evaporation or sublimation area, L is the distance between the substrate and the source material, m is the mass of the impinging atom or molecule, and k_B is the Boltzmann constant. For the typical deposition rate of 0.1-1 ML/min, the equilibrium vapor pressure, usually of the range 10^{-5} - 10^{-4} mbar, can be calculated from Equation (2.1). The source temperature can then be estimated from the vapor pressure plots for different elements (Oura et al. (2013)).

Molecular beam epitaxy (MBE) is an advanced technique for the growth of high-quality epitaxial thin films, which are obtained by precisely controlling the beam fluxes and growth parameters. Depending on the experimental design and deposited material, various types of deposition sources can be used.

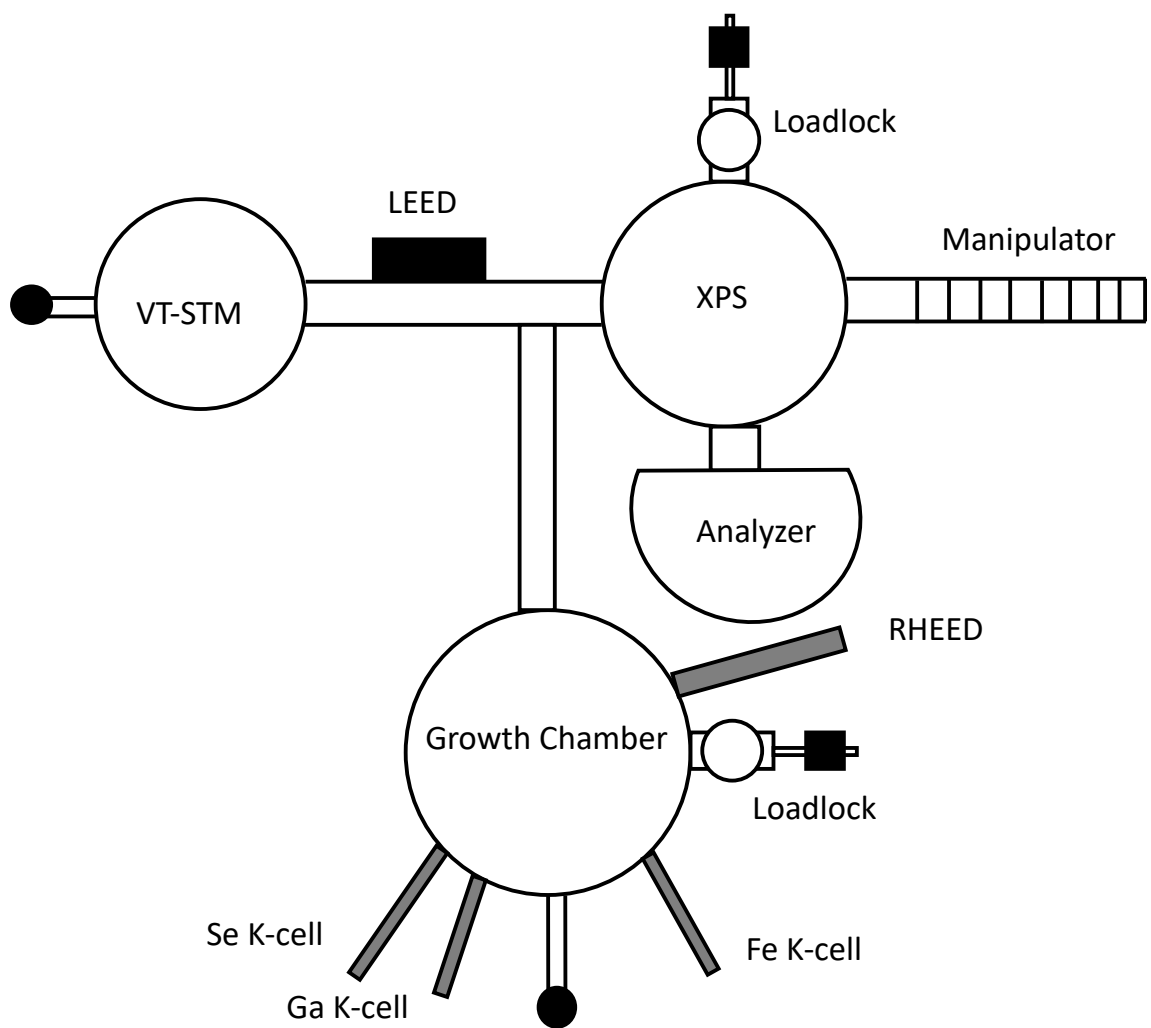


Figure 2.1: Schematic diagram of the growth and analysis chamber.

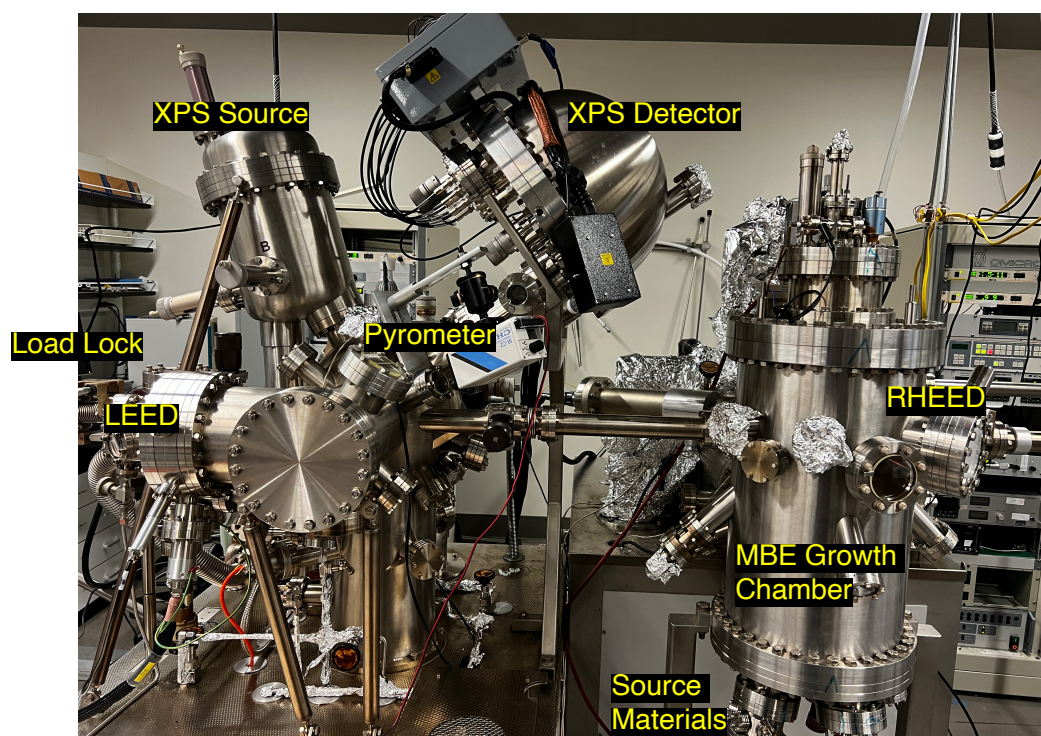


Figure 2.2: MBE growth and analysis chamber in the laboratory.

For a highly stable deposition rate, a Knudsen cell (or simply K-cell, also known as effusion cell) is used (Knudsen (1934)). The K-cell consists of a crucible that contains the source material. The crucibles used in this experiment are Pyrolytic Boron Nitride (PBN) and Alumina (Al_2O_3), which are surrounded by a filament heater and radiation shielding. The temperature of the crucible is monitored by the thermocouple attached to the base of the crucible, and the heating is controlled by a PID temperature controller. A pinhole aperture is placed at the top of the crucible to control the emission flux. It also has a movable shutter to start and end the deposition quickly. These K-cells are also connected with a water cooling system to reduce transmitted heat and degassing of the cell. In some K-cells (*e.g.*, our Se-source), a custom-made filament is wrapped around the aperture to prevent clogging of the aperture. A schematic of a K-cell or effusion cell is shown in Figure 2.3.

The surface coverage and morphology are optimized by evaluating the deposition time, deposition rate, deposition position, annealing temperature, and annealing time. Optimizing the above-mentioned parameters is very important for sample preparation. A slight change in any of the parameters may result in different film quality.

2.3 Characterization Techniques

2.3.1 Low Energy Electron Diffraction

Low Energy Electron Diffraction (LEED) is a well-known technique to determine surface structures via Bragg diffraction of low-energy electrons. It is often used to check the crystalline quality of the surface, though it is also possible (but quite difficult) to determine atomic positions from the scattering intensities. Other frequently used diffraction methods, such as X-ray or neutron diffraction, probe the structure of the bulk and are not sensitive to the atomic arrangement at the surface. This is due to the fact that (charge-neutral) photons and neutrons do not

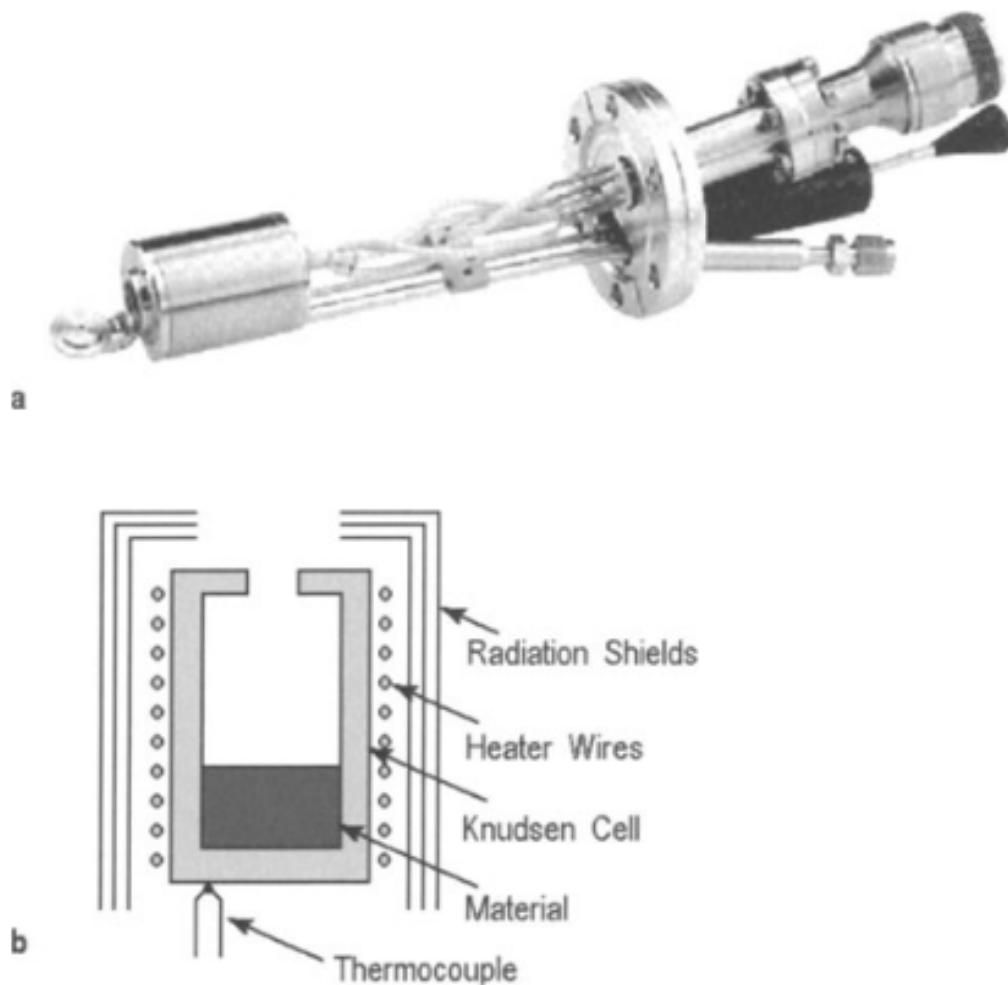


Figure 2.3: (a) Effusion cell; (b) a schematic diagram of an effusion cell head (Oura et al. (2013))

interact strongly with electrons in the crystal. Thus, they have a large penetration depth (Zangwill (1988)). So, for accurate and detailed studies of the surface atomic structure, it is best to use electrons because they have a short inelastic mean free path. Figure 2.4 shows a curve of the inelastic mean free path of electrons in various materials as a function of their kinetic energy. The data points follow a ‘universal curve’ for different materials with a minimum mean free path between 30 and 200 eV. Also, the de-Broglie wavelength of these low-energy electrons is of the order of the interatomic spacings in solids, and hence, they satisfy the condition for atomic diffraction.

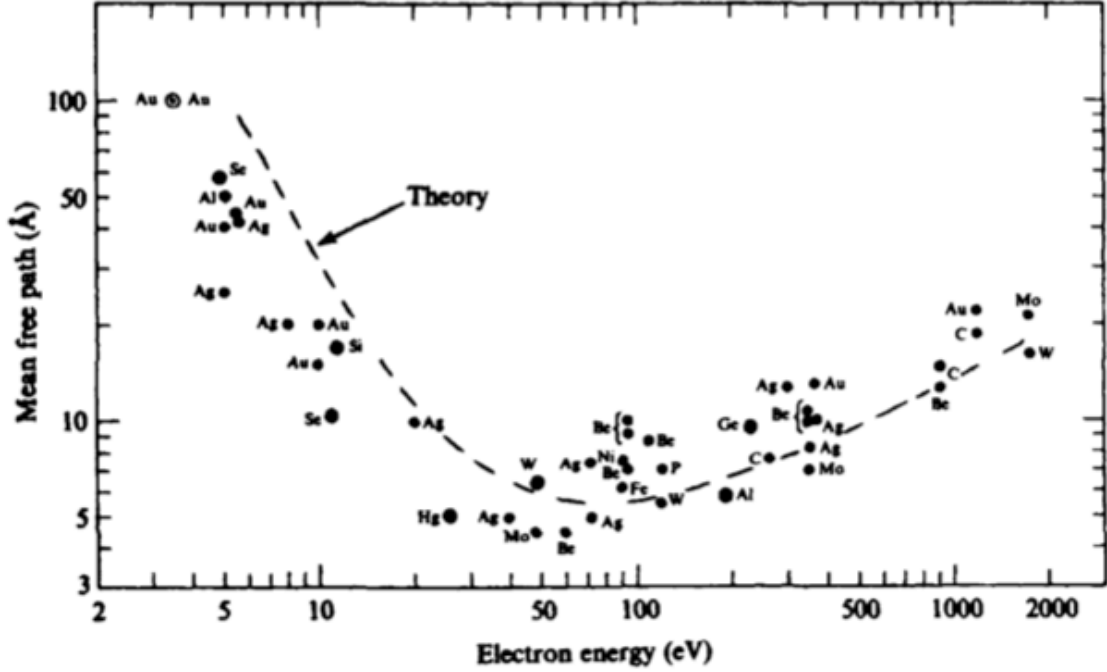


Figure 2.4: ‘Universal mean free path curve’ showing the mean free path of electrons versus electron energy for different materials. Figure taken from (Zangwill (1988)).

The UHV chamber contains a 4-grid retarding LEED system with a built-in electron gun, as shown in Figure 2.5. The electron gun, which produces a collimated beam of low-energy electrons, consists of a cathode filament with a Wehnelt cylinder and electrostatic lens for focusing the beam. The electrons are back-scattered from the sample and pass through the grids. The first grid is at ground potential so that the backscattered electrons travel through a field-free region. The second and third grids are negatively biased to filter inelastically scattered electrons. The fourth grid is grounded, and finally, the electrons are accelerated to a fluorescent screen that is biased at +5 kV. The screen lights up upon impact so that it directly visualizes the diffraction pattern. The latter represents the surface reciprocal lattice. The diffraction pattern can be inspected by eye or recorded with a digital camera.

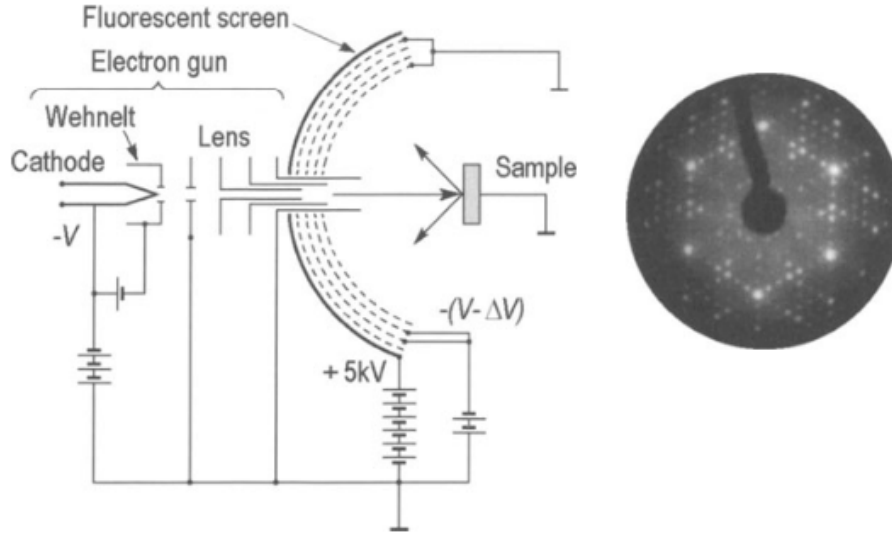


Figure 2.5: Left: Schematic diagram of a 4-grid LEED system. Right: LEED pattern of Si(111)7x7 surface. The figure is taken from (Oura et al. (2013)).

2.3.2 Reflection High-Energy Electron Diffraction

Reflection high-energy electron diffraction (RHEED) is a widely used characterization technique with a geometry that allows for real-time monitoring of the (changing) diffraction pattern during epitaxial growth. The RHEED system consists of an electron gun, a sample, and a fluorescent screen. The electron gun emits electrons with primary energies between 10 and 100 keV, which impinges on the sample surface at a grazing angle ($< 5^\circ$). Diffracted beams emitted at a grazing angle hit the fluorescent screen on the opposite side of the chamber. A schematic of the RHEED system is shown in Figure 2.6. The small incident angle makes it sensitive to the ordering of atoms at the surface or growth front of the film. The RHEED patterns provide information about the film's structure and morphology and can sometimes be used to calibrate the deposition rate.

The diffraction pattern observed in RHEED differs from that seen in LEED. The condition to observe constructive interference of the outgoing electrons in the RHEED experiment is best determined and visualized by the Ewald sphere construction (Ashcroft and Mermin (2014)). Figure 2.7 illustrates the Ewald construction for

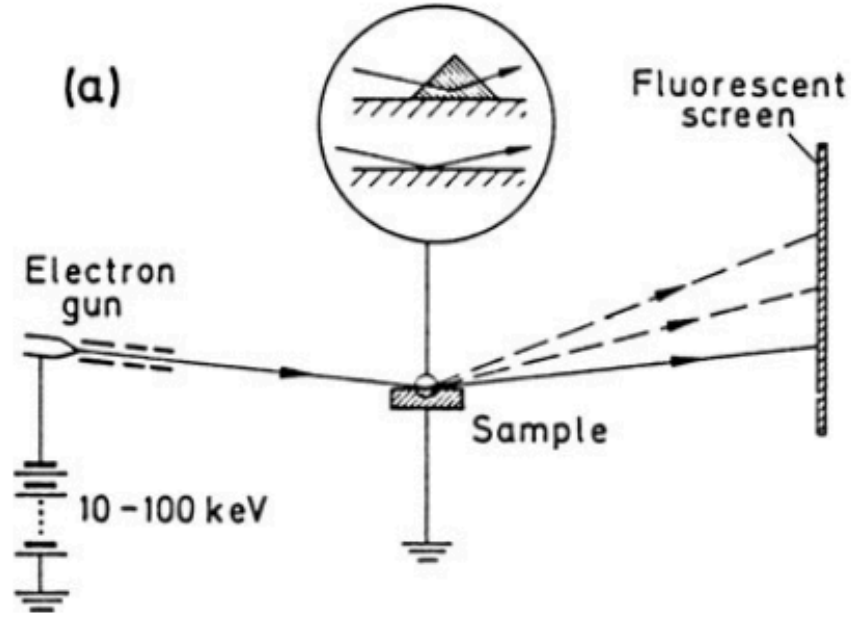


Figure 2.6: (a) Schematic of the RHEED set-up. The inset in the figure shows two different scattering situations: bulk scattering by a 3D island on top of the surface (top) and surface scattering on a flat surface (bottom). The figure is taken from (Lüth (2010)).

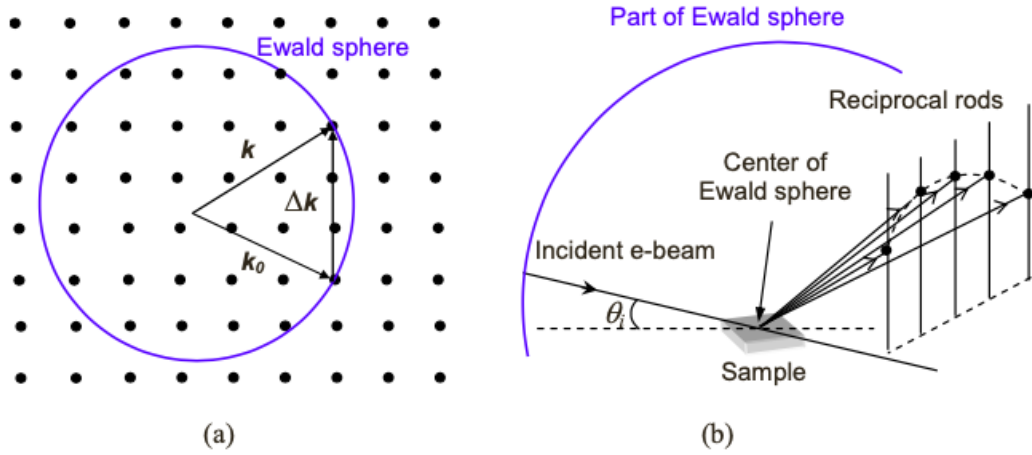


Figure 2.7: (a) Top view of the two-dimensional reciprocal lattice and Ewald sphere construction. Due to the lack of periodicity normal to the surface, each point represents a diffuse 'rod' (b) Systematic diagram showing the Ewald sphere's intersection with the reciprocal lattice rods. The figure is taken from (Hafez et al. (2022)).

the conditions of a RHEED experiment. The diameter of the Ewald sphere is much larger than a reciprocal lattice vector, as the primary energy of the electron beam is very high. Let us consider electrons with incoming momentum $\mathbf{k}_i$ and outgoing momentum $\mathbf{k}_o$. The Laue condition and conservation of energy gives:

$$\mathbf{k}_o - \mathbf{k}_i = \Delta\mathbf{K} \quad (2.2)$$

$$|\mathbf{k}_o| = |\mathbf{k}_i| = \frac{2\pi}{\lambda} \quad (2.3)$$

The Ewald construction, Figure 2.7, depicts these conditions in reciprocal space. The maximum intensity of the diffraction beam is obtained when the Laue diffraction condition is met:

$$\Delta\mathbf{K} = \mathbf{G}_m \quad (2.4)$$

where $\mathbf{G}_m$ is a vector of the reciprocal lattice where m refers to m^{th} diffracted beam. Figure 2.7(b) is a schematic diagram showing the Ewald sphere's intersection with the reciprocal lattice rods (due to the absence of periodicity perpendicular to the surface, the reciprocal lattice points along the third direction smear into diffuse 'rods', thus creating a 2D array of reciprocal lattice rods). The RHEED patterns depend on the structure and morphology of the probed surface; for example, the streaks are seen for two-dimensional crystalline surfaces, whereas for three-dimensional islands, a transmission diffraction pattern is observed. The streakiness originates from the fact that the reciprocal lattice rods are almost tangential to the Ewald sphere when the diffraction angle is small. Any type of broadening mechanism (such as finite size domains or thermal broadening) contributes to the streakiness of the pattern.

2.3.3 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), is a surface analytical technique that is widely used to study the chemical composition of surfaces and thin films (Chastain and King Jr

(1992)). It is based on the photoelectric effect. The technique was developed by Dr. Kai Siegbahn in mid-1960's, for which he was awarded the Nobel Prize in Physics in 1981 (Siegbahn (1967)). In this technique, the surface is irradiated with a monochromatic X-ray beam, and the energy of the outgoing photoelectrons electrons is analyzed. Generally, one uses Mg K α (1253.6 eV) or Al K α (1486.6 eV) radiation. We use the latter. The photoemission process is often described by the three-step model (Fadley (1978)), *i.e.*, an electron absorbs a photon, moves through the material towards the surface, and is ejected into the vacuum. The measured kinetic energy E_{kin} of the ejected electron is given by

$$E_{kin} = \hbar\omega - E_i - \phi \quad (2.5)$$

where $\hbar\omega$ is the energy of the photon, E_i is the binding energy of the atomic orbital from which the electron originates, and $\phi = E_{vacuum} - E_{Fermi}$ is the work function of the spectrometer (Oura et al. (2013)).

The schematic diagram of the experimental set-up for photoemission experiments is shown in Figure 2.8. It includes a monochromatic source of X-ray photons and an electron energy analyzer and detector to record the spectra of the photoemitted electrons. The photon source used in our laboratory is a so-called X-ray anode, in which X-rays are created by bombarding an Al target with high-energy electrons. The X-rays are monochromatized by a quartz crystal and directed towards the sample. The emitted electrons are dispersed using a hemispherical electron energy analyzer consisting of a series of lenses and concentric hemispheres to create an electric field such that only electrons with preselected kinetic energy will make it to the detector to be counted.

XPS is an important tool for obtaining information about the samples and is especially important when used as an *in situ* probe. It can be used to determine the chemical states and elemental composition of the sample, measure the thickness of thin films, and identify impurities present. An in-depth analysis of lineshapes further

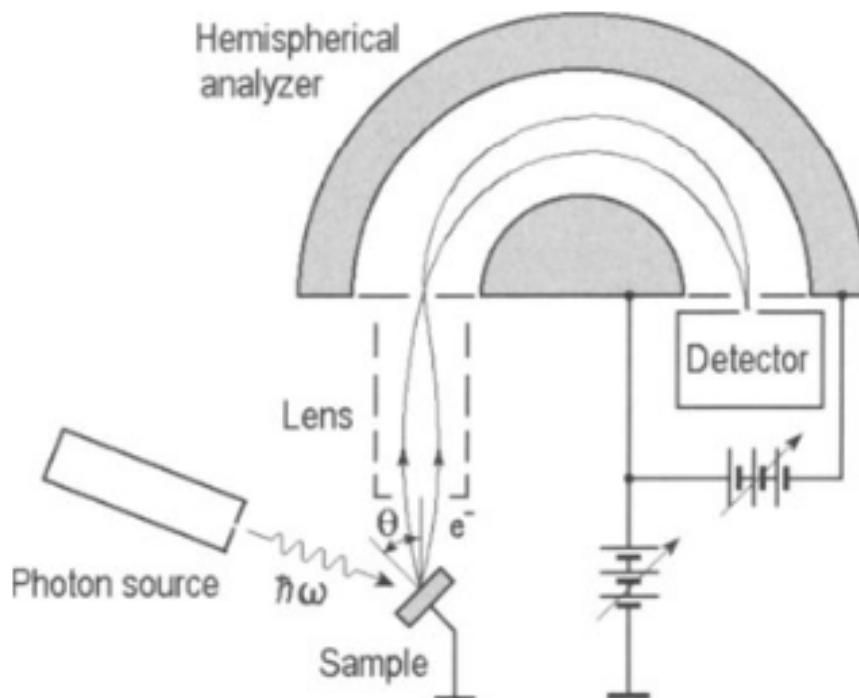


Figure 2.8: Schematic diagram of experimental set-up for XPS, showing the primary components- the photon source, sample, concentric hemispherical analyzer, and the detector. The figure is taken from (Oura et al. (2013)).

provides information about the various excitations in the solid. The core levels of each atom produce sharp peaks in the photoelectron spectrum at specific binding energies that are tabulated. The photoelectron spectrum thus serves as a fingerprint of the atomic species present on the surface. XPS spectra can be studied quantitatively to determine the compound's stoichiometry and to calibrate the coverage during thin film growth. XPS spectra of different thin films and the substrate collected in our laboratory will be analyzed and explained in detail in later chapters. The spectra will provide a better understanding of the samples' chemical composition and electronic structure.

Core-level spectra are typically fitted with a Voigt line profile, which is a Lorentzian line profile convoluted with a Gaussian. Instrumental broadening, which includes the energy broadening of the X-ray source and energy resolution

of the electron analyzer, contribute to the Gaussian width, whereas the Lorentzian width originates from the lifetime broadening of the core hole created during the photoemission process. However, in the case of metals, the line shape is often asymmetric because the sudden creation of the core hole is accompanied by a continuum of single-particle excitations near the Fermi level. The excitations steal some kinetic energy from the primary photoelectrons, thus creating a long tail on the high-binding-energy side of the spectrum. The asymmetry can be fitted with the Doniach-Sunjić line shape (Doniach and Sunjić (1970)). In order to fit the core level spectrum, one must decide on an appropriate protocol for subtracting the background. The most commonly employed background functions are the Shirley and Tougaard backgrounds (Shirley (1972), Tougaard (2021), Repoux (1992)).

The binding energy of the core level is specific to each element. However, the precise binding energies depend to some extent on the chemical oxidation state of the photo-ionized atom and its nearest neighbor atoms. A shift in binding energy, also known as a chemical shift, is observed whenever there is a change in the oxidation state or chemical environment. For example, when silicon is oxidized, its oxidation state becomes Si^{4+} . The Si^{4+} ion is more difficult to ionize than neutral Si, and hence, the Si^{4+} core level peaks appear at higher binding energy, as compared to those of bulk Si. Since the binding energy is referenced to the chemical potential, any shift in chemical potential due to e.g. charge doping or band bending will also shift the core levels (Chastain and King Jr (1992)). Details about core level shifts can be found in the review paper by (Egelhoff Jr (1987)).

With the exception of the ns core levels, all core level spectra are split due to the spin-orbit interaction of the orbital and spin angular momentum of the core hole. For example, the $2p$ core level spectrum consists of two peaks, corresponding to $j = l \pm 1/2$, which are referred to as the $2p_{1/2}$ and $2p_{3/2}$ peaks. Their intensity ratio is given by the ratios of their multiplicity $2j + 1$, or 2:4, respectively. For bulk silicon, the $2p_{1/2}$ peak appears at a binding energy of 99.4 eV, while the $2p_{3/2}$ peak appears at 100 eV, which amounts to a spin-orbit splitting of 0.6 eV.

Besides the primary core-level peaks in the XPS spectrum, one usually observes additional peaks, the so-called satellite peaks and Auger peaks. Satellite peaks are typically associated with the excitation of plasmons or excitons upon photoionization. The excitations lower the kinetic energy of the primary photoelectrons, thus producing peaks on the high binding-energy side of the main spectrum. Auger peaks result from the Auger process, where an electron from a higher energy level ‘drops down’ to fill the photo hole in the inner shell. The energy released in this process may be sufficient to excite a more weakly bound electron (the ‘Auger’ electron) into the continuum. This produces a final state with two holes. All these different peaks will be discussed in later chapters.

2.3.4 Scanning Tunneling Microscopy and Spectroscopy

The scanning tunneling microscope (STM) was developed in the early 1980s by Gerd Binnig and Heinrich Rohrer in the IBM research laboratory (Binnig et al. (1982)). They were awarded the Nobel Prize in Physics in 1986 for their revolutionary work. A schematic diagram of the STM set-up is shown in Figure 2.9, showing the main components. It consists of an atomically sharp tip, typically made from a W, PtIr, or Au wire, that approaches the sample surface to a distance of the order of 1 nm. This distance is so small that electrons can tunnel quantum mechanically from the tip to the sample or vice versa, depending on the applied bias. The motion of the tip is controlled by the piezoelectric ceramics, which convert electrical signals into mechanical expansion or contraction. By measuring the tunneling current as a function of the (x, y) coordinates on the surface, one obtains a topographical map of the surface. Here, an electronic feedback loop compensates for changes in the tunnel current during the scanning operation by adjusting the bias on the z -piezo so as to maintain a constant tunneling current. Changes in z -piezo bias correspond to vertical deflections of the STM tip and follow the atomic height profile of the surface. In this scanning mode, or ‘constant current mode’, the tunneling bias and tunneling

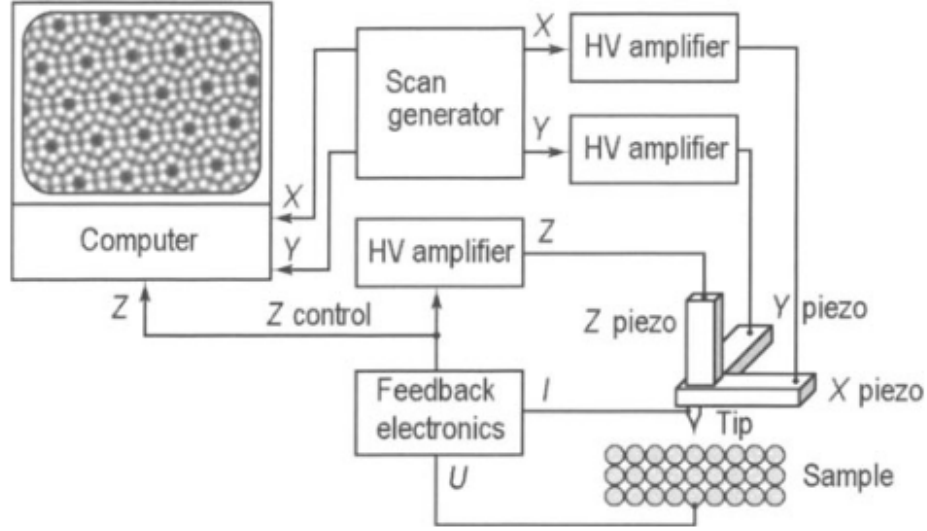


Figure 2.9: Schematic diagram of experimental set-up for STM showing the primary components- a tip, a sample, a scanner system, feedback electronics, and a computer system. The figure is taken from (Oura et al. (2013)).

current are kept constant. Alternatively, in constant-height mode, z and V are kept constant, while the current I is measured as a function of tip position. In both cases, one obtained similar images, although each method had its own advantages and disadvantages. The three piezo scanners are controlled by a computer system, which controls tip position, acquires data, and converts the data into a topographic image. To make all this work, the STM must be isolated from acoustic and floor vibrations, while the electronics must be extremely stable with minimal noise levels.

At a very close distance, the wave functions of the tip and the sample start to overlap. A tunneling current will flow through the vacuum gap when a bias voltage is applied between the tip and the sample. The tunneling current density j is given by:

$$j = \frac{D(V)V}{d} e^{-A\phi_B^{1/2}d} \quad (2.6)$$

where V is the bias voltage between the tip and the sample, d is the effective width of the tunneling gap, $D(V)$ reflects the electron state densities, A is a constant, and ϕ_B

is the effective barrier height of the junction. (Oura et al. (2013)). From the above equation, we see the tunneling current depends exponentially on the gap width d , and hence, the tunneling current is extremely sensitive to the tip-sample distance. When $\Delta d = 1 \text{ \AA}$, the tunneling current changes by an order of magnitude. The tunneling diagram is shown in Figure 2.10.

In scanning tunneling spectroscopy (STS), one measures the tunneling current flowing between the tip and the sample as a function of the applied voltage, while the electronic feedback loop is switched off (otherwise, the tip would move up and down with voltage). The tip height is set by choosing a current set-point. The current depends exponentially on the tip-sample distance and the electronic density of states near the surface. One can show (under several assumptions) that the dI/dV spectrum is proportional to the local density of states of the sample. By measuring the dI/dV spectrum at different locations on the surface for a given bias, one obtains a spatial map of the LDOS at that particular bias. STS is used to measure various electronic properties such as energy band structures, band gaps, surface states, impurity levels, *etc.*, and it can probe various quantum phenomena such as superconductivity, charge density waves, and magnetism.

2.3.5 Rutherford Backscattering Spectrometry

Rutherford Backscattering Spectroscopy (RBS) is a powerful analytical technique frequently used to determine the composition and structure of a material (Chu et al. (1978)). In this method, a sample is bombarded with high-energy ions, mostly helium ions, and the backscattered ions are counted as a function of their energies. The RBS spectrum provides information about the sample composition, impurities, stoichiometry of the material, *etc.*, for any species except for hydrogen. A simple illustration of the RBS technique is shown in Figure 2.11.

When the beam of high-energy ions reaches the sample, it interacts with the target atoms, and some ions are backscattered as a result of Coulomb interaction. This

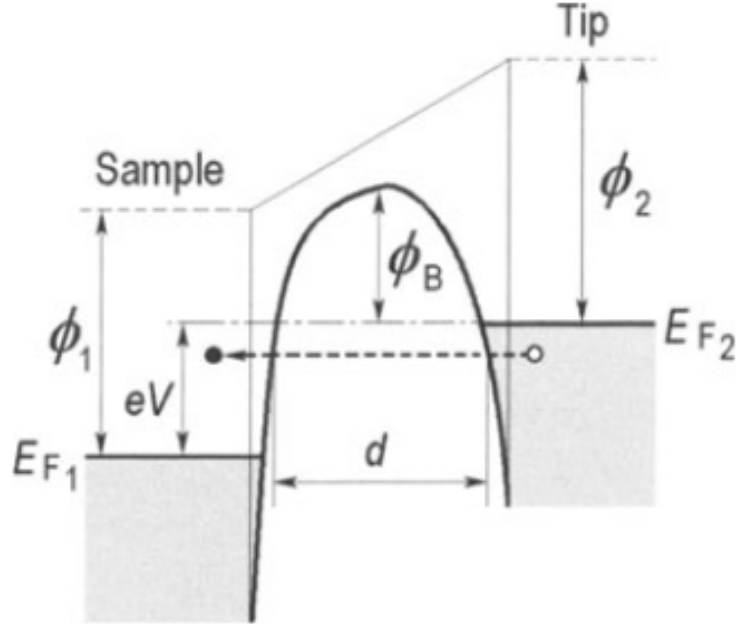


Figure 2.10: Energy diagram showing the tunneling of the STM tip and the sample. E_{F1} and E_{F2} represent the Fermi levels of the surface and the tip. ϕ_1 and ϕ_2 are the work functions of the surface and the tip, ϕ_B is the effective barrier height, d is the width of the tunneling gap, and V is the bias voltage. The figure illustrates the STM probing the empty state of the surface. Tunneling into the occupied states (not shown) is simply a case of reversing the sample polarity. The figure is taken from (Oura et al. (2013)).

elastic interaction can be treated as a classical two-body scattering problem. The velocity and scattering angle of the outgoing particle can be obtained as a function of the initial parameters of the incoming ion. If E_0 is the energy of the incident ions and E_1 is the energy of the backscattered ions, it can be written as $E_1 = K.E_0$ where K is a kinematic factor given as (Chu (2012)):

$$K = \left(\frac{(M_1/M_2)\cos\theta + \sqrt{1 - (M_1/M_2)^2(\sin^2\theta)}}{1 + (M_1/M_2)} \right)^2 \quad (2.7)$$

where M_1 and M_2 are the masses of the projectile and target atom, respectively, and θ is the scattering angle. K is a function of (M_1/M_2) , which means that He ions backscattered by heavier atoms will have higher energies, and hence they appear at

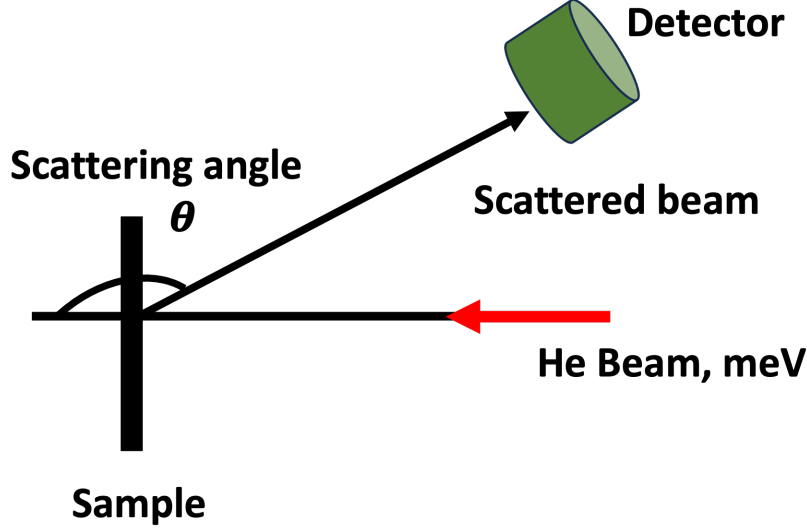


Figure 2.11: Schematic diagram of RBS experimental system.

higher energies in the RBS spectrum. The above equation, however, does not describe the probability of observing a backscattering event. This is given by differential cross-section:

$$\frac{d\sigma}{d\Omega} = \left(\frac{Z_1 Z_2 e^2}{4E_0} \right)^2 \frac{1}{(\sin \theta/2)^4} \quad (2.8)$$

where Z_1 and Z_2 are the atomic numbers of the projectile ion and the target nucleus. When the incident ions travel through the sample, the interaction of the projectile ions with the surrounding atoms and electrons reduces their energy. The ‘stopping power’ is given by $S = -dE/dx$ (Hartmann et al. (1997)) where x is the travel distance through the sample. This also means that ions backscattered from greater depths have relatively less energy by the time they reach the detector. In summary, the measured energy of the scattered ions provides information about the mass of the target nucleus and the depth distribution of the elements in the sample. The different peaks in the measured spectrum correspond to different elements, and their positions and shapes give information about the composition and thickness of the layers in the sample. The area under the peak gives the concentration of the element present in the sample. The experimental data is then compared with theoretical simulations to

obtain quantitative information about the composition of the sample. The theoretical calculations can be done using the SIMNRA software ([Max-Planck-Institut \(2021\)](#)). We have used this technique to calculate the growth rate of FeSe on GaSe:Si substrate. The details will be discussed in Chapter [4](#). The details of the RBS technique can be found elsewhere ([Chu et al. \(1978\)](#), [Nastasi et al. \(2014\)](#), [Almenara \(2011\)](#)).

Chapter 3

Growth and Characterization of GaSe on Si (111)

3.1 Introduction

Following the discovery of high-temperature (70 K) superconductivity in one unit-cell thick FeSe films on the SrTiO₃(001) substrate (Qing-Yan et al. (2012)), many researchers have tried to replicate this on a variety of other oxide substrates, such as SrTiO₃(110) (Zhang et al. (2016a), Zhou et al. (2016)), BaTiO₃(001) (Peng et al. (2014)), anatase TiO₂(001) (Ding et al. (2016)), rutile TiO₂(001) (Rebec et al. (2017)), and MgO(001) (Zhou et al. (2018)), all with different lattice constants and crystal orientations. All of these substrates enhance the superconducting T_c to temperatures well above that of bulk FeSe. FeSe has also been grown on graphitized SiC (Zhang et al. (2016b)), graphene, (Song et al. (2011)), GaAs (Takemura et al. (1997)), LaAlO₃ (Tsukada et al. (2011)), LiF (Wang et al. (2022)), and CaF₂ (Wang et al. (2022), Qiu et al. (2017)), showing little or no enhancement of T_c .

The main objective of this project is to grow FeSe thin films on the Si(111) substrate, which will be discussed in detail in chapter 4. Our initial attempt of growing FeSe on Si (explained in chapter 3.3) resulted in the formation of unwanted

iron silicides. To alleviate this problem, the Si substrate was first terminated with a monatomic layer of GaSe, as will be discussed in Section 3.6. The GaSe layer passivates the surface of Si(111) and potentially facilitates van der Waals growth of 2D materials. Hexagonal FeSe films were then grown on the GaSe passivated Si(111) surface.

3.2 Si(111) surface reconstruction and passivation

Silicon is the backbone of modern technology, mostly in the fields of electronics and material science. It is used in a wide range of applications because of its versatile properties and its vast abundance. Integration of other commonly used materials into silicon technology is not straightforward because of the lattice and/or chemical mismatch between Si and those other materials. By growing a hetero-epitaxial buffer layer in between the two materials, one may prevent interdiffusion and relieve the lattice strain with a minimal amount of misfit dislocations. A particularly promising approach is to first passivate the silicon surface both chemically and electronically by exposing an atomically clean Si(111) surface to a flux of atomic hydrogen, arsenic, or Ga plus Se. Figure 3.1 shows the ball-and-stick models of the corresponding surface terminations.

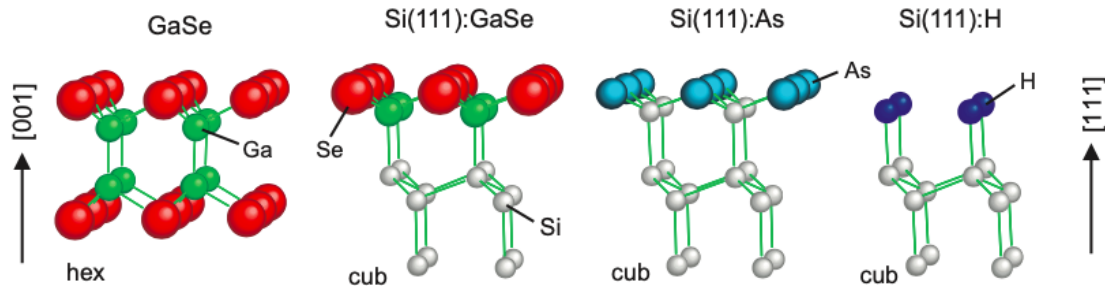


Figure 3.1: Structure of bulk GaSe and Si(111) passivated surfaces. Passivation is done by exposing an atomically clean Si(111) surface to a flux of Ga and Se, As, and atomic H, respectively. Figure is taken from (Rudolph et al. (2005)).

The chemical bonds are all saturated, thus eliminating the dangling bond surface states in the band gap of Si(111). The surface is, therefore, relatively inert, similar to the surfaces or interfaces of 2D van der Waals materials. Bulk gallium selenide (GaSe) exhibits a layered hexagonal structure, with each unit cell consisting of four monoatomic layers, Se-Ga-Ga-Se (Figure 3.2). It is a quasi 2D van der Waals compound with a band gap of 2.1 eV.(Fernelius (1994)). When the Si(111) surface is exposed to a beam of Ga and Se atoms, the incoming Ga atoms bond to the outermost Si atoms at the silicon surface. (Meng et al. (2001), Meng et al. (2000), Rudolph et al. (2000a)). Each Si atom binds to one Ga atom, and each Ga atom binds to one Si atom (below) and three Se atoms (above).

A simple way to view this is to slice the Se-Ga-Ga-Se slabs of bulk GaSe in half and to place a Se-Ga- half-slab on top of the Si atoms. The Ga atom needs to steal one electron from the Se to form four covalent bonds, leaving the Se atoms with five valence electrons, three of which are used to form the backbonds to the Ga atoms and two of which that fill a lone-pair dangling bond orbital on the Se atom. The structure of bulk GaSe and Si(111) surface terminated with GaSe bilayer is shown in Figure 3.2. A similar kind of surface termination was also achieved by As-deposition (Uhrberg et al. (1987)) and H-deposition (Ohba et al. (1997)) on Si(111) surface.

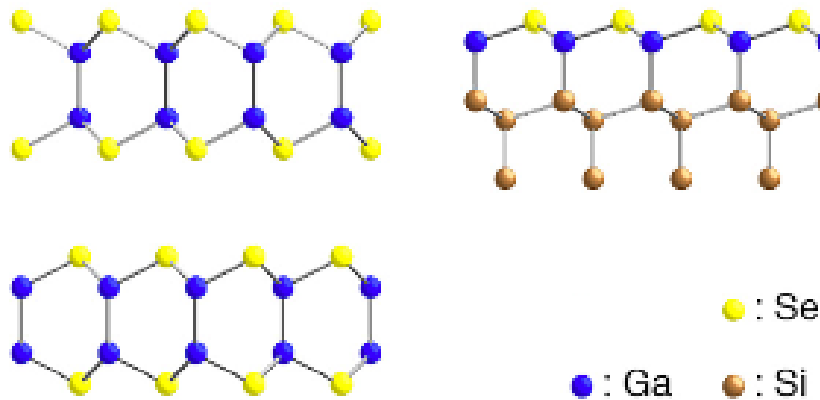


Figure 3.2: Left: Structure of bulk GaSe, Right: Structure of GaSe terminated Si surface. Figure is taken from (Ohtake and Sakuma (2019)).

The GaSe terminated Si(111) surface is reported to be a suitable substrate for van der Waals (vdW) growth of 2D materials. Van der Waals growth is an epitaxial growth mode characterized by weak van der Waals bonding between the substrate and film, thus enabling single-crystalline heteroepitaxial layer growth irrespective of lattice mismatch (Koma (1992)). This allows the layered materials to grow in a relaxed state, even when the lattice mismatch is very large. Ideally, strain is fully relieved in the first layer without the formation of misfit dislocations. A schematic illustration of conventional, van der Waals, and quasi-van der Waals epitaxy is shown in Figure 3.3. The combination between two-dimensionally and three-dimensionally bound materials is quasi-van der Waals epitaxy.

Jaegermann et al. have grown lattice-mismatched GaSe films on different Si substrates. For Si(111) and Si(110) substrates, a Si-Ga-Se van der Waals-like termination was obtained, and the subsequent growth of GaSe produces the layered hexagonal GaSe crystal structure of bulk GaSe. However, for Si(100), the surface was terminated by a Se adatom layer, and no Ga-Se surface termination was achieved. GaSe grown to this surface results in diffuse diffraction streaks of four-fold symmetry on a diffuse background, indicating microfacetting along the [100] direction (Jaegermann et al. (2000)).

In the case of Si and GaSe, the lattice mismatch is about 2.4%. Vinh et al. also claimed to have grown epitaxial GaSe on Si(111) (Vinh et al. (1997)). Fritsche et al. reported preparing a Si(111):GaSe van der Waals surface by sequential deposition of

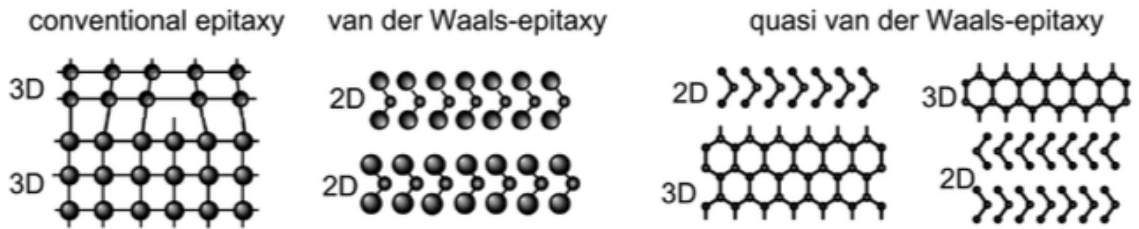


Figure 3.3: The schematic illustration of conventional, van der Waals, and quasi-van der Waals epitaxy. Figure is taken from (Jaegermann et al. (2000)).

Ga and Se on the Si(111)7 $\times$ 7 surface. The authors concluded that there is no charge transfer between the Si substrate and GaSe bilayer (Fritsche et al. (2002)). Ohtake and Sakuma have grown epitaxial MoSe₂ on GaSe-passivated Si(111). This procedure prevented the formation of the thermodynamically stable MoSi₂ phase and facilitated the growth of epitaxial MoSe₂ thin films (Ohtake and Sakuma (2019)).

GaSe passivation has also been tried with other substrates. Yonezawa et al. have grown GaSe thin films on Ge(111) via van der Waals epitaxy (Yonezawa et al. (2019)). Figure 3.4 shows a cross-sectional scanning transmission electron microscopy (STEM) image of the vdW interface between GaSe and Ge(111). Lee et al. grew GaSe by van der Waals epitaxy on GaN (Lee et al. (2017)), see Figure 3.5. GaSe has also been grown on a variety of other substrates like WS₂ (Lang et al. (1994)), GaAs(111) (Rumaner et al. (1998), Tatsuyama et al. (1997)), GaAs(110) (Rudolph et al. (2000b)), GaAs(001) (Tatsuyama et al. (1997)), and c-sapphire (Wu et al. (2015)).

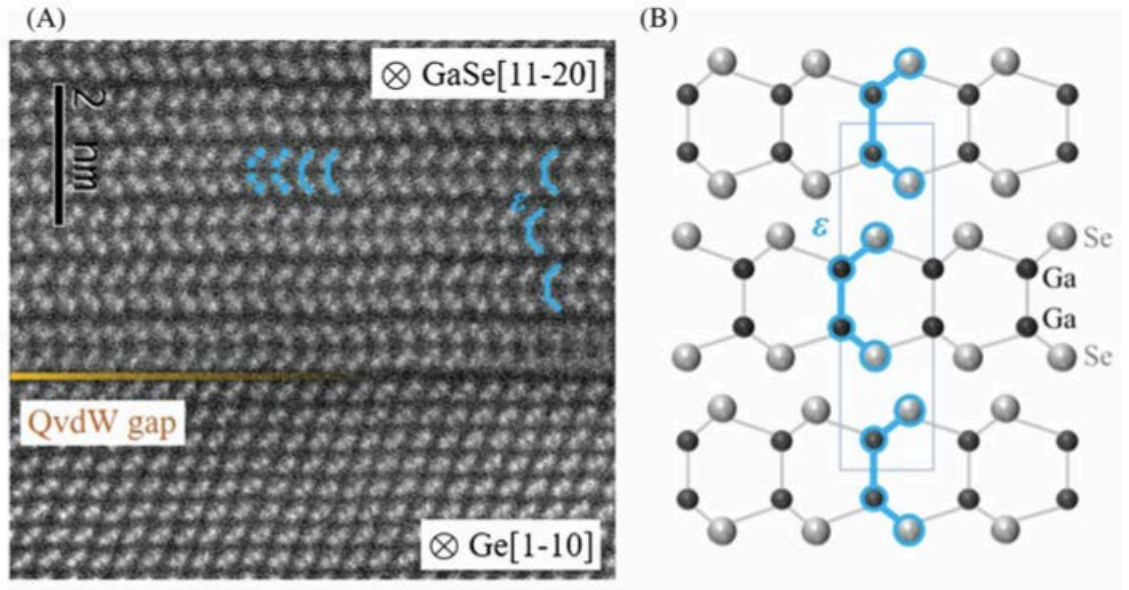


Figure 3.4: A) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of the GaSe/Ge(111) interface B) GaSe layers in ϵ -type stacking. Figure is taken from (Yonezawa et al. (2019)).

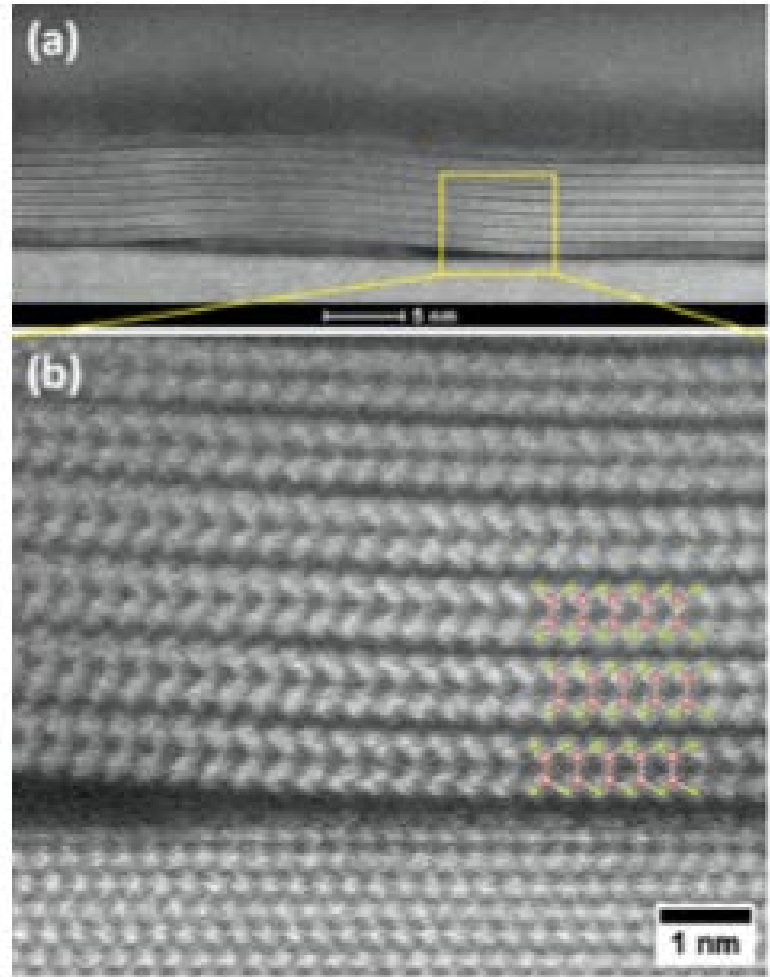


Figure 3.5: a) Cross-sectional scanning transmission electron microscopy (STEM) image of GaSe film grown at GaN substrate. b) Magnified image from the boxed area in (a). Figure is taken from (Lee et al. (2017)).

3.3 Fe and FeSe growth on Silicon

Our main goal is to check whether the GaSe termination of the Si(111) surface prevents silicide formation during the attempted growth of epitaxial FeSe. We first attempted to grow a FeSe film directly onto the Si(111)7×7 substrate without an intermediate GaSe layer and measured the Fe 2*p* and Si 2*p* core level spectra with XPS. For reference, we also deposited pure Fe directly onto Si(111), which is sure to produce FeSi and/or FeSi₂. Figure 3.6 shows the corresponding Fe 2*p* spectra. The Fe coverage is the same for both spectra. Note that the spectra are almost identical, suggesting that FeSe deposition results in silicide formation. We compare our spectra with those of Fe silicide measured by Ohtsu et al., which are shown in Figure 3.7 (Ohtsu et al. (2013)). The spectrum looks very similar to the ones obtained in our experiment, Figure 3.6.

Taking a closer look at the Fe 2*p*_{3/2} region in Figure 3.8, we find that the spectra for the FeSe and Fe deposits on Si are indeed very similar. There is a small shift between the spectra of about 0.1 eV, but this is well within the instrumental resolution of the XPS spectrometer. In Figure 3.9, we compare the Fe 2*p* spectra of the FeSe deposited on Si(111) and that of epitaxial FeSe grown on SrTiO₃. Their lineshapes are very different, and we tentatively conclude that the FeSe deposited on Si(111) has little in common with epitaxial FeSe. The epitaxial FeSe film on STO was synthesized by Mr. Xiyu Peng in Prof. Weiering’s group, and the corresponding XPS spectrum was measured by Mr. Kaleb McClure in Prof. Mannella’s group. These experiments clearly highlight the need to passivate silicon before attempting the growth of epitaxial FeSe.

3.4 GaSe phase diagram

The Si(111) surface can be passivated by growing a layer of GaSe. However, it is important to note that there are also other competing phases of Ga-Se compound.

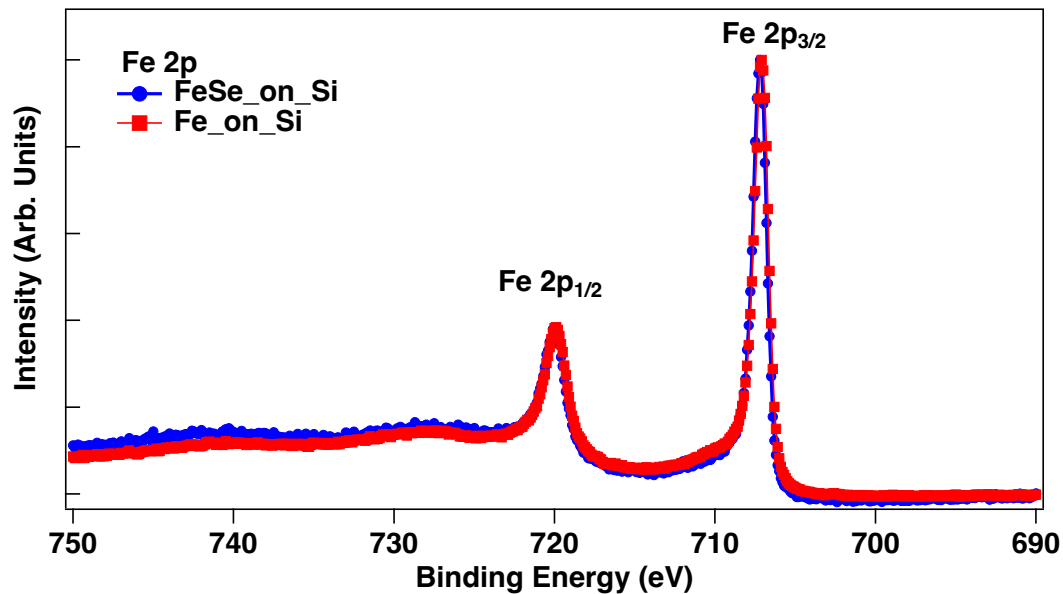


Figure 3.6: Comparison of Fe 2p core-level XPS spectra after growing FeSe and Fe films on Si(111), after Shirley background subtraction.

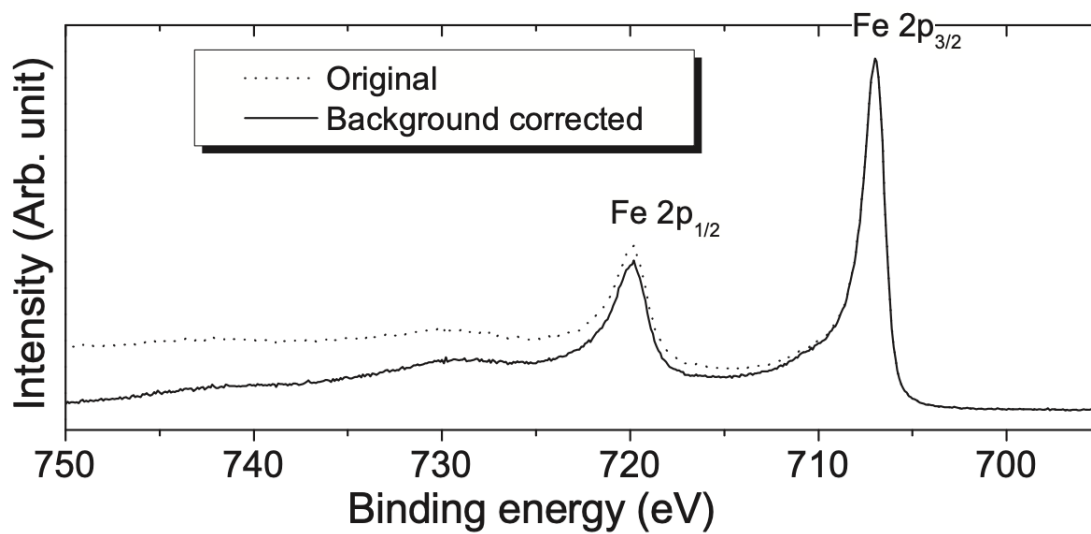


Figure 3.7: XPS spectrum for a ‘fractured’ FeSi surface after Tougaard background subtraction. This figure taken from [Ohtsu et al. \(2013\)](#).

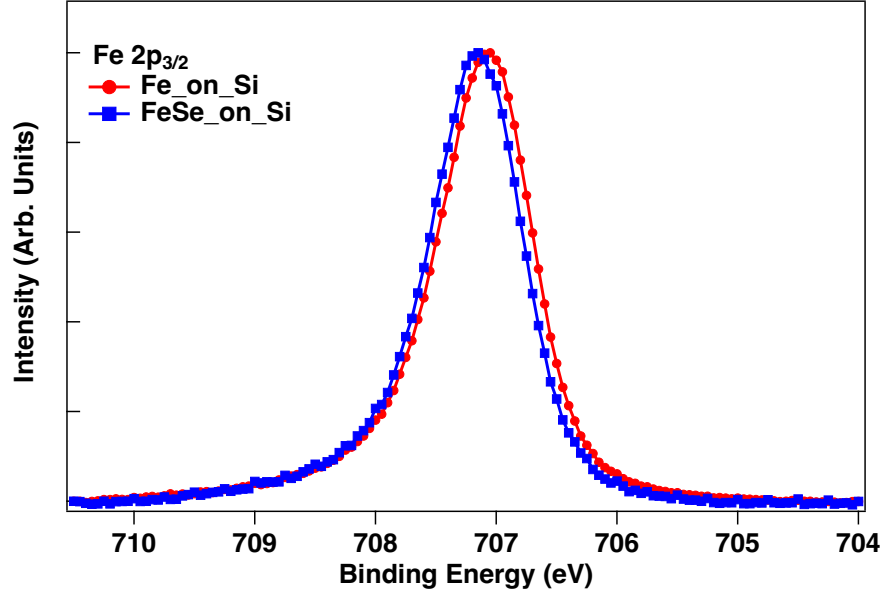


Figure 3.8: XPS spectra of Fe 2p_{3/2} region for Fe and FeSe deposits on Si(111), after Shirley background subtraction.

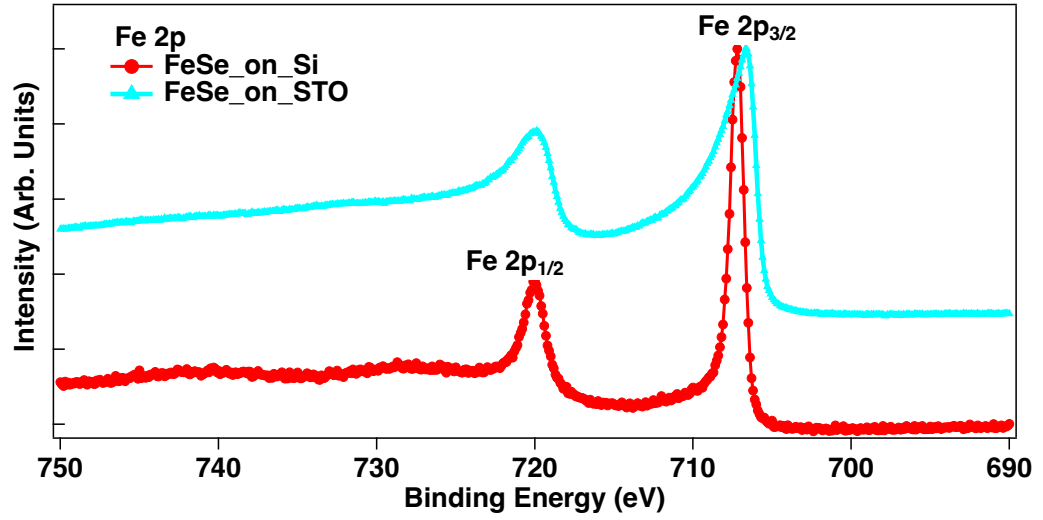


Figure 3.9: XPS spectra of Fe 2p core-level for FeSe films grown on Si and STO substrates.

The phase diagram of Ga-Se is shown in Figure 3.10. It is evident from the phase diagram that there are two stable phases, GaSe and Ga₂Se₃. It is *a priori* not clear which phase would be obtained in MBE because MBE growth requires large amounts of excess Se vapor, due to its low sticking coefficient at the typical growth temperature. While GaSe has a layered hexagonal crystal structure with lattice parameters $a = 3.76 \text{ \AA}$ and $c = 16.02 \text{ \AA}$. Ga₂Se₃ has a cubic structure with lattice parameter $a = 5.445 \text{ \AA}$. The in-plane lattice constant of hexagonal FeSe is fairly close to that of the Si(111) surface (3.84 $\text{\AA}$). The lattice match improves for the cubic Ga₂Se₃ phase when growing it in the (111) orientation: 3.85 $\text{\AA}$. This suggests that the growth of Ga₂Se₃ might be preferred. Ultimately, the Se content of the film is determined by the supersaturation conditions of the Se flux (Okamoto (2009), Suzuki and Mori (1974)).

3.5 Experimental protocols and calibration

The experiments were carried out in an ultra-high vacuum system consisting of the MBE chamber and the analysis chamber equipped with RHEED, LEED, and XPS. Si(111) wafers, arsenic doped with a resistivity of 0.002 $\Omega\text{-cm}$, were cut into 3 mm x 10 mm pieces and mounted onto a molybdenum sample holder. The Si sample was degassed overnight at around 600 $^{\circ}\text{C}$ and then flashed to about 1200 $^{\circ}\text{C}$ in UHV to remove the native oxide layer and to obtain an atomically clean and well-ordered Si(111)7 $\times$ 7 surface. The temperature of the substrate was measured with an optical pyrometer. The presence of the 7 $\times$ 7 reconstruction was confirmed with both LEED and RHEED, as shown in Figure 3.11.

The cleanliness of the surface was also checked with XPS, Figure 3.12. The usual contaminants, *i.e.*, carbon and oxygen, were not visible in the XPS spectrum. Once a substrate is prepared, the GaSe layer is grown next.

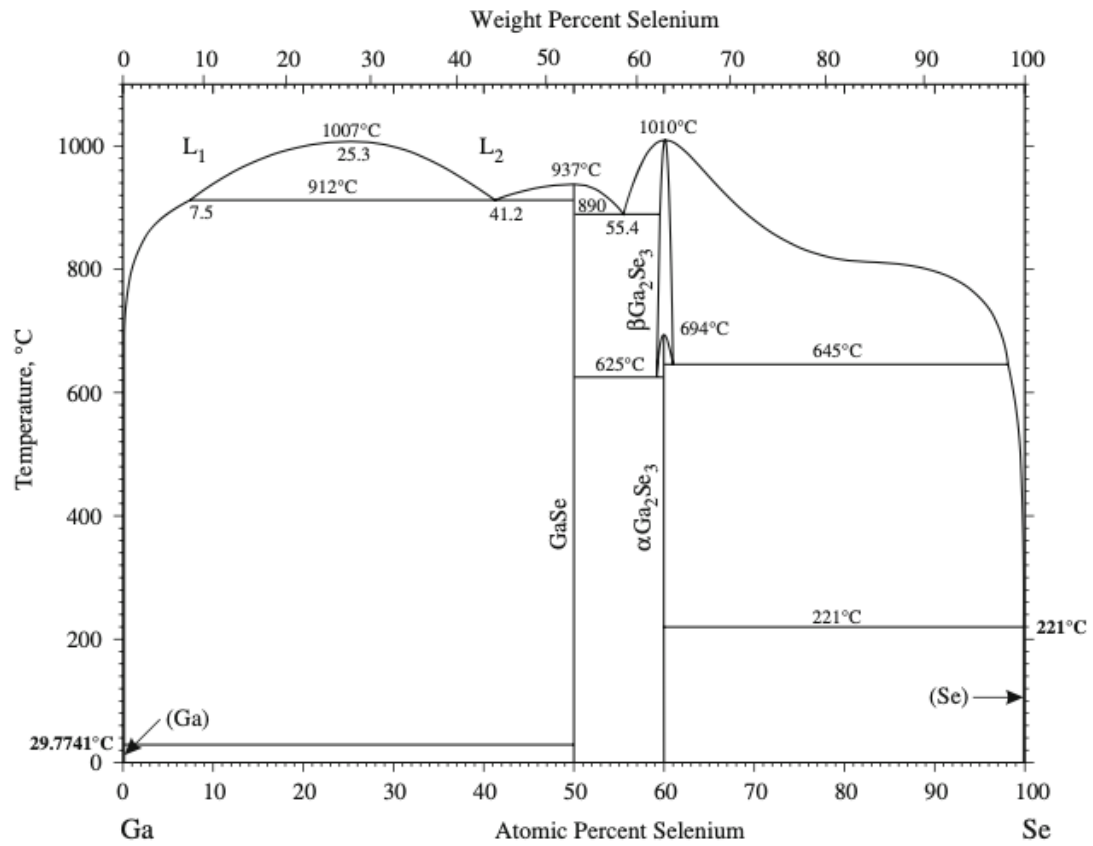


Figure 3.10: Phase diagram of Ga-Se. The figure is taken from (Okamoto (2009)).

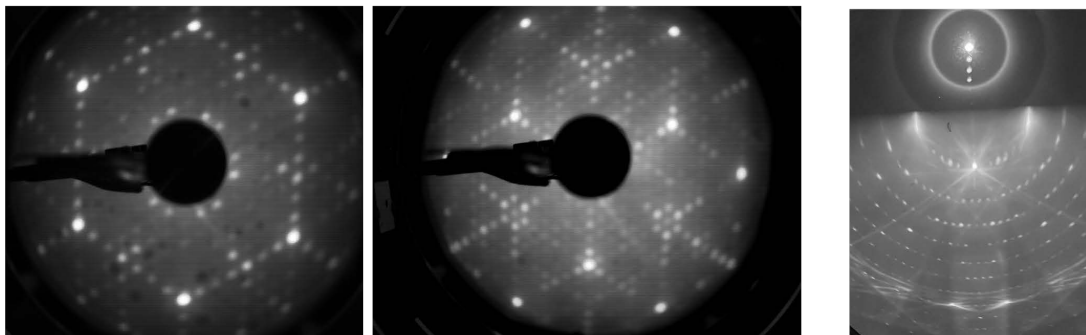


Figure 3.11: Left, center: LEED pattern of the Si(111) 7×7 surface reconstruction taken at a beam energy of 57 eV and 110 eV. Right: RHEED pattern of the same substrate. The beam energy of RHEED is 15 KeV.

The deposition rate of Ga was calibrated by measuring the deposition time required to form the gallium-induced $\sqrt{3} \times \sqrt{3}$ surface reconstruction on Si(111), which has a known Ga coverage of 1/3 ML (one ML is defined as the areal density of atoms in the Si(111) plane: 7.83×10^{14} atoms per cm^2). The Si substrate was kept at 550 °C during the growth. First of all, a program was written in Labview to monitor the CCD camera intensity of the diffraction spots in RHEED during Ga deposition. The interface of the program is shown in Figure 3.13. We then select the region of interest on the RHEED screen where we wish to monitor changes in the diffraction intensity. A real-time graph of the RHEED intensity versus time is displayed on the screen and saved as a text file. In our experiment, we monitored the 1/3rd and 2/3rd order spots of Ga-induced $\sqrt{3} \times \sqrt{3}$ reconstruction separately. The change in intensity with respect to time is then plotted and fitted, as shown in Figure 3.14. It takes about 70 seconds before the Ga-induced $\sqrt{3} \times \sqrt{3}$ reconstruction shows up in RHEED. The corresponding diffraction intensity then increases linearly with time, as expected for single-phase growth, until other phases start to form at

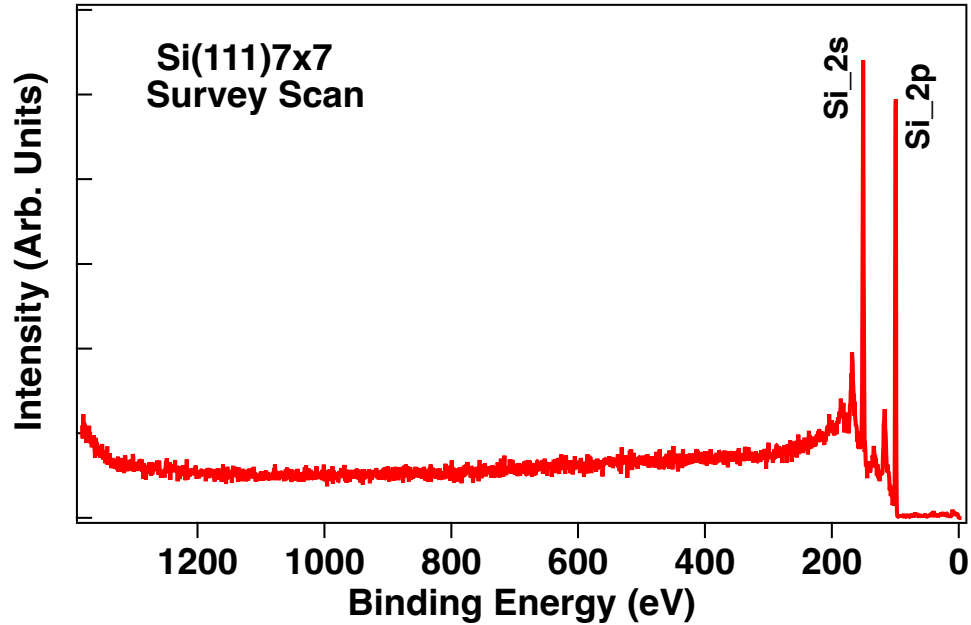


Figure 3.12: XPS spectrum of Si (111) 7×7 measured with a pass energy of 100 eV. The Si 2p and Si 2s core level peaks are labeled.

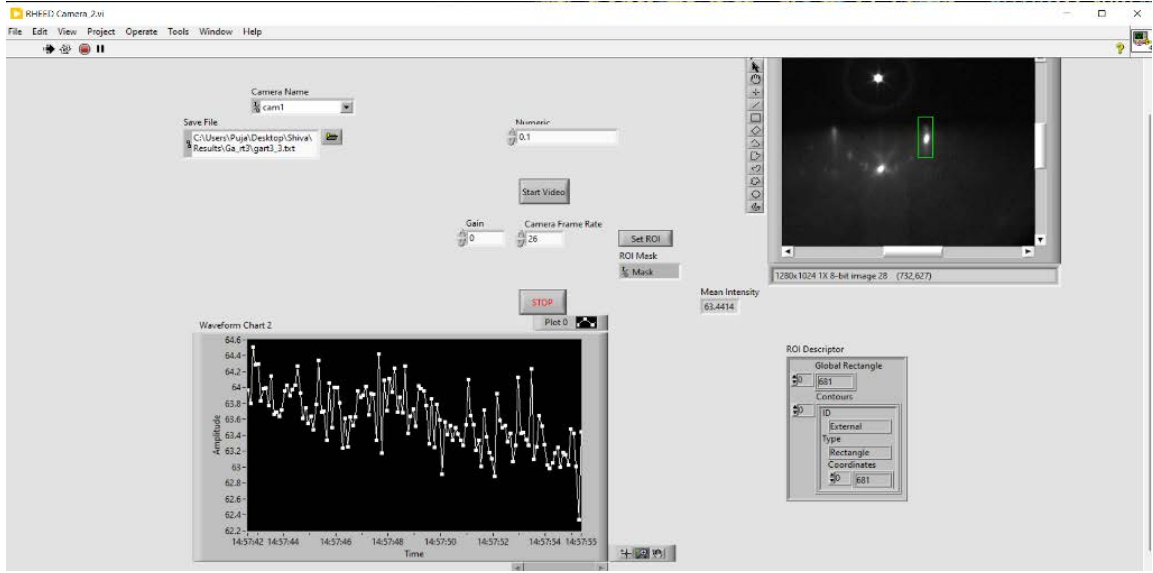


Figure 3.13: Interface of labview program to monitor the RHEED intensity in real time.

the expense of the $\sqrt{3} \times \sqrt{3}$ phase. The deposition time corresponding to the kink in the graph (173 seconds) is then assumed to be the time needed to grow 1/3 ML of Ga. It is important not to overshoot the kink coverage because this may lead to Ga clustering, which is detrimental to the GeSe film quality. This graph shows the intensity variation of the 2/3rd spot of the Ga-induced $\sqrt{3} \times \sqrt{3}$ reconstruction. A very similar result is obtained for the 1/3rd spot, producing the exact same deposition time (within 1 %). For a complete ML of GaSe, we would need to deposit three times longer. For a complete bilayer of GaSe, one needs to deposit Ga for a total of 6×173 seconds. If the Ga source temperature is changed, the calibration would have to be redone. The temperature of the Se effusion cell was adjusted such that the Se vapor pressure exceeded that of Ga by a factor of 8 to 10. This heavy over saturation is needed as few Se atoms stick to the GaSe passivated surface when the substrate is kept at 550 °C. The LEED pattern of the Ga-induced $\sqrt{3} \times \sqrt{3}$ reconstruction on Si(111) is shown in Figure 3.15. The corresponding RHEED pattern is also shown.

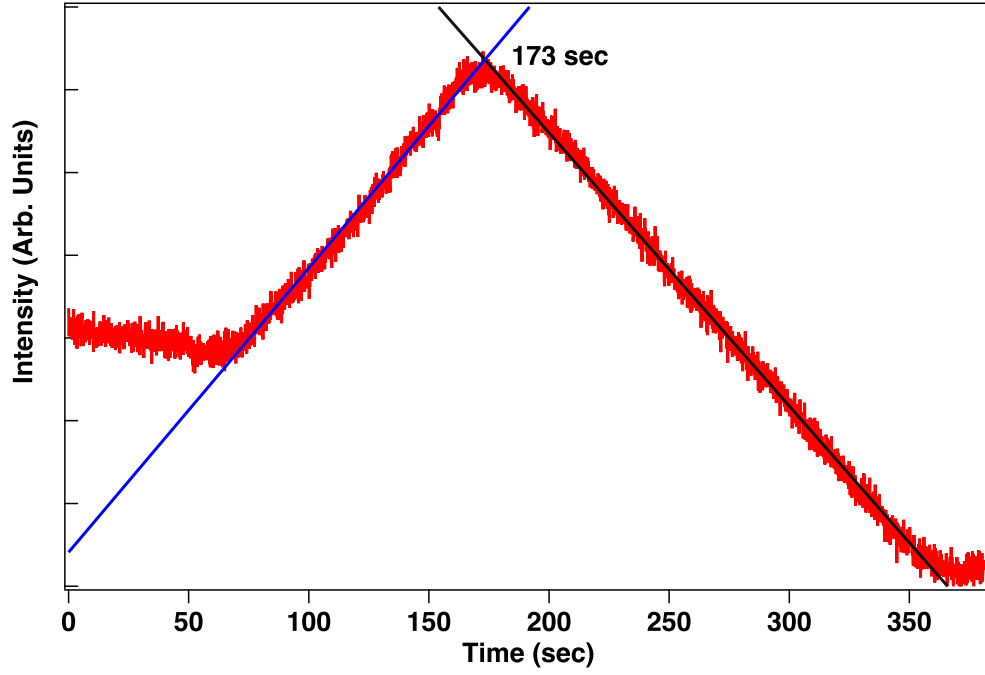


Figure 3.14: Intensity of the $(2/3,2/3)$ diffraction spot in RHEED of the Ga-induced $\sqrt{3} \times \sqrt{3}$ surface plotted as a function of deposition time. The intensity increases with time, reaches a maximum, and then starts to decrease, all in a linear fashion. The two linear segments are fitted with straight lines whose intersection corresponds to the optimal $1/3$ ML coverage for forming the $\sqrt{3} \times \sqrt{3}$ phase of Ga on Si(111).

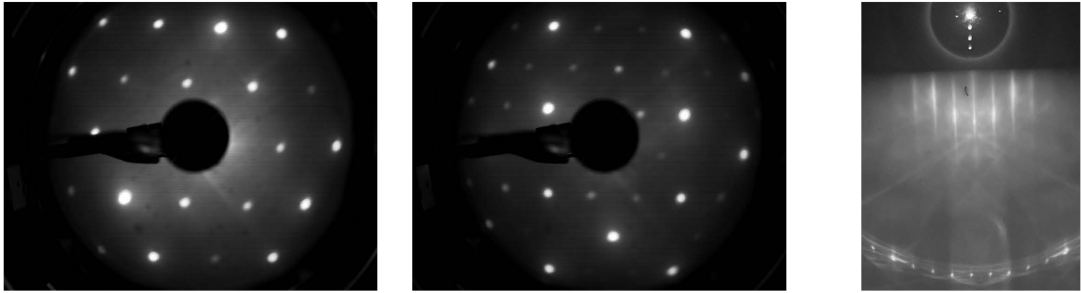


Figure 3.15: Left, center: LEED pattern of the Ga-induced $\sqrt{3} \times \sqrt{3}$ reconstruction on Si(111) taken with a beam energy of 57 eV and 110 eV. Right: RHEED pattern of the same sample. The beam energy in RHEED is 15 KeV.

3.6 Van der Waals passivation of Si(111)

When GaSe is deposited on Si(111)7×7, the growth quality strongly depends on the substrate temperature. It is found that a GaSe passivated Si(111) surface is formed at a substrate temperature of 500 °C to 600 °C. The passivated surface is a monolayer GaSe layer, which fully passivates the dangling bonds of the Si(111) surface, and the 7×7 surface reconstruction is completely gone. Additional Ga and Se deposition at these temperatures does not increase the film thickness, as the Se atoms no longer appear to stick (Meng (2000), Ohta et al. (2004)). The GaSe passivated surface is the template for the subsequent growth of GaSe and FeSe thin films at substrate temperatures well below 500 °C.

Figure 3.16 shows the RHEED pattern for the Si(111)7×7, and GaSe passivated Si (111) surface. The beam energy of the RHEED is 15 KeV. To passivate the 7×7 surface, a monatomic GaSe layer was grown at a substrate temperature of 550 °C. Se and Ga were evaporated from separate effusion cells. Figure 3.16 also shows the hexagonal LEED pattern of the passivated Si surface at beam energies of 57 eV, 90 eV, and 110 eV. The contrast variation in the diffraction spots suggests a threefold rotational symmetry, as expected for the Si(111) substrate.

The XPS survey scan is shown in Figure 3.17. All the core level peaks are shown in the figure. This includes the Ga 2s, Ga 2p_{3/2}, Ga 2p_{1/2}, Ga 3d, Se 3s, Se 3p, Se 3d, Si 2p, Si 2s core levels. In addition, there are several Auger peaks that belong to Ga or Se. The intensity of Ga 2p is quite large compared to the other peaks, as its photoemission cross-section is very large.

The Si 2p spectrum was recorded after GaSe passivation and is shown in Figure 3.18. The peak was fitted using the Voigt function for both the 2p_{3/2} and 2p_{1/2} peaks. The spin-orbit splitting obtained from the fitting is 0.602 eV, consistent with the literature value (Čechal et al. (2006)), and the branching ratio of 0.503 is very close to the theoretical value of 0.5. The Gaussian width for both peaks was 0.3 eV. We also recorded the Si 2p spectrum of the pristine Si(111) 7×7 surface, which

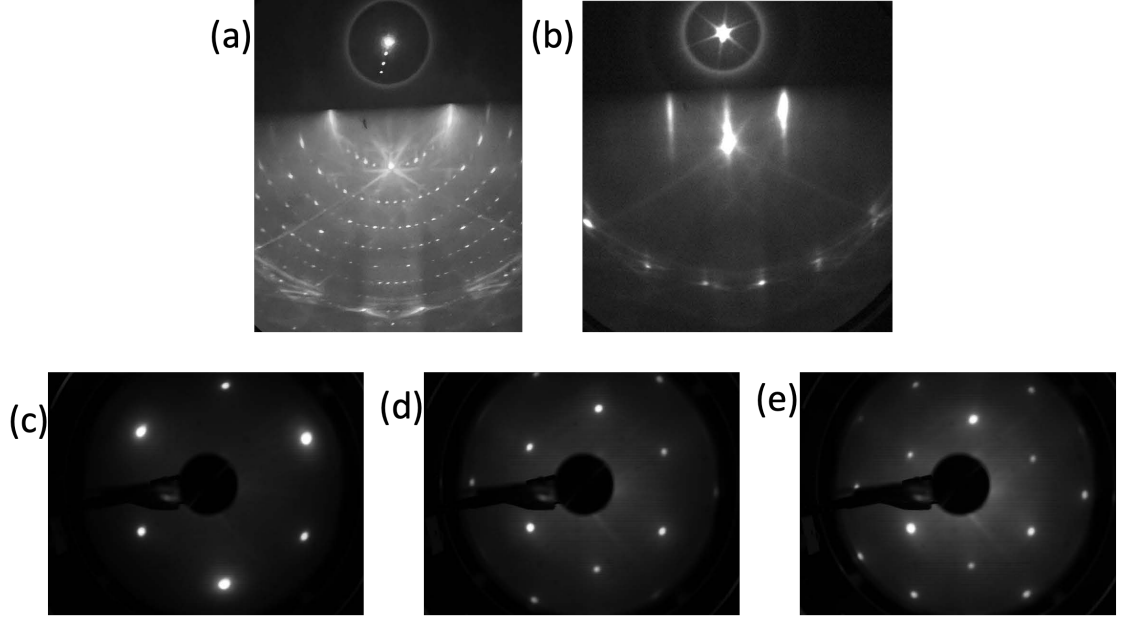


Figure 3.16: RHEED pattern of (a) Si(111)7 $\times$ 7 and (b) the GaSe passivated Si(111) surface. The beam energy of RHEED is 15 KeV. The LEED patterns of GaSe passivated Si (111) were recorded with beam energies of (c) 57 eV, (d) 90 eV, and (e) 110 eV. The patterns originate from the same sample, before and after deposition.

is shown in Figure 3.19. Though the spin-orbit splitting was close to 0.6 eV, the branching ratio was way off, 0.73. The Gaussian width for both peaks was kept at 0.3 eV. The large discrepancy between the experimental and theoretical branching ratios indicates that the experimental spectrum contains multiple unresolved peaks. This is to be expected because the 7 $\times$ 7 reconstruction is very complex, with various atomic sites, each with a different atomic coordination. The 2*p* spectrum thus contains contributions from the adatoms, restatoms, and dimer atoms of the reconstruction, each of which appears at slightly different binding energy, which is the cause of the apparently wrong branching ratio when fitted with only one spin-orbit doublet. The main contribution still originates from the bulk atoms due to the relatively large inelastic mean free path of the Si 2*p* photoelectrons. A more realistic fit of the 7 $\times$ 7 spectrum with multiple spin-orbit doublets can be obtained using high-resolution spectra acquired with synchrotron radiation, see e.g. (Čechal et al. (2006)). The parameters obtained in our fitting are summarized in Table 3.1.

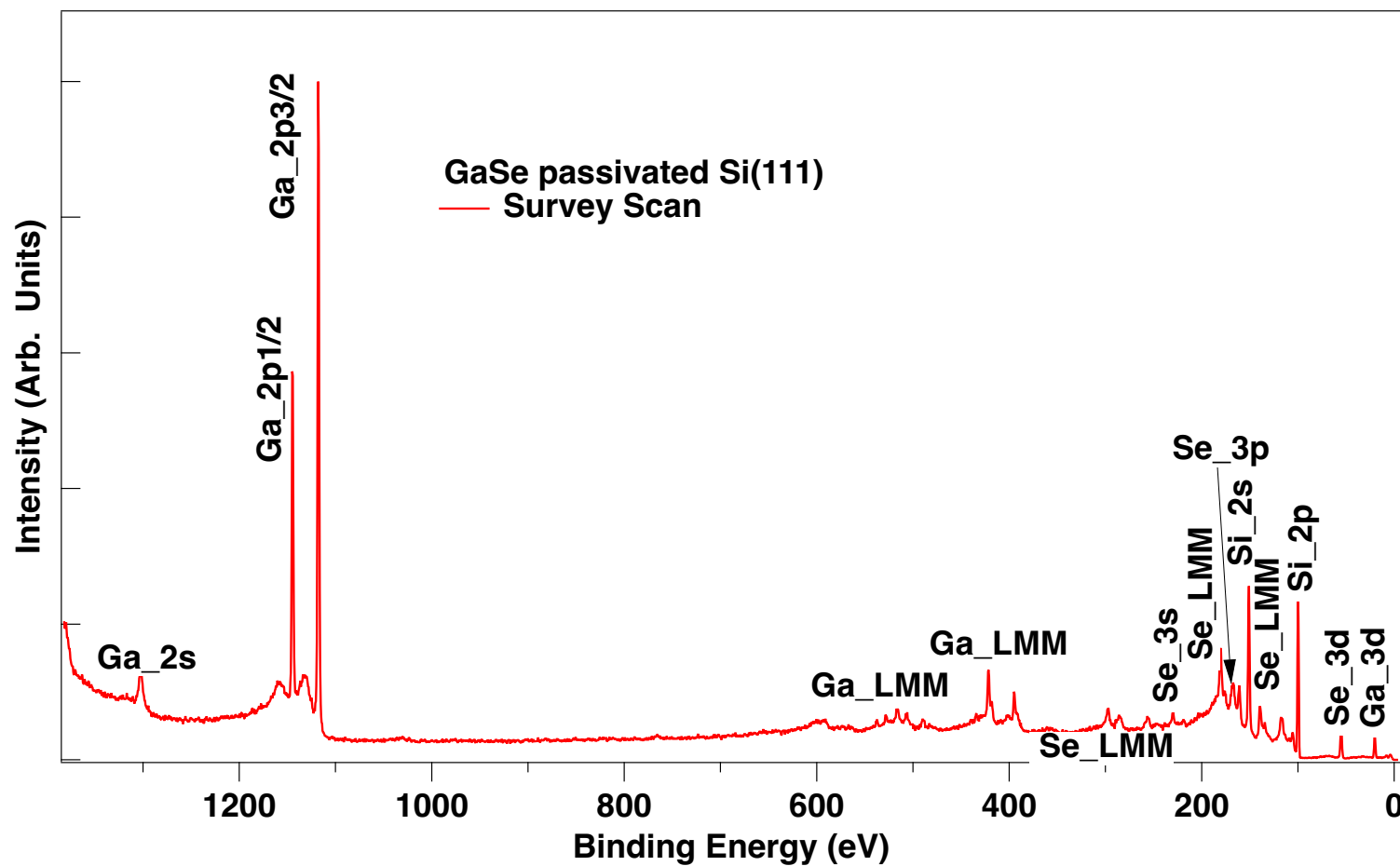


Figure 3.17: XPS spectrum of GaSe terminated Si(111). The core level peaks of Ga, Se, and Si are labeled in the spectrum.

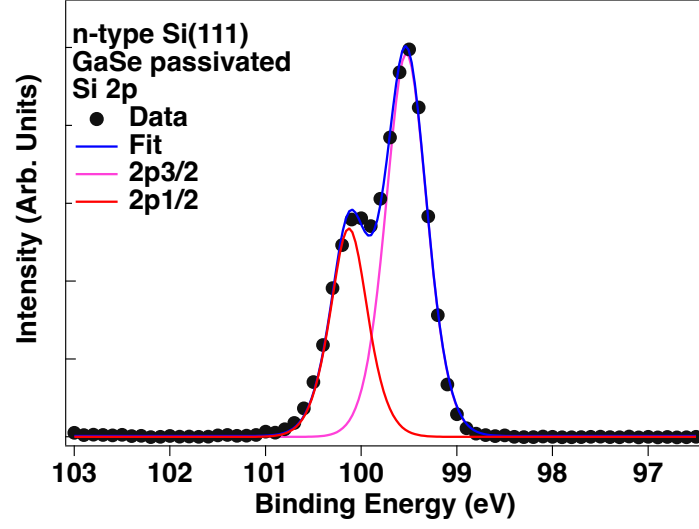


Figure 3.18: XPS spectrum of Si $2p$ core level peak of GaSe passivated Si(111). It is fitted with two Voigt line shapes after Shirley background subtraction.

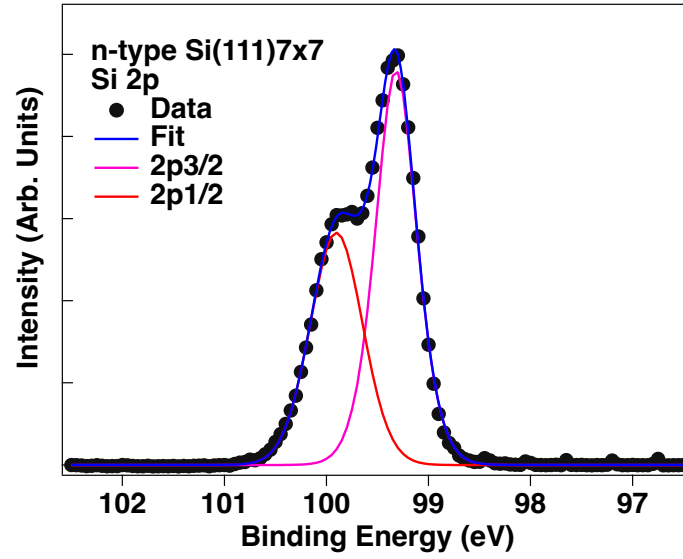


Figure 3.19: XPS spectrum of Si $2p$ core level peak of Si(111)7 $\times$ 7. It is fitted with two Voigt line shapes after Shirley background subtraction.

Table 3.1: Fitting parameters of the Si 2*p* spectrum for Si(111)7×7 and GaSe passivated n-type Si(111), shown in Figure 3.18 and 3.19 respectively.

Parameters	Si(111)7×7	GaSe passivated Si(111)
2p 1/2 position (eV)	99.90	100.13
2p 3/2 position(eV)	99.32	99.53
$\Delta_{s.o.}$ (eV)	0.59 ± 0.01	0.60 ± 0.01
Area Ratio	0.73	0.50
Gaussian width (eV)	0.3 eV	0.3 eV

The substrate used in this experiment is a n-type Si(111). We will follow up with a more detailed analysis of the photoelectron spectra in Chapter 5.

Figure 3.20 shows the STM image, 5 nm × 5 nm, of the GaSe passivated Si (111) surface, which clearly shows a hexagonal lattice, as expected. The small undulation of the atoms rows in the image is due to the thermal drift of the tip during the data acquisition. Figure 3.21 shows the STS spectra of the same sample. The first plot contains five point spectra, acquired at the same location in the forward and backward scans. The spectra are nearly identical, indicating the tip and the temperature were very stable. The center plot shows the average of all five STS spectra. The STS spectrum on the right is the normalized dI/dV spectrum, which shows a band gap of about 2.1 eV (Fernelius (1994)). This matches the band gap of bulk GaSe. All spectra were recorded at 77 K.

The GaSe passivated surface on Si(111) can also be prepared by using a Ga_2Se_3 effusion cell (as opposed to a pure Ga source) in combination with a Se effusion cell. The corresponding RHEED and LEED patterns are shown in Figure 3.22. Both diffraction patterns are sharp and have low background intensity. XPS spectra of GaSe passivated Si(111), obtained using the two different growth methods described above, are also identical. This indicates that the Si(111) surface can be passivated either way.

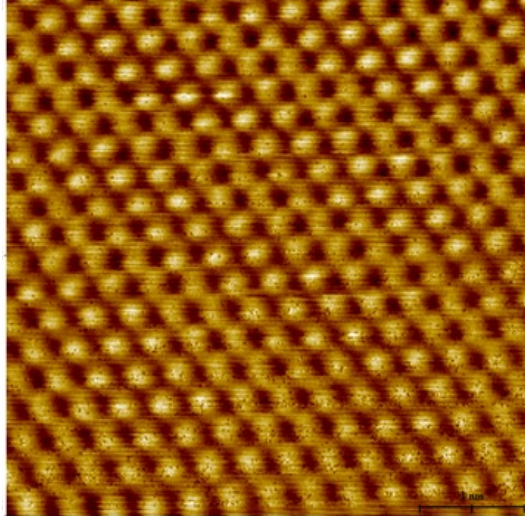


Figure 3.20: STM image of the GaSe passivated Si(111) surface. The area of the scanned image is $5 \text{ nm} \times 5 \text{ nm}$.

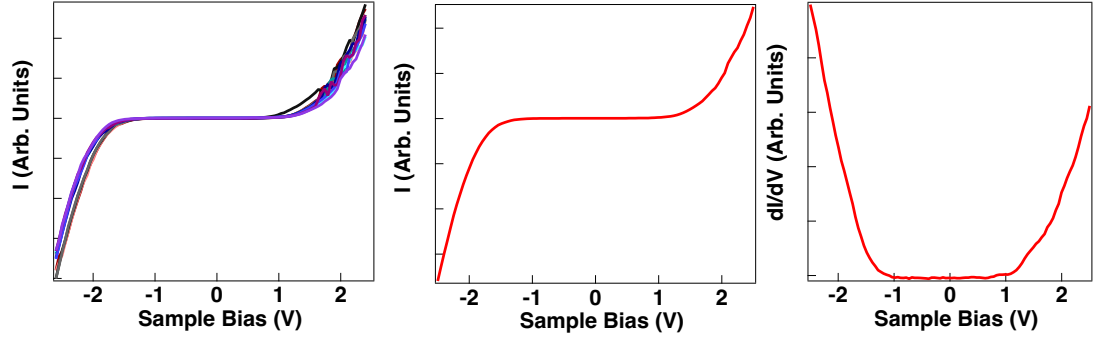


Figure 3.21: Left: I-V spectra of GaSe passivated Si (111) surface. The STS at the same point was taken for five repetitions with each forward and backward scan. Center: The average of the first STS. Right: Normalized dI/dV of the same STS spectra. All the spectra were obtained at 77 K.

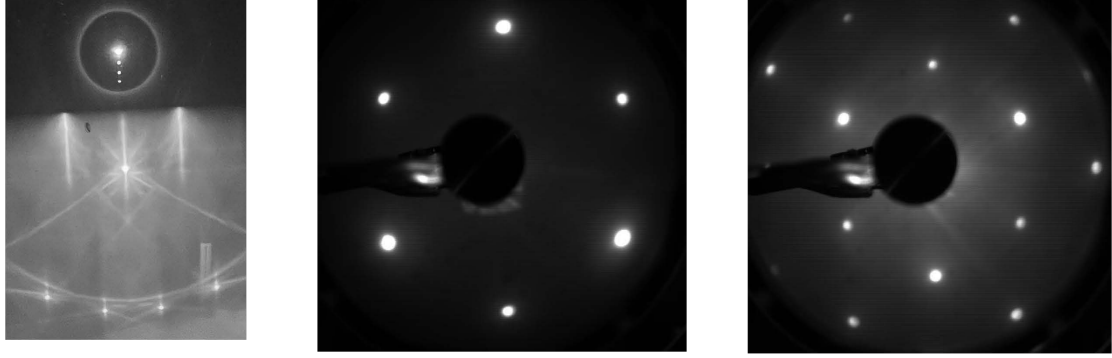


Figure 3.22: Left: RHEED pattern of GaSe terminated Si(111). The beam energy of RHEED is 15 KeV. Center, Right: LEED pattern taken at a beam energy of 57 eV and 110 eV from the same sample. The MBE source material is Ga_2Se_3 .

3.7 Van der Waals epitaxy Ga_2Se_3

After Si(111) is passivated with GaSe, attempts were made to grow thicker epitaxial GaSe films because it is not *a priori* clear how thick the buffer layer should be to completely suppress silicide formation during FeSe growth. Multilayer growth required lowering of the substrate temperature as no material was accumulated beyond 1 ML when the substrate temperature remains above 500 °C. This was verified in our experiment via LEED, RHEED, and XPS.

Figure 3.23 compares the RHEED and LEED patterns after growing 1 ML of GaSe, with and without additional deposition for two more hours. The additional deposition would correspond to a film thickness of at least six unit cells, had it been grown at the same rate as the passivation layer. A one-unit-cell thick film is equivalent to the Se-Ga-Ga-Se bilayer slab shown in Figure 3.2. The slab thickness corresponds to the *c*-axis of bulk GeSe. Note that the RHEED and LEED patterns are identical. Moreover, the XPS survey spectra do not change at all after two hours of additional deposition, as is shown in Figure 3.24. Figure 3.25 shows the Si 2*p*, Se 3*d*, Ga 2*p*_{3/2}, and Ga 3*d* core levels with or without the additional two hour deposition. There was no change in the lineshape or intensity of the core level spectra, indicating that no material is accumulated beyond the first layer at a substrate temperature of 550 °C.

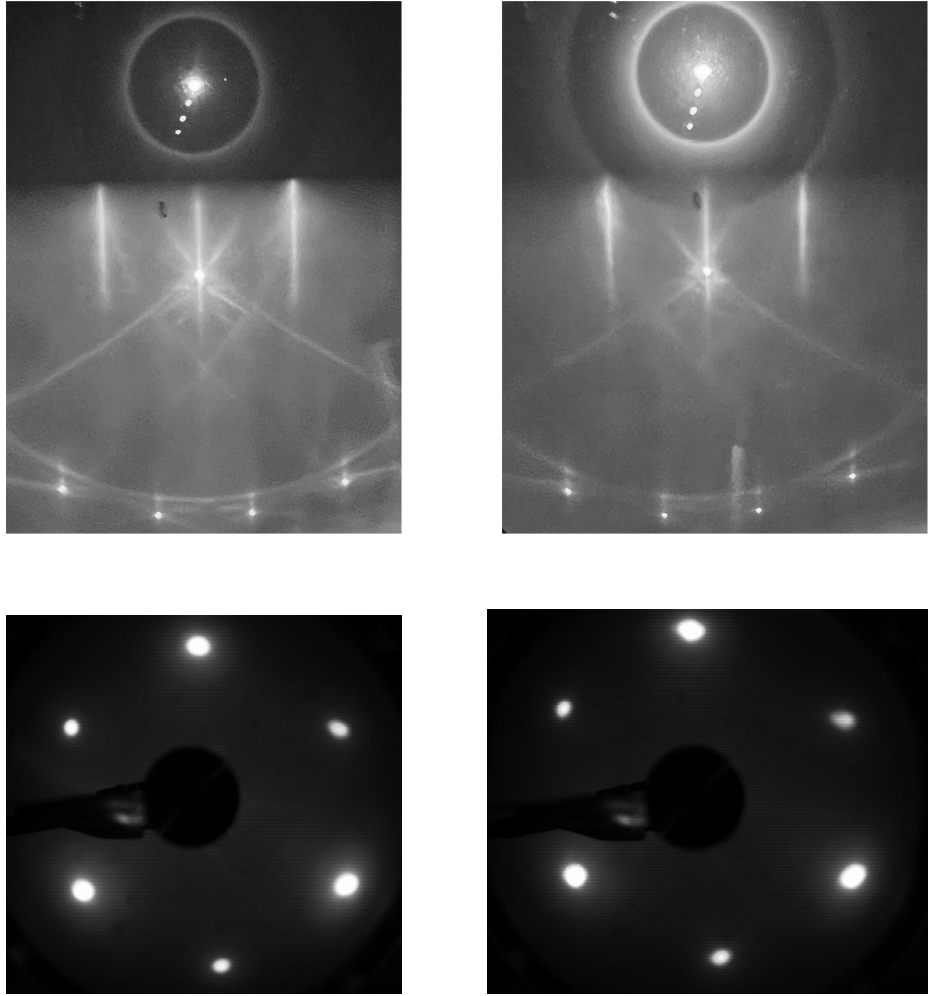


Figure 3.23: Left: RHEED and LEED pattern of GaSe passivated Si surface. Right: RHEED and LEED pattern of the same sample after two additional hours of deposition at 550 °C. The LEED is taken at the beam energy of 57 eV, and the beam energy of RHEED is 15 KeV.

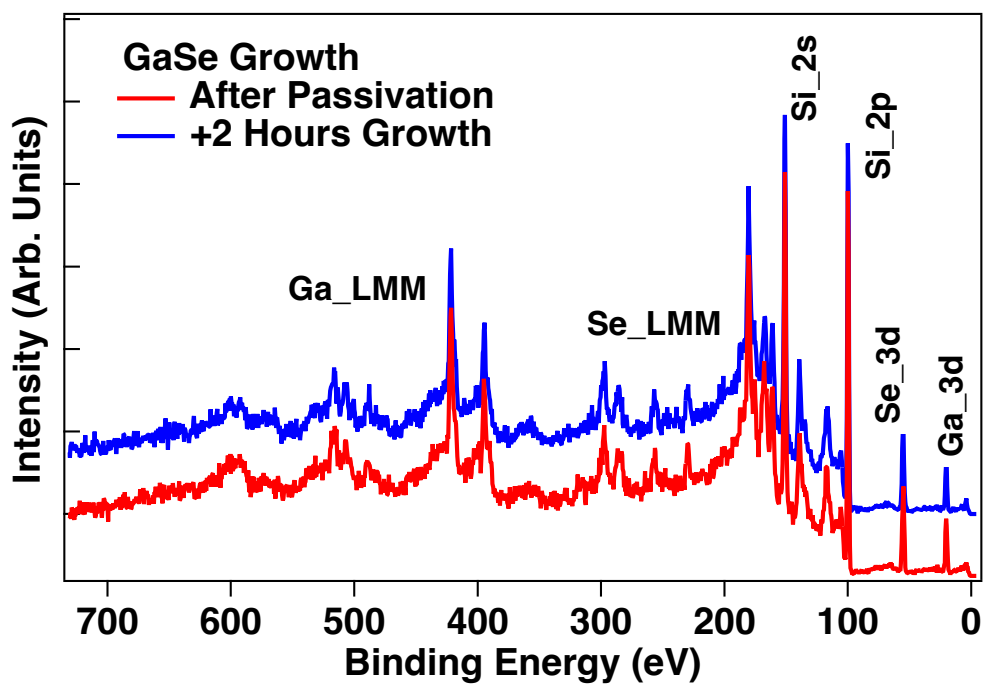


Figure 3.24: XPS spectra of the GaSe passivated Si surface, before and after two more hours of GaSe deposition. The substrate temperature was 550 °C. An offset is added to the spectra for better visualization.

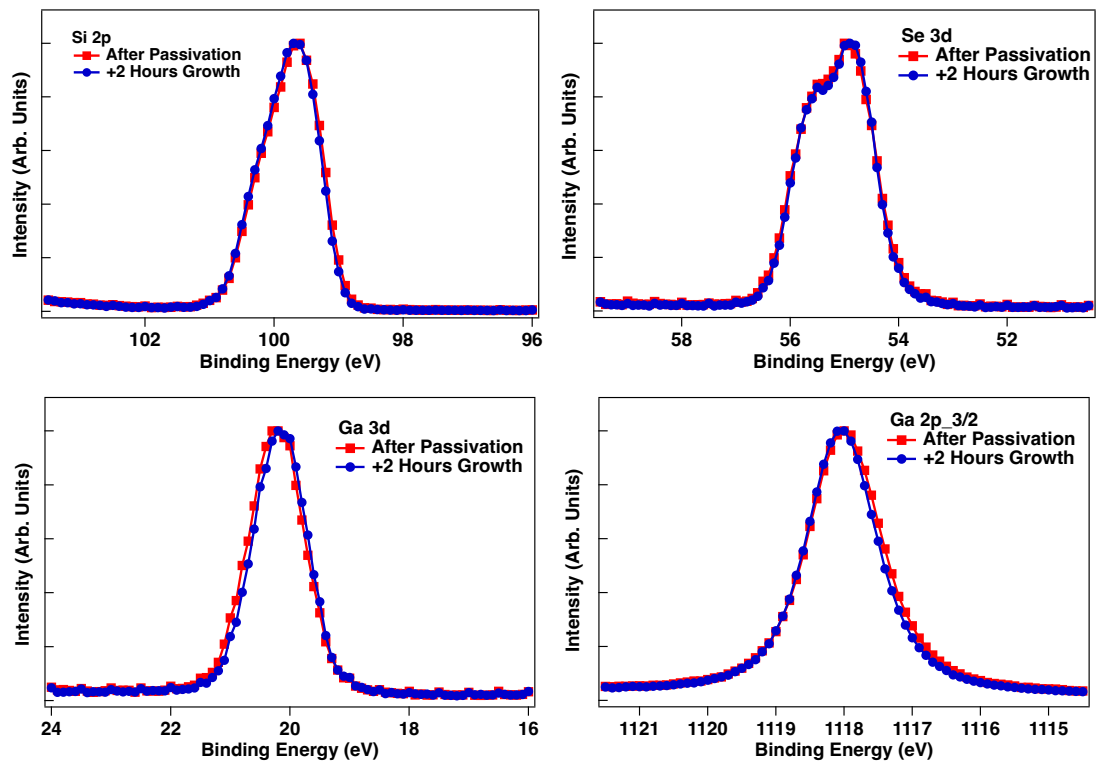


Figure 3.25: XPS core level spectra, before and after two hours of additional deposition. The growth temperature was 550 °C. From top left clockwise: Si 2p, Se 3d, Ga 2p_{3/2} and Ga 3d spectrum, respectively.

Thick GaSe films can be grown by reducing the substrate temperature to, *e.g.*, 300 °C. However, the film is not as smooth as the passivated GaSe:Si(111) surface. After growing a film with a nominal thickness of 3 unit cells at 300 °C, the RHEED pattern exhibits 3D transmission spots, suggesting that the growth film is becoming rough (Figure 3.26). Careful analysis of the RHEED pattern indicates that we grew cubic Ga₂Se₃ instead of hexagonal GaSe. This will be discussed in detail below.

Let us first review the hexagonal space lattice and its reciprocal lattice. The primitive translational vectors of the hexagonal space lattice are given by:

$$\begin{aligned}\vec{a}_1 &= \left(\sqrt{3}\frac{a}{2}\right)\vec{x} + \left(\frac{a}{2}\right)\vec{y} \\ \vec{a}_2 &= -\left(\sqrt{3}\frac{a}{2}\right)\vec{x} + \left(\frac{a}{2}\right)\vec{y} \\ \vec{a}_3 &= c\vec{z}\end{aligned}\tag{3.1}$$

The volume of the primitive cell is given by

$$V = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = \left(\frac{\sqrt{3}}{2}\right)a^2c\tag{3.2}$$

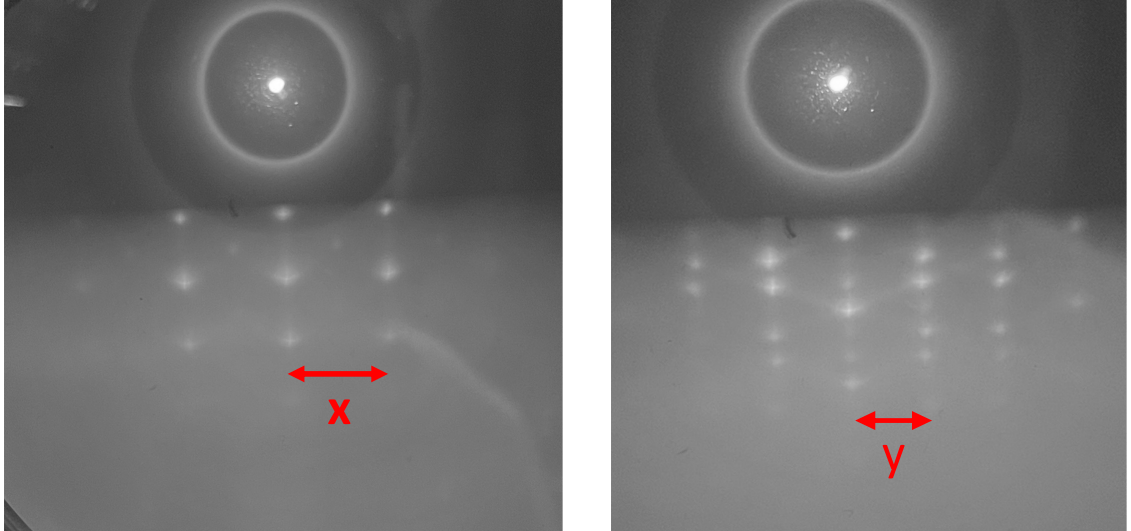


Figure 3.26: RHEED pattern recorded at different azimuthal angles, 30° apart after Ga and Se are deposited at 300 °C.

The primitive translational vectors of the reciprocal lattice are given by:

$$\begin{aligned}\vec{b}_1 &= \frac{2\pi}{V}(\vec{a}_2 \times \vec{a}_3) = \left(\frac{2\pi}{\sqrt{3}a}\right)\vec{x} + \left(\frac{2\pi}{a}\right)\vec{y} \\ \vec{b}_2 &= \frac{2\pi}{V}(\vec{a}_3 \times \vec{a}_1) = -\left(\frac{2\pi}{\sqrt{3}a}\right)\vec{x} + \left(\frac{2\pi}{a}\right)\vec{y} \\ \vec{b}_3 &= \frac{2\pi}{V}(\vec{a}_1 \times \vec{a}_2) = \left(\frac{2\pi}{c}\right)\vec{z}\end{aligned}\tag{3.3}$$

The lengths of the reciprocal lattice vectors are calculated as follows:

$$\begin{aligned}|\vec{b}_1| &= \sqrt{\vec{b}_1 \cdot \vec{b}_1} = \frac{4\pi}{\sqrt{3}a} \\ |\vec{b}_2| &= \sqrt{\vec{b}_2 \cdot \vec{b}_2} = \frac{4\pi}{\sqrt{3}a} \\ |\vec{b}_3| &= \sqrt{\vec{b}_3 \cdot \vec{b}_3} = \frac{2\pi}{c}\end{aligned}\tag{3.4}$$

The in-plane angle between the translational vectors of the hexagonal space lattice and its reciprocal lattice is 30° , which can be deduced from the scalar products $\vec{a}_1 \cdot \vec{b}_1$ and $\vec{a}_2 \cdot \vec{b}_2$. Altogether, the reciprocal lattice is also hexagonal but 30° rotated, see Figure (3.27).

Figure 3.26 shows the RHEED patterns of a 3 UC thick film. The 3D island spots are clearly visible. The two RHEED patterns were taken at two different azimuthal angles, 30° apart. The distance between the streaks, namely x and y in the figure, was calculated using the line profile in Igor Pro software. The ratio $x/y \sim \sqrt{3}$. Thus, the horizontal distance x in the first figure is measured along the (11) direction in reciprocal space, whereas the distance y is measured along the (10) direction, as illustrated in Figure 3.28. Accordingly, the incident RHEED beam is pointing along the $(\bar{1}1)$ and $(\bar{1}2)$ direction of reciprocal space, respectively.

Now that the direction of the RHEED pattern is verified, we calculate the lattice constant along the vertical direction on the screen, as shown in Figure 3.29. For the RHEED pattern along the (11) direction, the ratio of the vertical distance $3c^*$ between the spots to the horizontal distance between the spots a^* is found to be 0.622.

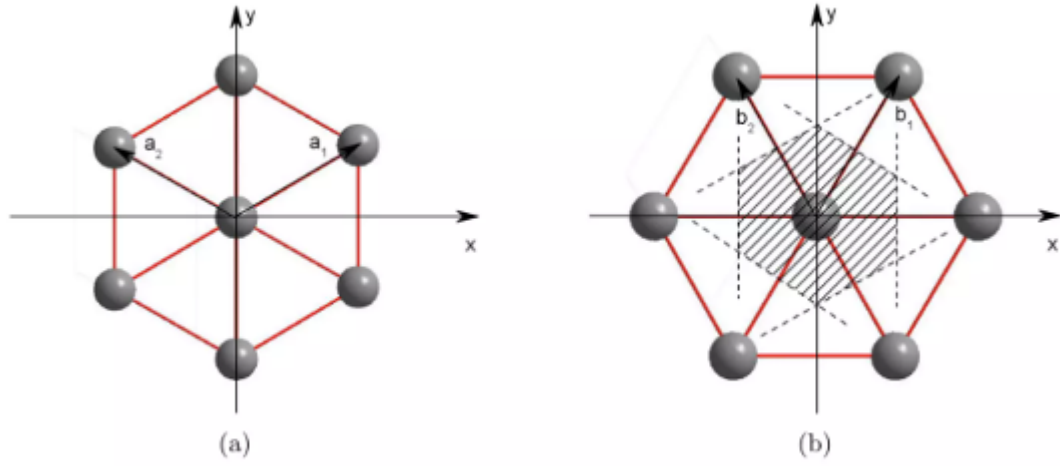


Figure 3.27: (a) Hexagonal lattice in xy plane. The angle between the unit cell vectors a_1 and a_2 is 120° . (b) Reciprocal lattice of the hexagonal lattice. The reciprocal space lattice is also hexagonal but rotated 30° with respect to the real space lattice. The angle between the unit cell vectors b_1 and b_2 is 60° . The shaded area is the Brillouin zone.

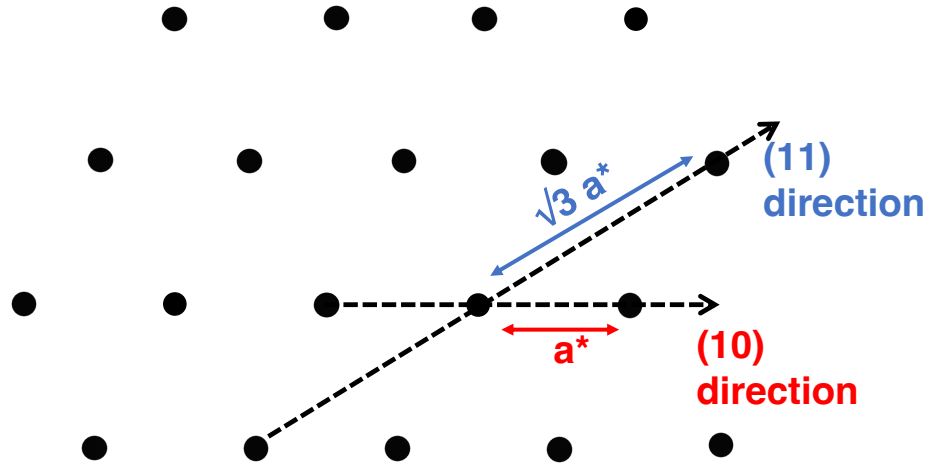


Figure 3.28: Hexagonal reciprocal space lattice. The RHEED patterns in Figure 3.26 are oriented along the (11) and (10) directions.

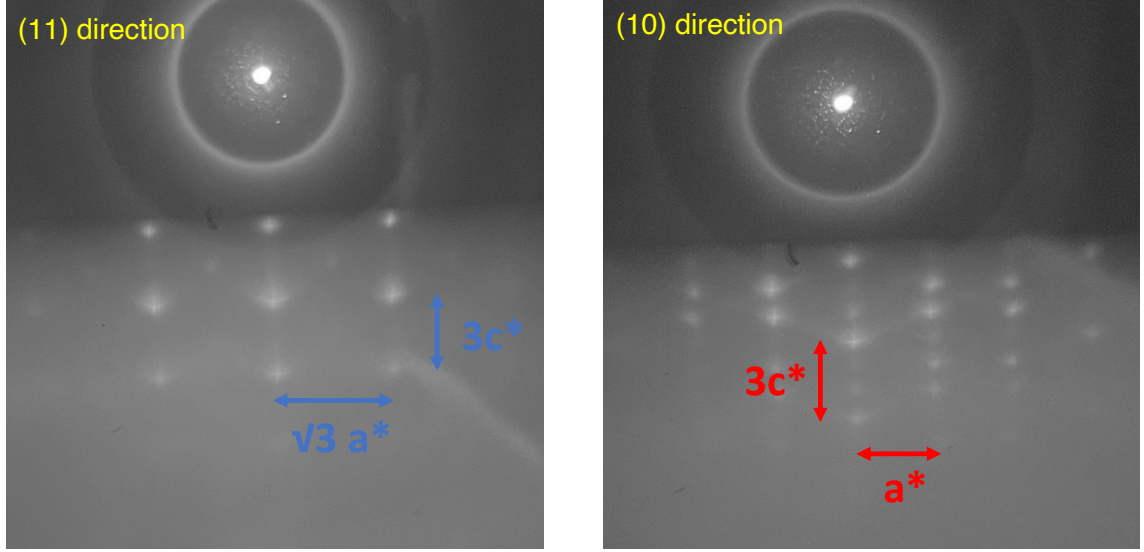


Figure 3.29: Left: RHEED pattern along the (11) direction in reciprocal space. The ratio $3c^*/a^* = 0.622$. Right: RHEED along the (10) direction in reciprocal space. The ratio $3c^*/a^* = 1.04$. The faint spots in between the main spots along the vertical direction are separated by a distance c^* .

However, in the (10) direction, we see extra spots in between the main spots along the vertical direction that are separated by a distance c^* .

For the RHEED pattern along the (11) direction, the ratio of the vertical and horizontal spacing is :

$$\frac{3c^*}{\sqrt{3}a^*} = \frac{3a}{2c} = 0.622$$

where the numerical value is obtained from the experiment. Since the main RHEED streaks of the film appear at the same position as those of the Si(111) substrate, we infer that $a = 3.84 \text{ \AA}$. Accordingly, $c = 9.26 \text{ \AA}$

The cubic lattice constants of Si and Ge_2Se_3 are $5.43 \text{ \AA}$, i.e., identical. The repeat distance along the [111] direction is then $\sqrt{3} \times 5.43 \text{ \AA} = 9.4 \text{ \AA}$. This number is very close to the $9.26 \text{ \AA}$ value obtained from the experiment. In fact, it is off by only 1.5%. We tentatively conclude that we grew the cubic $\alpha\text{-Ga}_2\text{Se}_3$ phase in our MBE experiment, where each layer grows in the (111) orientation. This essentially continues the ABC stacking of the Si(111) substrate. The cubic phase has a zinc blende crystal structure (like GaAs), but 1/3 of the Ga cations are missing. In the

following, we will corroborate this conjecture by indexing all the diffraction spots seen in RHEED.

The zinc blende lattice is face-centered cubic, Figure 3.30. The reciprocal lattice is then body-centered cubic (bcc), as shown in Figure 3.31. The reciprocal lattice constant of this bcc lattice is $4\pi/a_c$, where a_c is the cubic lattice constant of the fcc lattice in real space. In terms of the conventional reciprocal lattice constant of $2\pi/a_c$, the center of the bcc unit cell in reciprocal space can be indexed as (111), while the (100), (010) and (001) lattice points are missing. These correspond to the systematic extinctions in kinematic diffraction theory for fcc lattices. The diffraction indices should be either all odd or all even.

Referring back to the RHEED patterns in Figure 3.26, it is evident that we need to re-index our spots in the bcc setting. The in-plane (11) direction in reciprocal space in the hexagonal setting is equivalent to the $[1\bar{1}0]$ direction in the cubic setting. Along the bottom row of spots in the RHEED pattern, we can index the reflections as $(\bar{2}20)$, $(\bar{1}10)$ (000), $(1\bar{1}0)$, $(2\bar{2}0)$, etc., see Figure 3.32.

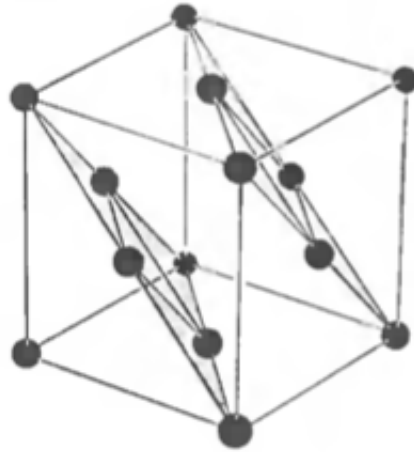


Figure 3.30: FCC lattice where the shaded planes correspond to hexagonal (111) planes. ABC stacking of such planes, shown in the shaded area, constitutes an FCC lattice structure. The figure is taken from (Ashcroft and Mermin (2014)).

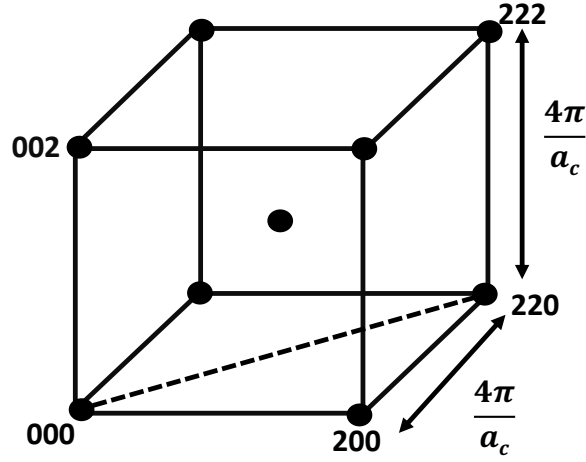


Figure 3.31: BCC unit cell in reciprocal space. The reciprocal lattice constant is $4\pi/a_c$ where a_c is the lattice constant of the fcc unit cell in real space. The three Miller indices of each reciprocal lattice point have to be all even or all odd.

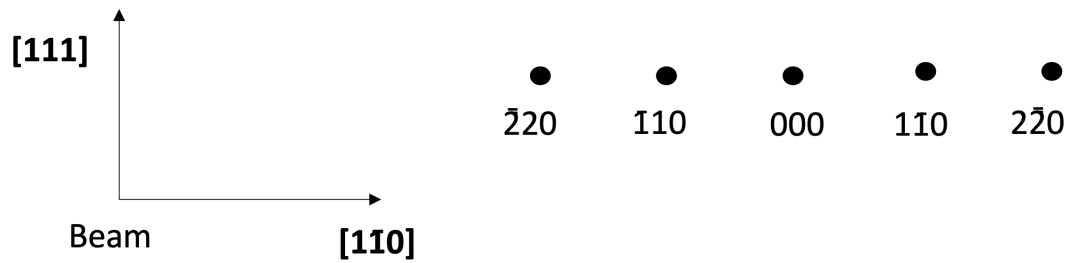


Figure 3.32: Left: Cartoon showing the $[111]$ and $[1\bar{1}0]$ direction in reciprocal space. The incident RHEED beam is perpendicular to the plane. Right: Possible indices along the horizontal direction of the RHEED pattern in Figure 3.26.

However, since the (hkl) indices should be all odd or all even for the diffraction condition for this type of crystal structure, the $(1\bar{1}0)$ and $(\bar{1}10)$ reflections are forbidden, and marked out by the red crosses, shown in Figure 3.33. Moving vertically away from the (000) reflection, the first reflection should be the (111) reflection. The second row can now be indexed by adding (111) to the indices of the bottom row (see Figure 3.34).

Likewise, we can index the reflection of the RHEED pattern along the (10) direction in Figure 3.26, or the $(\bar{1}\bar{1}2)$ direction in the cubic setting. This generates a row of spots with indices $(44\bar{8})$, $(22\bar{4})$, (000) , $(\bar{2}\bar{2}4)$, and $(\bar{4}\bar{4}8)$, etc, where the mixed even/odd indices are once again absent, see Figure 3.35. Note the presence of the (006) reflection in the third row from below. This allows for the existence of additional spots, such as the (002) and (004) reflections, since their indices are all even. Similarly, in between the (000) and $(44\bar{2})$ reflections, we can find the $(11\bar{1})$ and $(22\bar{2})$ reflections, not shown in this figure.

We can now index all the transmission spots in RHEED, if we allow for the existence of twin domains on the surface. Our patterns are very similar to those of Roy et al. for fcc stacked Ag nanoislands on an oxidized Si(111)7×7 surface. The twins are rotated by 180° (Roy et al. (2012)). Figure 3.36 shows the experimental RHEED diffraction pattern of fcc Ag, along with the simulated diffracted pattern for the A-type and B-type twins. Type A and Type B have different stacking orders (i.e., ABCABC versus ACBACB). When the simulated patterns of the A-type and B-type domains are superimposed, they perfectly match our RHEED patterns. We thus conclude that we have grown the zinc blende phase of Ga_2Se_3 .

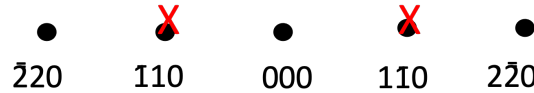


Figure 3.33: Forbidden indices marked by red crosses, because (hkl) should be all odd or all even.

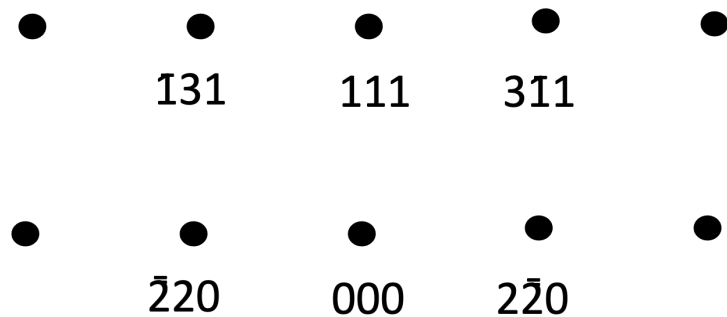


Figure 3.34: The first two rows of the (11) diffraction pattern in Figure 3.26. Mixed even/odd indices are left out.

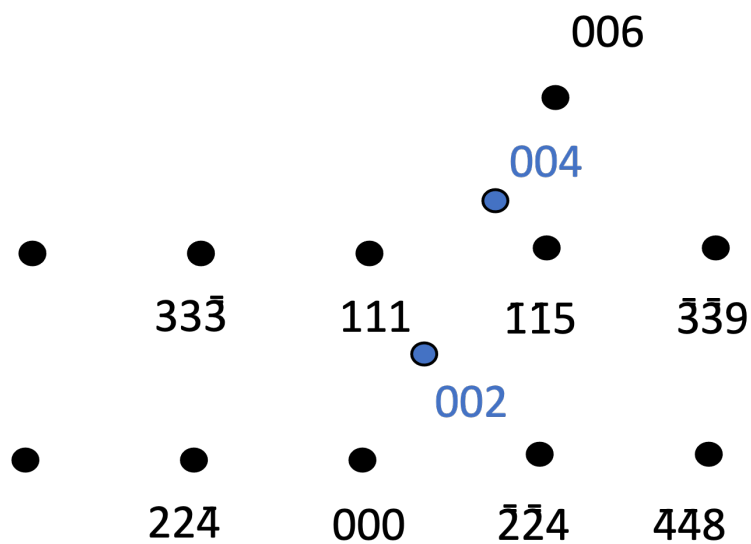


Figure 3.35: Additional (002) and (004) reflections appear in between the (000) and (006) reflections.

3.8 Conclusions

We have shown that direct deposition of FeSe onto Si(111)7×7 produces Fe silicides. In order to grow epitaxial FeSe on Si(111), a buffer layer is needed, though it is not *a priori* clear how thick the buffer layer should be. We successfully passivated the Si(111)7×7 surface with a single GaSe layer and obtained a high-quality van der Waals surface at growth temperatures between 500 °C and 600 °C. We also learned that the growth ceases after 1 ML if the substrate temperature remains above 500 °C. This is attributed to the low sticking coefficient of Se on the passivated surface. However, additional layers can be deposited at 300 °C, though the film quality quickly deteriorated with thickness. RHEED patterns indicate island formation, while LEED spots are broadened and riding on top of a strong diffuse background. The transmission patterns in RHEED can be indexed assuming fcc stacking. This strongly indicates that we have grown the zinc-blende α -Ga₂Se₃ phase. In the next chapter, we will show that a single layer GaSe on Si(111) fully suppresses silicide formation and facilitates the growth of fully relaxed hexagonal FeSe.

Chapter 4

Structure and Growth of FeSe on Si(111):GaSe

4.1 Bulk phase diagram

Superconducting FeSe thin films on STO are tetragonal. There are several competing crystallographic phases, however. The bulk phase diagram of FeSe is shown in Figure 4.1. The vertical red line at 50 atomic percent (*i.e.*, perfectly stoichiometric FeSe) is drawn for reference. The tetragonal PbO-type structure, referred to as β -FeSe, exists on the slightly Fe-rich side of the 50% line, with a composition ranging from 49.0 to 49.4% Se. The δ -FeSe phase crystallizes in the hexagonal NiAs structure, but it is unstable below about 350 °C. At this temperature, the NiAs phase is slightly Fe deficient, and the Fe vacancies order into a hexagonal superstructure with the nominal composition Fe₇Se₈. The question is whether the stoichiometric NiAs phase can be grown out-of-equilibrium with, *e.g.*, MBE. The crystal structure data for the various compounds in the FeSe phase diagram are shown in Figures 4.2 and 4.3. Along with the Fe and Se flux ratio and growth temperature, the choice of substrate will also be very important for the MBE synthesis of hexagonal FeSe.

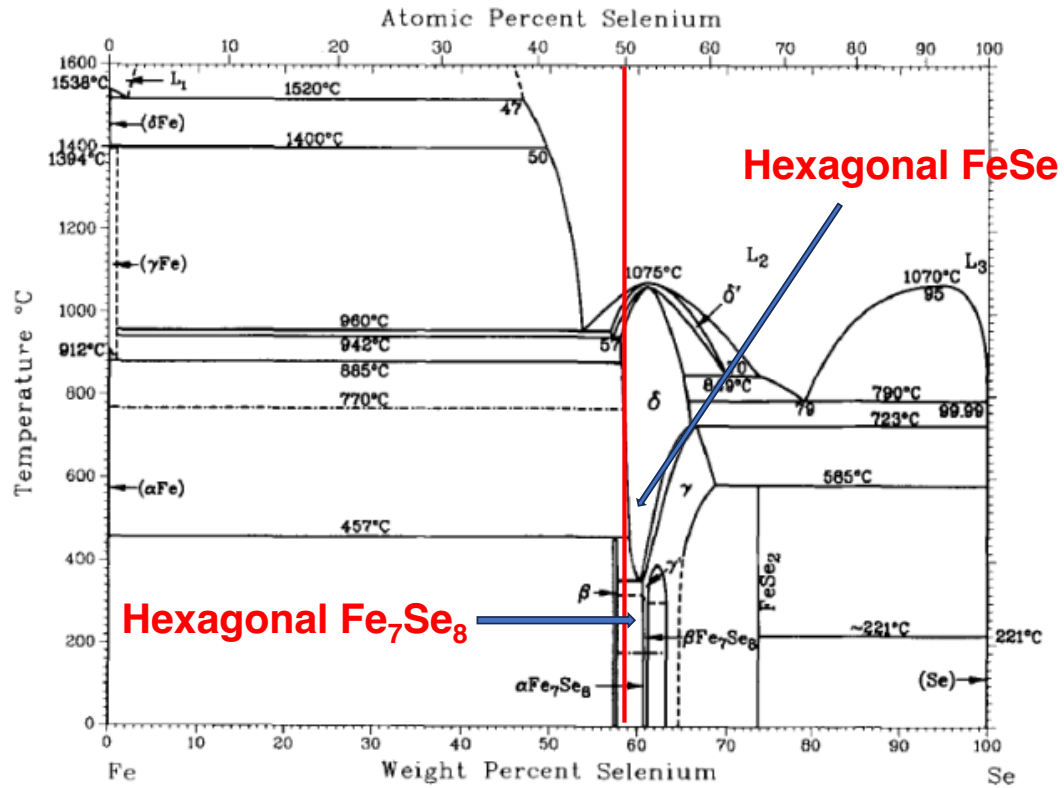


Figure 4.1: Iron-Selenium phase diagram. The figure is taken from (Okamoto (1991)).

Phase	Composition, at. % Se	Pearson symbol	Space group	Strukturbericht designation	Prototype
(δ Fe).....	~0	<i>cI2</i>	<i>Im$\bar{3}m$</i>	A2	W
(γ Fe).....	~0	<i>cF4</i>	<i>Fm$\bar{3}m$</i>	A1	Cu
(α Fe).....	~0	<i>cI2</i>	<i>Im$\bar{3}m$</i>	A2	W
β	49 to 49.4	<i>tP4</i>	<i>P4/nmm</i>	B10	PbO
δ'	48.5 to 62	...	...	...	...
δ	49.5 to 58	<i>hP4</i>	<i>P6$_3$/mmc</i>	B8 ₁	NiAs
γ'	?	<i>mC7</i>	<i>C2/m</i>	...	...
γ	? to 61	<i>mC14</i>	<i>C2/m</i>	...	...
β Fe $_7$ Se $_8$	53.3	<i>hP45</i>	<i>P3$_1$21</i>	...	...
α Fe $_7$ Se $_8$	53.3	<i>aP120</i>	...	...	...
FeSe $_2$	66.7	<i>oP6</i>	<i>Pnnm</i>	C18	FeS $_2$ (marcasite)
(γ Se).....	100	<i>hP3</i>	<i>P3$_1$21</i>	A8	γ Se

Figure 4.2: Iron-Selenium crystal structure data. The figure is taken from (Okamoto (1991)).

Phase	Composition, at. % Se	Lattice parameters, nm			Comment	Reference
		<i>a</i>	<i>b</i>	<i>c</i>		
δ Fe.....	0	0.29315	...	...	At 1394 °C	[Massalski2]
γ Fe.....	0	0.36467	...	...	At 915 °C	[King2]
α Fe.....	0	0.28655	...	...	At 25 °C	[King1]
β	?	0.3773	...	0.5529	...	[33Hag]
	47.9	0.3771	...	0.5521	At 20 °C	[68Gro]
		0.3785	...	0.5534	At 105 °C	[68Gro]
		0.3803	...	0.5553	At 220 °C	[68Gro]
		0.3809	...	0.5565	At 290 °C	[68Gro]
		0.3824	...	0.5580	At 390 °C	[68Gro]
		0.3829	...	0.5585	At 440 °C	[68Gro]
	49.5	0.3775	...	0.5527	...	[79Sch2]
	51	0.377	...	0.553	...	[75Red]
δ	?	0.362	...	0.588	...	[25Als]
	~50	0.3644	...	0.5821	...	[33Hag]
	51	0.361	...	0.593	...	[75Red]
	51.5	0.3635	...	0.5881	...	[79Sch2]
	52.9	0.3633	...	0.5911	...	[82Ter]
	53.1	0.3548	...	0.5733	...	[56Hir]
	53.3	0.3617	...	0.5886	At 20 °C	[68Gro]
		0.3628	...	0.5875	At 65 °C	[68Gro]
		0.3639	...	0.5867	At 105 °C	[68Gro]
		0.3643	...	0.5860	At 120 °C	[68Gro]
		0.3646	...	0.5852	At 130 °C	[68Gro]
		0.3661	...	0.5826	At 165 °C	[68Gro]
		0.3668	...	0.5821	At 205 °C	[68Gro]
		0.3680	...	0.5829	At 295 °C	[68Gro]
		0.3685	...	0.5835	At 340 °C	[68Gro]
		0.3694	...	0.5846	At 370 °C	[68Gro]
		0.3696	...	0.5852	At 405 °C	[68Gro]
		0.3701	...	0.5862	At 495 °C	[68Gro]
	54.3	0.3619	...	0.5864	...	[79Sch2]

Figure 4.3: Iron-Selenium lattice parameter data. The figure is taken from (Okamoto (1991)).

When FeSe is grown on the (001) surface of cubic STO, the tetragonal phase will be favored as the square lattice symmetries of substrate and film match. There still is a significant lattice mismatch, however, which makes it difficult to understand the intricacies of the incommensurate FeSe/STO interface. Likewise, we can expect that the hexagonal FeSe will be favored on the triangular Si(111) substrate. With the GaSe van der Waals termination, we expect the lattice mismatch will not play a significant role.

4.2 Experimental protocols and calibration

All experiments were carried out in an ultra-high vacuum system. The samples were grown in an MBE chamber equipped with RHEED for real-time monitoring of the structure. The FeSe films were grown on the GaSe passivated Si(111) surface (GaSe passivation was discussed in Chapter 3). XPS and LEED experiments were done in the analysis chamber which is connected to the MBE chamber. The sample was transferred between the two chambers using a magnetic transfer arm. STM studies were conducted *ex-situ* after transferring the samples to the variable-temperature and low-temperature STM chambers with a vacuum suitcase. The pressure inside the vacuum suitcase was better than 2×10^{-10} mbar.

The growth rate of the film is determined by the Fe flux. Since the films are grown at temperatures of the order of 400°C, Se atoms will have a very low sticking coefficient, meaning that the Se flux has to be about ten times higher. We calibrated the Fe flux using ex-situ Rutherford Backscattering Spectrometry (RBS) at the Tennessee Ion Beam Materials Laboratory (IBML). To this end, we deposited pure Fe onto a mica and Si substrate for 30 minutes and 60 minutes. This way, we checked the consistency of our calibration methods and made sure that the measured Fe thickness was linear with deposition time. For the RBS measurement, we used a beam of He ions with a beam energy of 1 MeV or 2 MeV. Both substrates produced almost identical results, and the Fe deposition rate was indeed constant.

Figure 4.4 shows the RBS spectrum after Fe was deposited for 30 minutes on a mica substrate. The peak corresponding to 756 keV is the Fe peak. The step-like features at lower channels correspond to potassium, silicon, aluminum, and oxygen in the substrate, respectively. These atoms with the lower atomic mass appear at a lower energy range in the RBS spectrum. The inset provides a closer look at the Fe peak. The blue line is the SIMRNA fit, which gives us the area density of the Fe atoms on the surface. In this experiment, we measured an area density of 20×10^{15} atoms/cm². This value is then used to calculate the deposition rate of FeSe. The Fe lattice is body-centered cubic (bcc). Accordingly, the film thickness is $20 \times 10^{15} / 8.46 \times 10^{22} = 2.36 \times 10^{-7}$ cm = 2.36 nm (the number in the denominator is the atomic density of bcc Fe). When we grow FeSe instead of pure bcc Fe, we need to correct this number for the differences in Fe density as follows: after 30-minute deposition at the same growth rate, the hexagonal FeSe film should be $20 \times 10^{15} / 2.96 \times 10^{22} = 6.76 \times 10^{-7}$ cm = 6.76 nm thick. This corresponds to $6.76 / 0.589 = 11.5$ unit cells. So, to grow a 1 unit-cell thick hexagonal FeSe film, it would take $30 / 11.5 = 2.6$ minutes, i.e., 2 minutes and 36 seconds of deposition time. Likewise, it would take 2 minutes and 7 seconds to grow a 1 unit-cell thick tetragonal FeSe film. The used lattice parameters of bcc Fe, hexagonal FeSe, and tetragonal FeSe are shown in Table 4.1.

The experiment was also performed by depositing Fe for 60 minutes on mica. The graph is not shown here, but the fit provides an areal density of 39×10^{15} Fe atoms/cm². Compared to 20×10^{15} atoms/cm² for a 30-minute Fe deposition on the same substrate, this value is off by only 2.5%.

Figure 4.5 shows the RBS spectrum after Fe was deposited for 60 minutes on silicon. The blue line is a fit using SIMRNA software. The smaller peak corresponds to Fe, and the other sharp peak in the graph corresponds to the silicon substrate. The inset is a zoom-in image of the Fe peak. The fit provided the areal density of Fe to be 39×10^{15} atoms/cm², identical to the value obtained in 60-minute Fe deposited on mica. Compared to 20×10^{15} atoms/cm² for a 30-minute Fe deposition on mica, this value is only off by 2.5%.

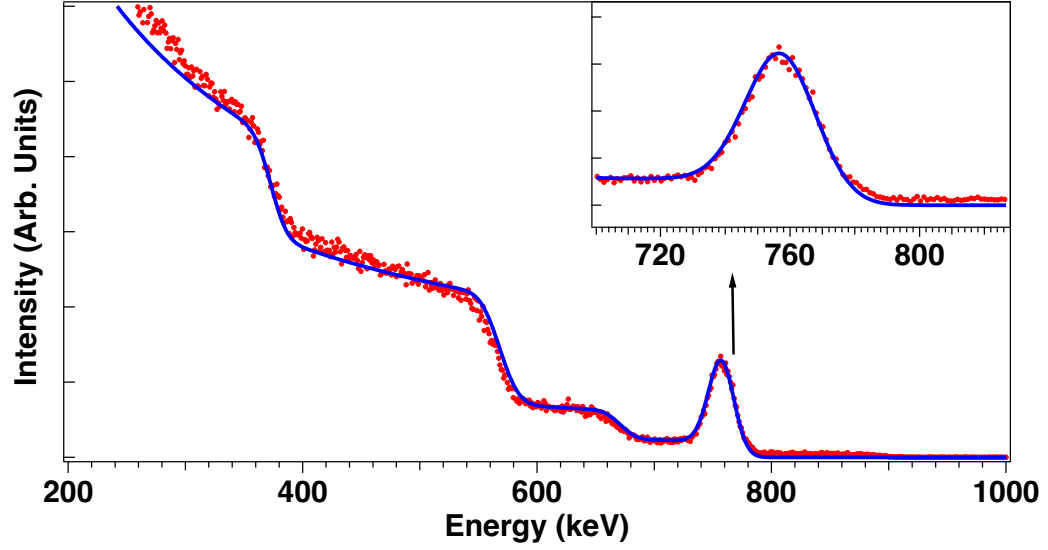


Figure 4.4: RBS spectrum of Fe deposited for 30 minutes on mica. The RBS measurements employed a 1.0 MeV He^+ beam. The blue line is a fit using the SIMRNA software. The inset zooms in on the Fe peak.

Table 4.1: Lattice parameters and atomic densities of bulk Fe, hexagonal FeSe and tetragonal FeSe.

Parameters	Fe	FeSe - Hexagonal	FeSe - Tetragonal
Crystal Structure	BCC	Hexagonal (NiAs Structure)	Tetragonal (PbO Structure)
Lattice Constant	$a = 2.87 \text{ \AA}$	$a = 3.64 \text{ \AA}, c = 5.89 \text{ \AA}$	$a = 3.77 \text{ \AA}, c = 5.52 \text{ \AA}$
Volume	$23.64 \text{ \AA}^3$	$67.58 \text{ \AA}^3$	$78.46 \text{ \AA}^3$
No. of atoms/unit cell	2	2	2
Density	$2/23.64 = 8.46 \times 10^{22} \text{ atoms/cm}^3$	$2.96 \times 10^{22} \text{ atoms/cm}^3$	$2.55 \times 10^{22} \text{ atoms/cm}^3$

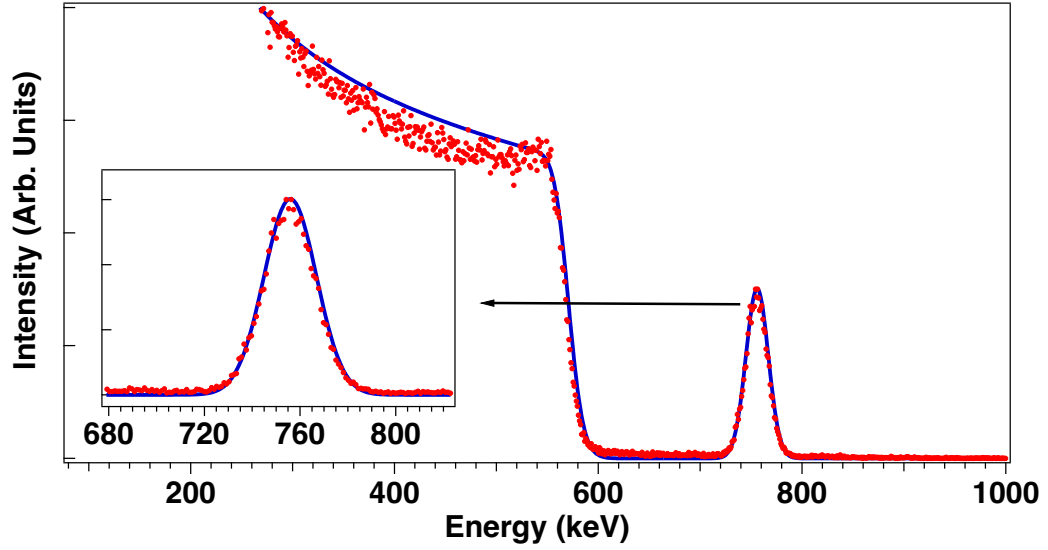


Figure 4.5: RBS spectrum of Fe deposited for 60 minutes on Si substrate. The RBS measurements used a 2.0 MeV He^+ beam. The blue line is a fit using SIMRNA. The inset zooms in on the Fe peak.

Based on the results obtained from the different experiments mentioned above, it can be concluded that the Fe growth is consistent, reproducible, and linear over time.

4.3 Stoichiometry and Thin Film Morphology

After determining the growth rate of FeSe by RBS, FeSe was grown on the GaSe passivated Si(111) surface. Our first attempt was to use a substrate temperature similar to the one that is typically used for FeSe deposition on STO, which is around 450 °C. However, the growth rate turned out to be extremely slow, presumably due to the low sticking coefficient of Se on the Si(111):GaSe van der Waals surface. However, FeSe can grow easily at a substrate temperature of 300 °C.

Figure 4.6 shows the LEED and RHEED pattern of a 1 UC thick FeSe film grown on Si(111):GaSe. The beam energy in LEED was 82 eV, and the beam energy in RHEED was 15 KeV. The LEED pattern exhibits almost perfect six-fold symmetry, unlike that of the Si(111) substrate, which has three-fold rotational symmetry. The RHEED streaks are also sharp, indicating a smooth film morphology. The XPS

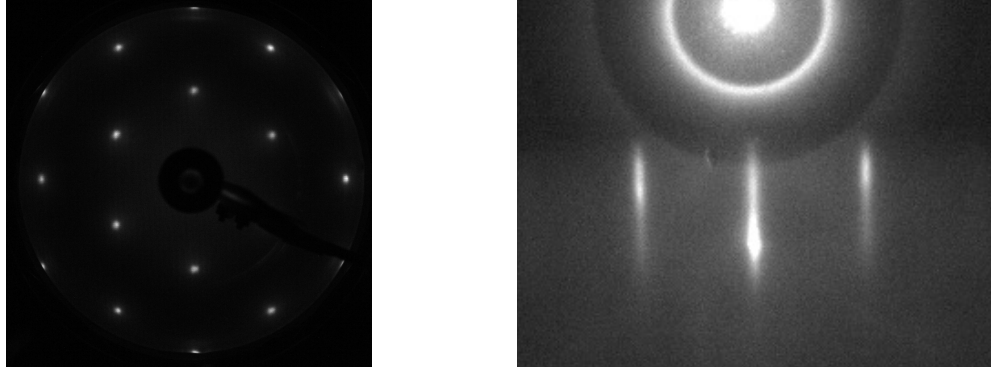


Figure 4.6: (a) LEED and (b) RHEED pattern of a 1 UC thick FeSe film grown on the GaSe passivated Si(111) surface. The LEED pattern is taken at a beam energy of 82 eV. The beam energy of RHEED is 15 KeV.

survey spectrum is shown in Figure 4.7. The spectrum shows the core levels and Auger spectra of Ga, Fe, Se, and Si. As expected, the substrate Si peaks remain visible as the film was only 1 UC thick. A detailed discussion of the core level spectra will be presented in Chapter 5.

To understand how the FeSe film nucleates on the passivated Si(111):GaSe substrate, we grew a 0.2 UC thick FeSe film. This means that we deposited for 20% of the time needed to form a complete 1 UC thick FeSe layer. As we will see, the growth mode of the film is not perfectly layer-by-layer, meaning that the thicknesses indicated below should be interpreted as nominal thicknesses.

Figure 4.8 shows a large-scale STM image of a 0.2 UC thick FeSe deposit on a GaSe passivated p-type Si(111) wafer. Figure 4.8 (a) and Figure 4.8 (c) are 900 nm $\times$ 900 nm images taken at two different parts of the sample. Figure 4.8 (b) and Figure 4.8 (d) are zoomed-in images of (a) and (c), respectively, with a scan area of 300 nm $\times$ 300 nm. The step edges and terraces of the Si(111) substrates can be clearly seen. The FeSe film mostly nucleates at the step edges, although one can observe FeSe nuclei at the center of the terraces. The baby clusters are mostly triangular, suggesting the FeSe film is hexagonal. All the images were acquired at a bias voltage of 2.5 V.

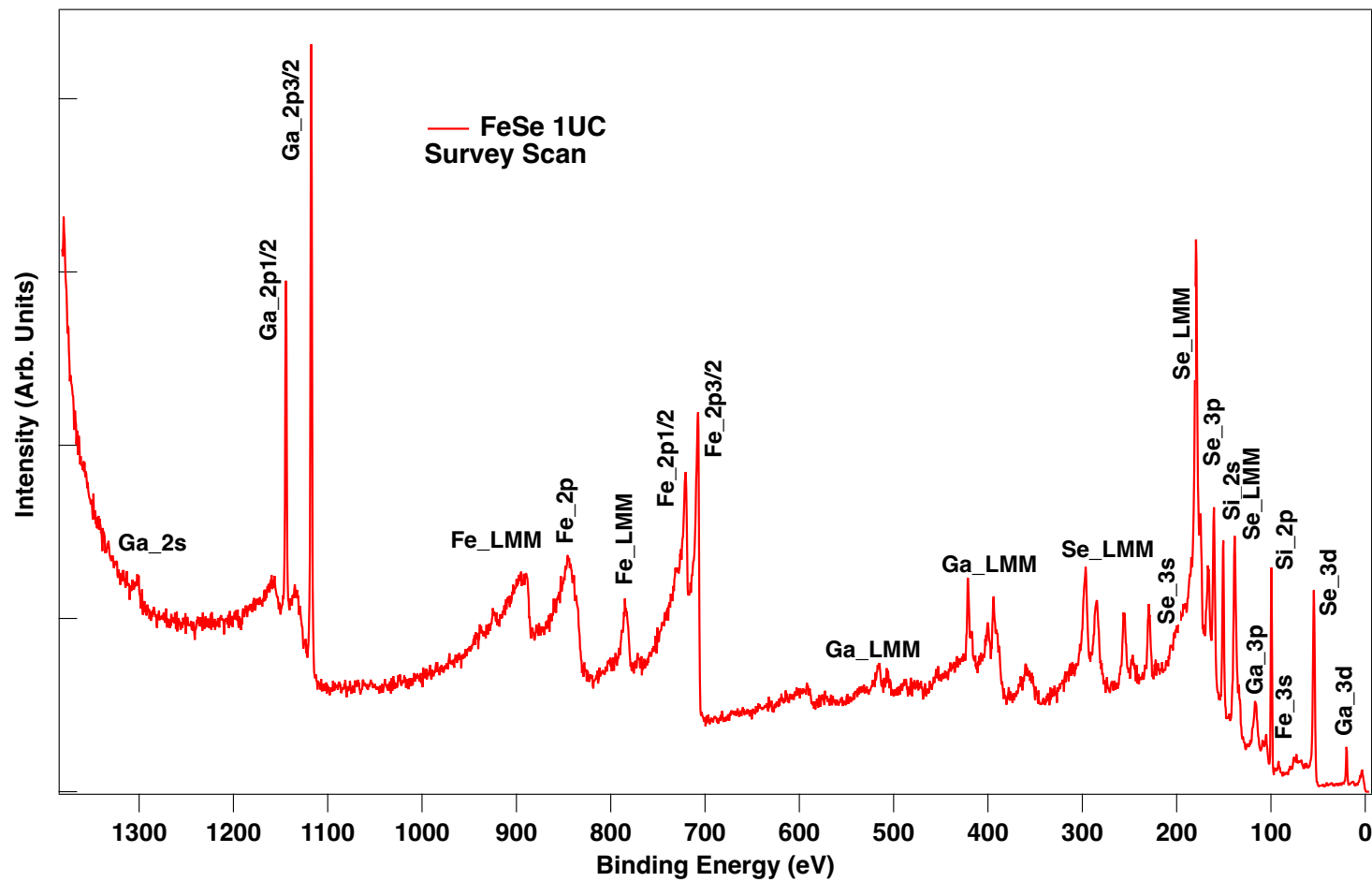


Figure 4.7: XPS spectrum of a 1 UC thick FeSe film grown on Si(111):GaSe. The core level peaks are all labeled.

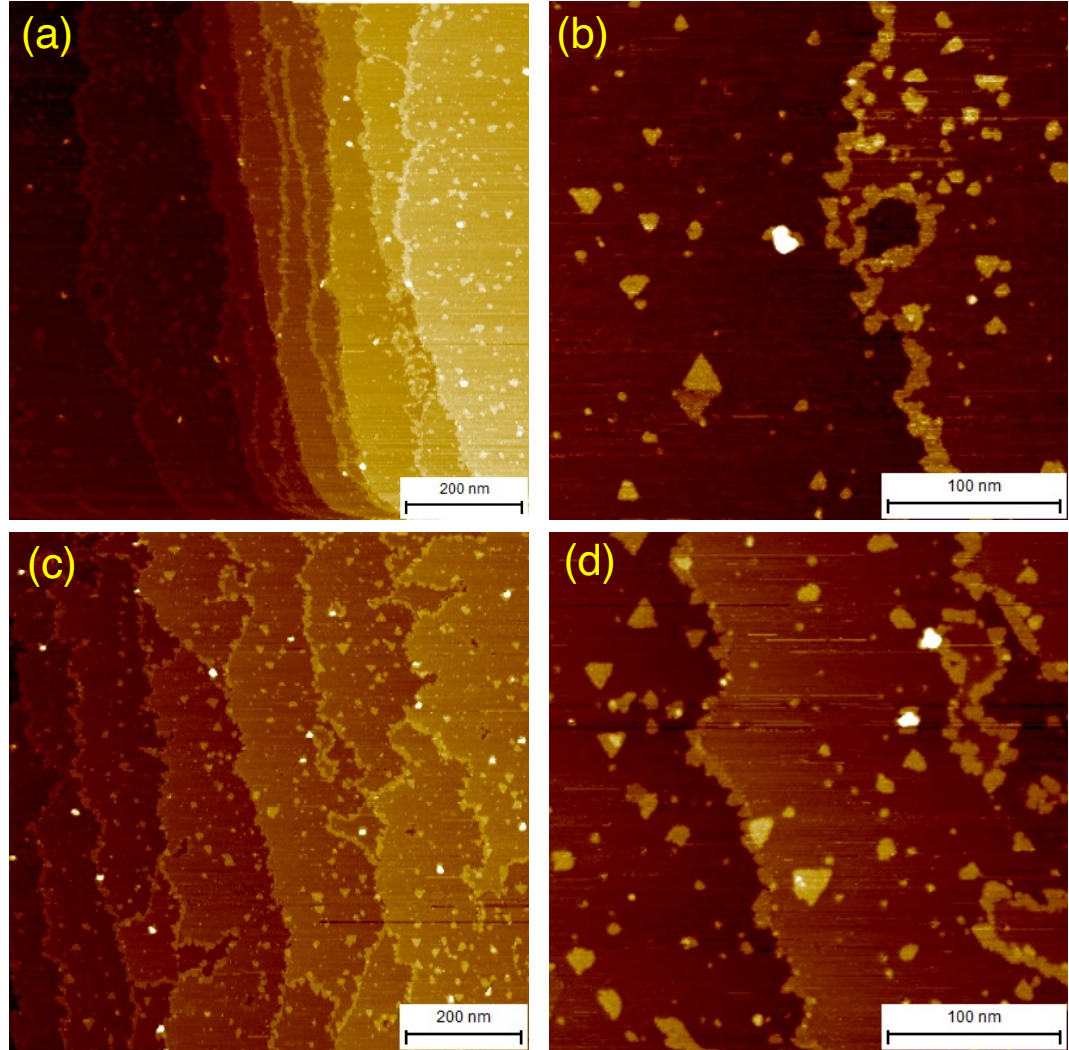


Figure 4.8: Large scale STM image of a 0.2 UC thick FeSe film grown on p-type Si(111):GaSe. The area of the scanned region is (a), (c) $900\text{ nm} \times 900\text{ nm}$ and (b), (d) $300\text{ nm} \times 300\text{ nm}$.

The islands have flat tops, but their heights differ quite a bit. Figure 4.9 (a) and Figure 4.9 (b) are images taken at two different parts of the sample on a $100\text{ nm} \times 100\text{ nm}$ scale. They were acquired at a bias voltage of 2 V. The first figure reveals island heights of 0.88 nm and 0.58 nm, which are labeled ‘C’ and ‘E’, respectively. The second figure reveals an additional island height of 0.68 nm islands, labeled ‘D’. Figure 4.10 reveals an island height of 0.29 nm in between the red horizontal lines.

Figure 4.11 shows the STM image for a 1 UC thick FeSe film. Figure 4.11 (a) and Figure 4.11 (b) are images with a scanned area of $300\text{ nm} \times 300\text{ nm}$ and $100\text{ nm} \times 100\text{ nm}$, respectively. Image (a) was acquired at a bias voltage of 2.5 V, and image (b) at 2 V. Even though the nominal film thickness is 1 UC, we can see the nucleation of the second layer on top of the first. Some intermediate layers of FeSe are also seen. In this image, the exposed substrate is labeled ‘SU’. The first and second layers are labeled ‘1’ and ‘2’, respectively. The 1st layer is 0.88 nm high with respect to the substrate, and the 2nd layer is 0.68 nm high with respect to the first layer. Some layer heights are half the height of the second UC, i.e., 0.34 nm. In addition, we also have an intermediate layer labeled ‘IN’, which is 0.60 nm high.

Figure 4.12 shows the STM image for a 2 UC thick FeSe film. Figure 4.12 (a) and Figure 4.12 (b) are images with a scanned area of $300\text{ nm} \times 300\text{ nm}$ and $100\text{ nm} \times 100\text{ nm}$, respectively. Both images were acquired at a bias voltage of 2 V. Ideally, for a 2 UC thick film of FeSe, we would expect the film thickness to be twice the *c*-axis, but the film does not grow layer by layer. We observe areas that are 1 UC, 2UC, and 3 UC thick. These are all labeled in the figure. We find that about 60% of the surface area is covered with a 1 UC thick film; 23% is covered with a 2 UC thick film, and 17% of the area is covered with a 3 UC thick film, consistent with a nominal coverage of 2 UC (and thus in excellent agreement with the RBS calibration). The second and third UC of FeSe are both 0.60 nm high, which is very close to the *c*-axis of hexagonal FeSe.

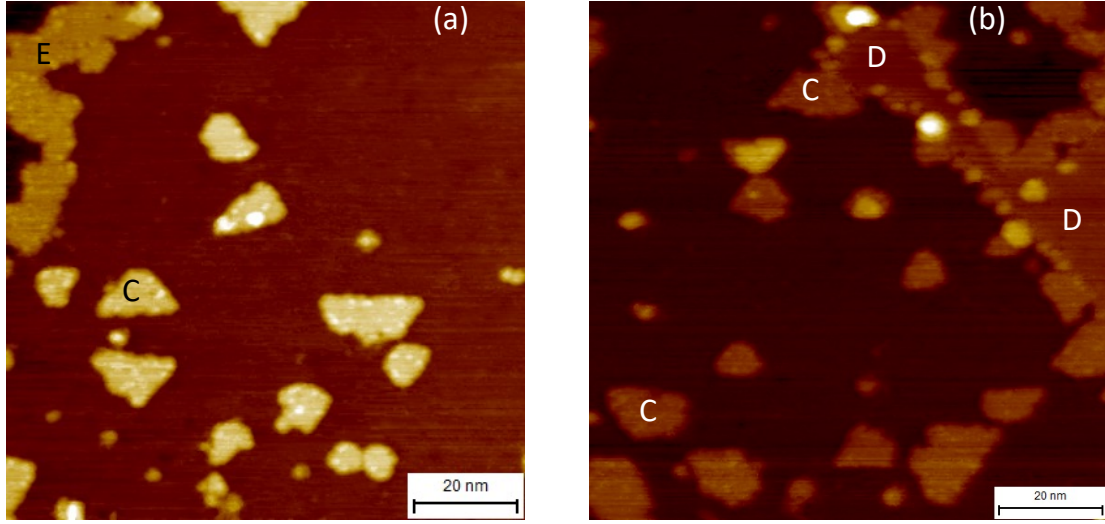


Figure 4.9: STM image of a 0.2 UC thick FeSe film grown on p-type Si(111):GaSe. The area of the scanned region is 100 nm $\times$ 100 nm. The two images were taken at different parts of the sample. The capital letters indicate the different heights of the baby clusters.

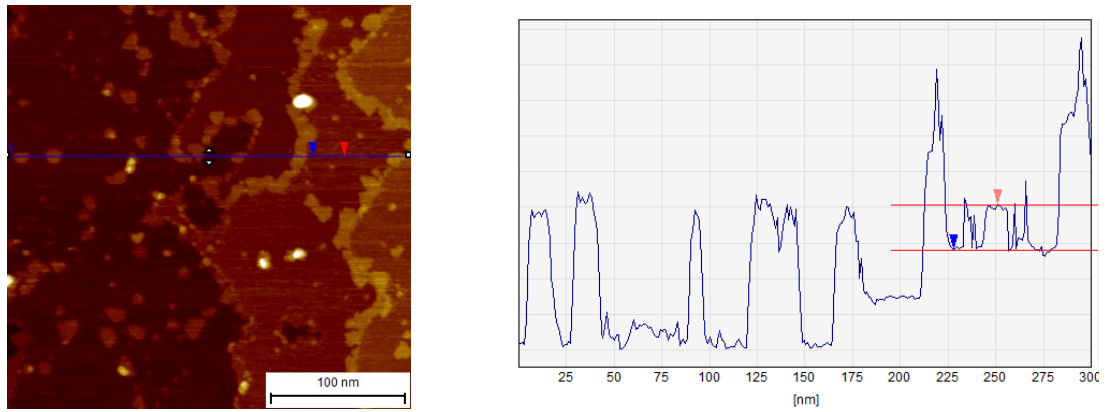


Figure 4.10: STM image of a 0.2 UC thick FeSe deposit on p-type Si(111):GaSe. The area of the scanned region is 300 nm $\times$ 300 nm. A line profile shows the island height of 0.29 nm on the right.

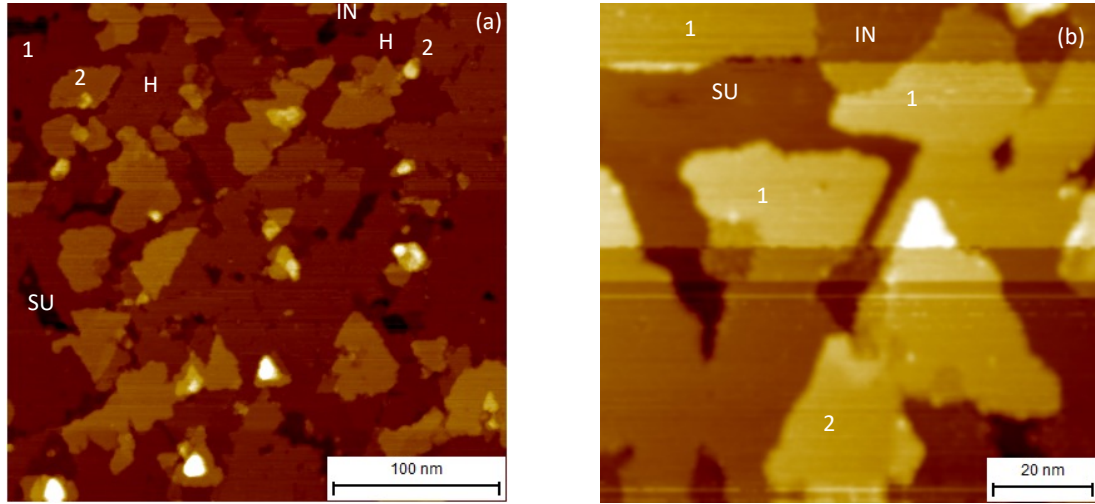


Figure 4.11: STM image of a 1 UC thick FeSe film grown on p-type Si(111):GaSe. The area of the scanned region is (a) 300 nm $\times$ 300 nm and (b) 100 nm $\times$ 100 nm. The different layer heights are labeled in the figure.

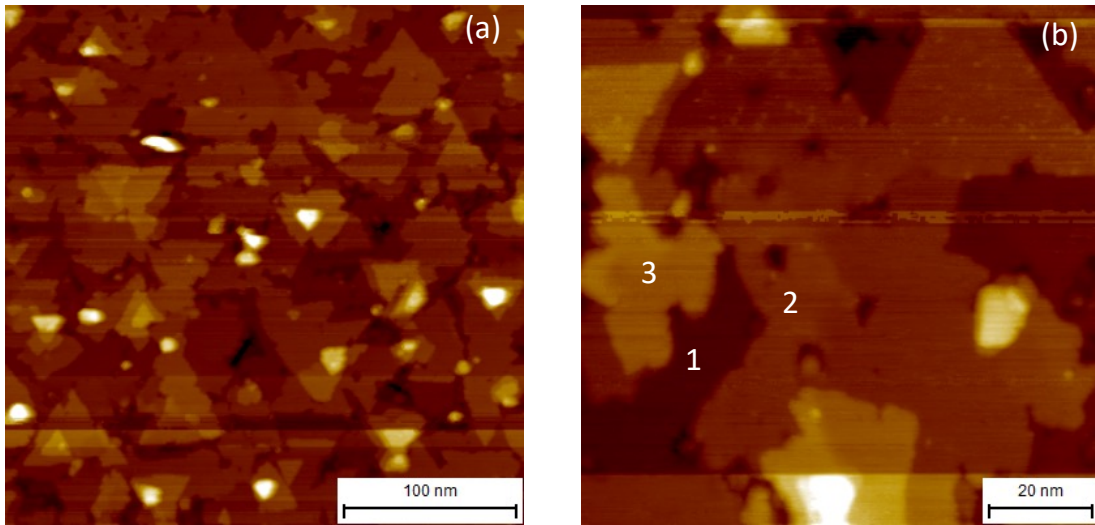


Figure 4.12: STM image of a 2 UC FeSe grown on p-type Si(111):GaSe. The area of the scanned region is (a) 300 nm $\times$ 300 nm and (b) 100 nm $\times$ 100 nm. The different UC thicknesses are labeled in (b).

In summary, the step heights observed in STM are 0.29 nm, 0.34 nm, 0.58 nm, 0.60nm, 0.68nm, and 0.88 nm. The step heights correspond to an integer number times $c/2$, except for the 0.34 and 0.68 nm step heights. The 0.58 nm and 0.60 nm heights are close (within error) to the c -axis of hexagonal FeSe. The 0.29 nm height is $c/2$, whereas 0.88 nm corresponds to $3c/2$. This is shown in Figure 4.13.

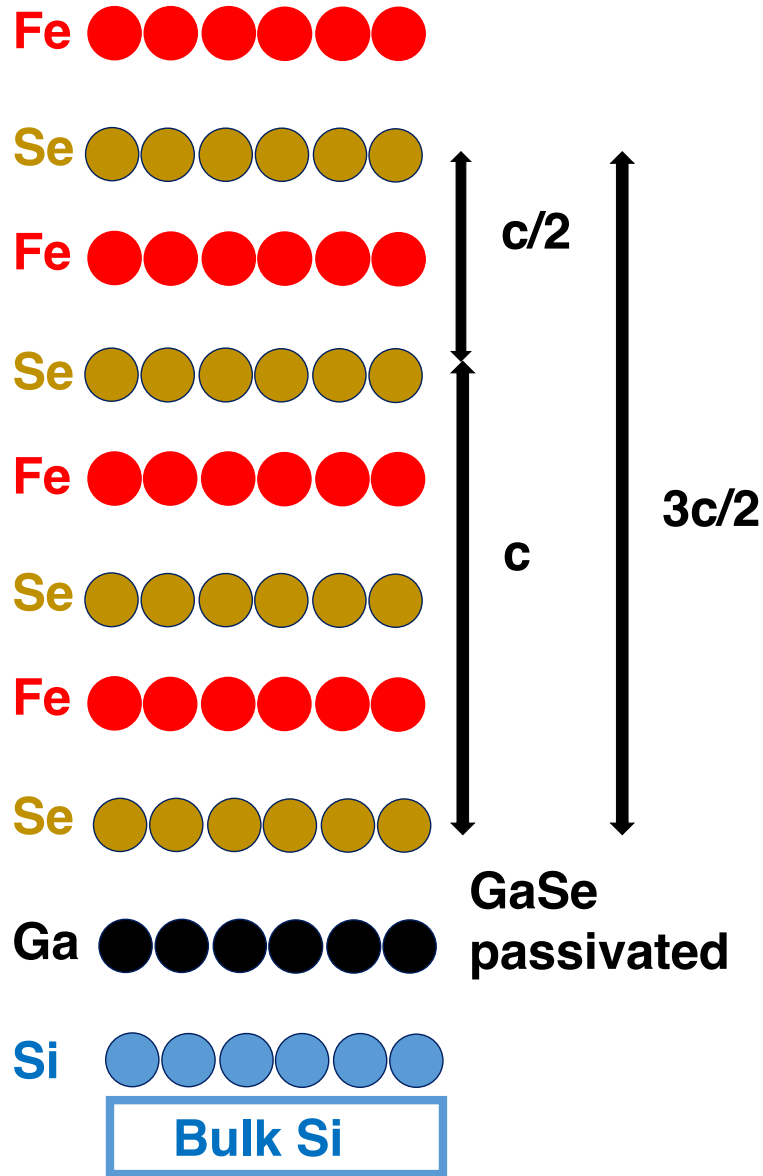


Figure 4.13: Cartoon showing the Si substrate, the GaSe passivation layer, and the FeSe layers on top. The vertical distance ' c ' indicates the c -axis of a UC FeSe film.

It is likely that stable islands are all terminated with a Se layer. Selenium in FeSe has a closed shell electron configuration, whereas Fe does not. Hence, it is expected that the surface free energy of the Se-terminated surface is the lowest. Given the fact that the 2 UC thick FeSe film grows in multiple units of $c/2$, we conclude that the Fe atoms go down first, i.e., there is no double Se layer at the Si(111):GaSe and FeSe interface; hence, there is no van der Waals growth, and the lattice constants of the islands are dictated by the substrate.

There is no easy interpretation for the observation of 0.34 nm and 0.68 nm step heights on the 0.2 UC and 1 UC films. Since they are not seen in the 2 UC thick film, they may be metastable. Indeed, there are no known bulk phases that would match those step heights. One possible interpretation is the presence of interstitial Fe or the presence of an additional Fe layer on top. The Fe atoms have a small ionic radius of about 0.08 nm (Huheey et al. (2006)), which would be roughly consistent with the 0.60-0.68 nm height difference. The presence of an extra Se layer seems unlikely as the Se atom is much bigger. Alternatively, incomplete strain relaxations at the interface may produce different island heights, though it should be noted that the FeSe film is under tensile strain, meaning that the step heights are expected to be smaller than those expected based on the bulk lattice constants, contrary to our observations. As a final note of caution, we remark that STM probes the LDOS, which can affect the measured step height, i.e., the measured step heights may be somewhat different from the crystallographic layer spacings.

The previous images were all acquired on p-type Si(111). Figure 4.14 shows STM images of a 1 UC thick FeSe film grown on two different n-type Si(111):GaSe substrates. Their growth conditions were identical. The scan areas in Figure 4.14 (a) and (b) are $390 \text{ nm} \times 390 \text{ nm}$ and $130 \text{ nm} \times 130 \text{ nm}$, respectively, and both images were acquired at a bias voltage of 2.5 V. Again, we observe multiple layer thickness as well as some intermediate thicknesses labeled ‘H’. From the area fractions of the exposed substrate (SU) and those of the additional layers, we find that the coverage is indeed very close to 1 UC.

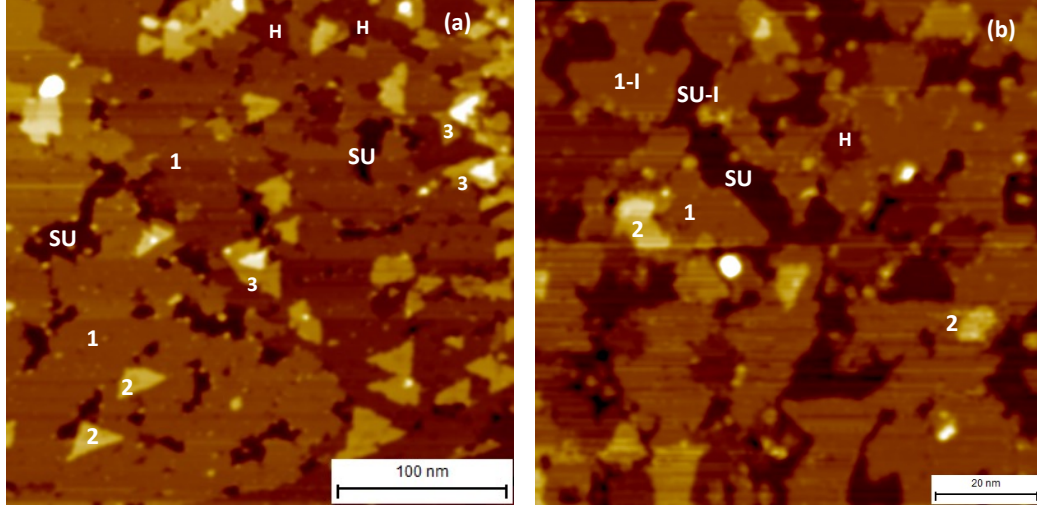


Figure 4.14: STM image of a 1 UC FeSe grown on n-type Si(111):GaSe. The area of the scanned region is (a) $390 \text{ nm} \times 390 \text{ nm}$ and (b) $130 \text{ nm} \times 130 \text{ nm}$. (a) and (b) are different samples prepared under the same growth conditions. The different layers are labeled.

We can clearly see the step edge of the Si substrate in Figure 4.14 (a), which is 0.314 nm high. The first UC is 0.78 nm high, while the second and third UCs of FeSe are 0.68 nm high. In Figure 4.14 (b), the heights of the intermediate layer and second UC thick layer of FeSe are identical to those in (a). The first UC height is also the same as the other image, but there are very few patches where the height of FeSe is 0.68 nm, labeled as 1-I in the figure. There are also some islands labeled as ‘H’, which are 0.34 nm. Note that the height of the 1 UC tall island on n-type Si(111):GaSe is 0.78 nm, which is smaller than those on p-type Si(111):GaSe (0.88 nm). We have no satisfactory explanations why the observed step heights on n-type Si(111) are limited to 0.68 and 0.78 nm, and why we do not observe 0.29 and 0.58 nm step heights seen on p-type Si(111):GaSe. The 0.78 nm height step possibly arises from an extra Se layer at the interface, as in van der Waals growth. All the different heights obtained on various samples are summarised in Table 4.2.

Figure 4.15 shows two small-scale STM images of a 1 UC thick FeSe film grown on n-type Si(111):GaSe. The scan areas are $39 \text{ nm} \times 39 \text{ nm}$ and $13 \text{ nm} \times 13 \text{ nm}$, and the images were acquired at a bias voltage of -1 V and -0.8 V, respectively. Here, we

Table 4.2: Summary of islands in different samples with the explanation of the heights.

Sample Type	Island Height (nm)	Explanation
0.2 UC p-type Si	0.30	$c/2$
	0.60	c
	0.68	$c + \text{extra Fe layer}$
	0.88	$3c/2$
1 UC p-type Si	0.60	c
	1 st UC = 0.88	$3c/2$
	2 nd UC = 0.68	$c + \text{extra Fe layer}$
	half UC = 0.34	
1 UC n-type Si	1 st UC = 0.78	$c + \text{Se extra layer}$
	2 nd UC = 0.68	$c + \text{extra Fe layer}$
	3 rd UC = 0.68	$c + \text{extra Fe layer}$
	half UC = 0.34	
2 UC p-type Si	1 st UC = 0.88	$3c/2$
	2 nd UC = 0.60	c
	3 rd UC = 0.60	c

are close to achieving atomic resolution. We can see three striped domains that are rotated 120° with respect to one another, consistent with the three-fold symmetry of the Si(111) substrate. The three domain stripes are labeled by lines for reference. A more detailed discussion of these stripe-like patterns will be provided in Chapter 6.

4.4 Tetragonal FeSe

The tetragonal FeSe phase is easily obtained via MBE growth on an oxide substrate such as STO. Here, we show that the tetragonal phase can also be obtained on Si(111):GaSe by adjusting the growth conditions. Here, we did not intentionally heat the Si(111) substrate, though it is exposed to thermal radiation coming from the Fe effusion cell. The substrate temperature is still close to 300°C . We do see evidence

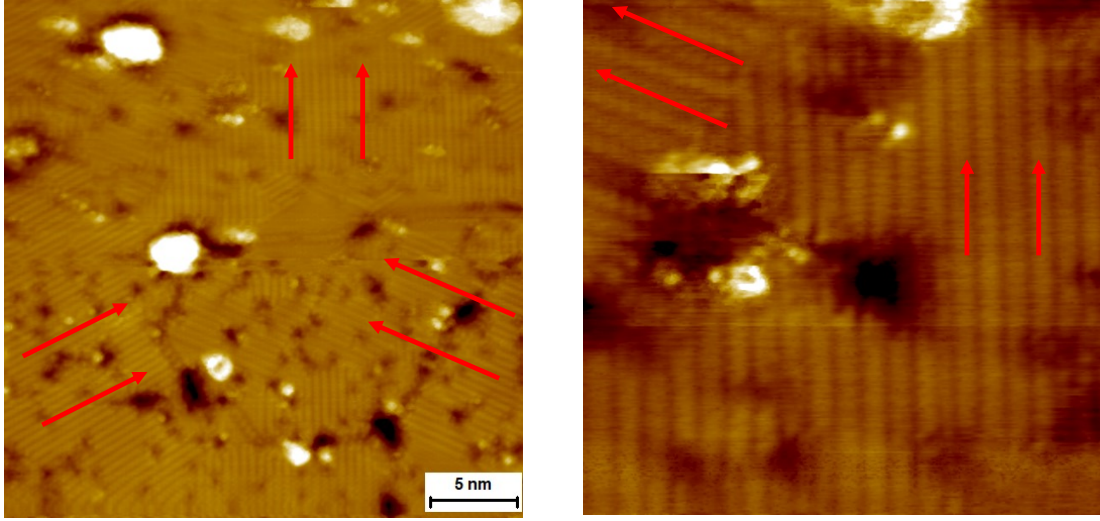


Figure 4.15: STM image of a 1 UC thick FeSe film grown on n-type Si(111):GaSe. The area of the scanned region is 39 nm $\times$ 39 nm (left) and 13 nm $\times$ 13 nm (right). The different domain orientations are marked in the figure.

of tetragonal FeSe domains in RHEED, LEED, and STM in the sample prepared by this method.

Figure 4.16 shows the RHEED pattern of a 3.3 UC thick FeSe film grown on n-type Si(111):GaSe. The distances between the RHEED streaks (in real space) correspond to distances along the high symmetry directions in reciprocal space. For instance, distance ‘2’ corresponds to the distance along the (11) direction in the reciprocal lattice of the Si(111) substrate, which is hexagonal. Distance ‘1’ is attributed to the FeSe overlayer and is exactly half the distance ‘2’. In addition, there are several other RHEED streaks that originate from the FeSe overlayer.

The corresponding LEED pattern is shown in Figure 4.17. The LEED is very faint, but the Si (10) reflection is clearly visible. The other twelve fuzzy spots seem to be located on a circle and originate from the FeSe layer. First, we checked if the LEED spots could originate from two 30° rotated hexagonal FeSe domains, which would also produce twelve spots in the LEED pattern. Figure 4.18 shows the cartoon depicting those two domains. The in-plane reciprocal lattice constant of hexagonal FeSe is 1.99 $\text{\AA}^{-1}$ and is 1.89 $\text{\AA}^{-1}$ for Si(111), see Table 4.3.

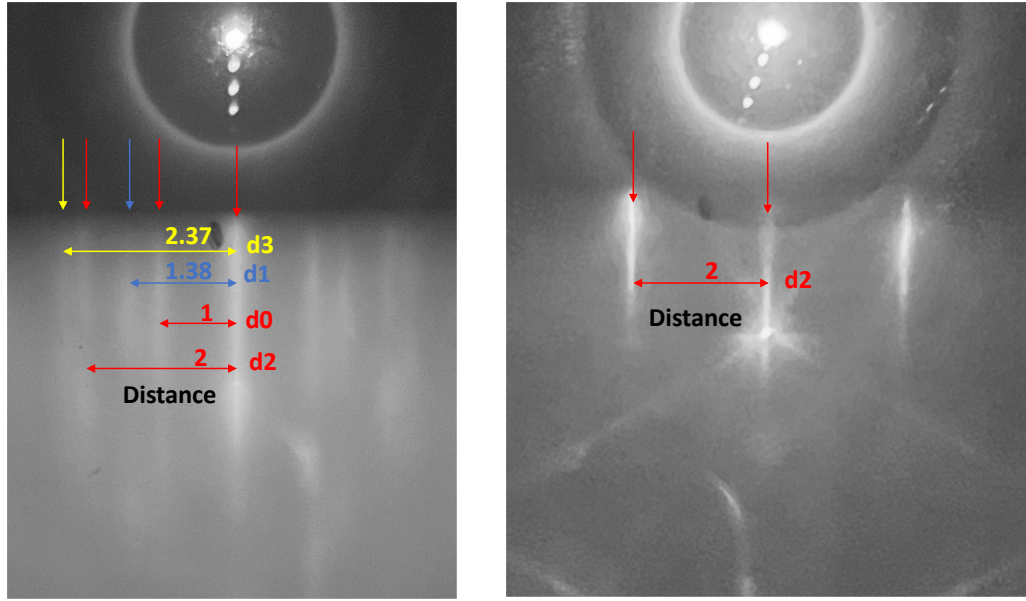


Figure 4.16: Left: RHEED pattern after growing a 3.3. UC thick FeSe film on Si(111):GaSe. Right: RHEED pattern of Si(111):GaSe. The beam energy of RHEED is 15 KeV.

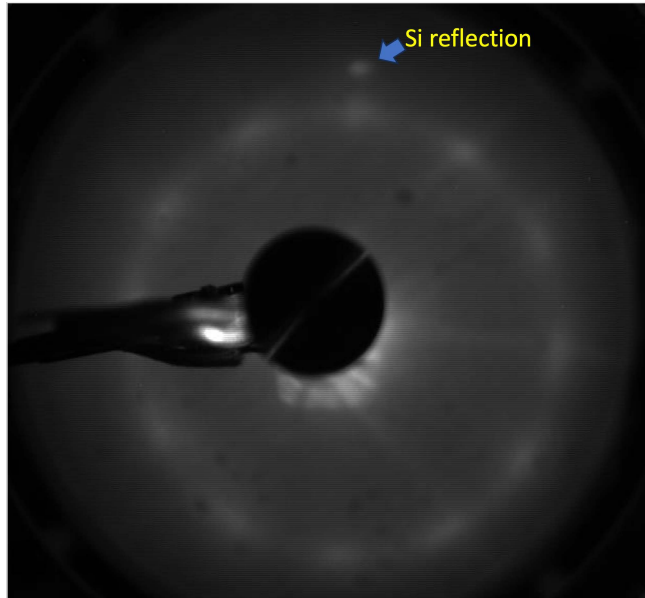


Figure 4.17: LEED pattern after growing FeSe on Si(111):GaSe at low temperature, corresponding to RHEED pattern of Figure 4.16. The beam energy of LEED is 51 eV.

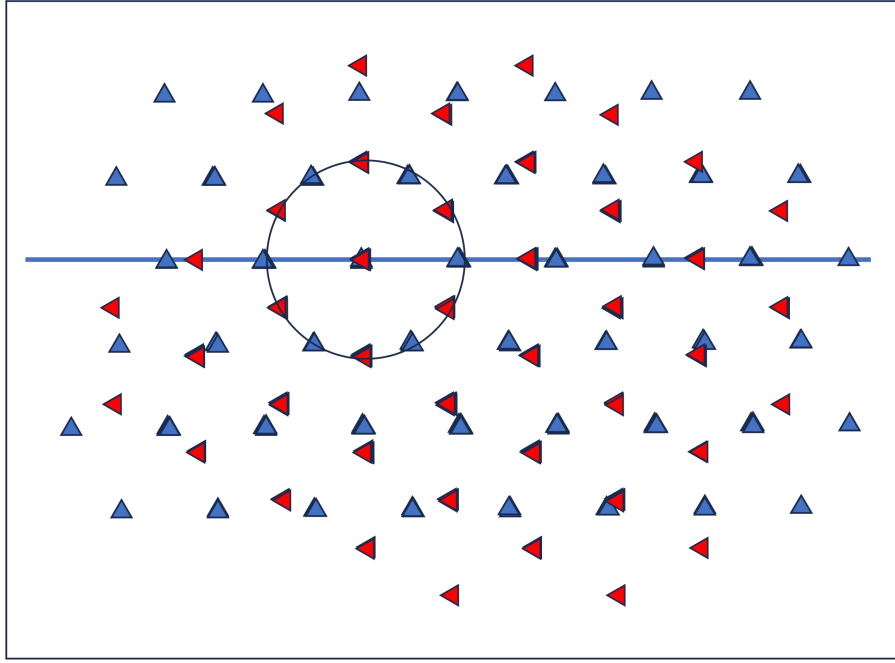


Figure 4.18: Cartoon showing two 30° rotated hexagonal FeSe domains in reciprocal space.

Table 4.3: Lattice constant in real space and reciprocal space of Si (111), hexagonal and tetragonal FeSe.

Crystal	Si (111)	FeSe:Hexagonal	FeSe:Tetragonal
a_1	$3.84 \text{ \AA}$	$3.64 \text{ \AA}$	$3.77 \text{ \AA}$
$ b_1 $	$4\pi/a_1\sqrt{3}$	$4\pi/a_1\sqrt{3}$	$2\pi/a_1,$
$ b_1 $	$1.89 \text{ \AA}^{-1}$	$1.99 \text{ \AA}^{-1}$	$1.67 \text{ \AA}^{-1}$
Diagonal	$ b_1 \sqrt{3}$	$ b_1 \sqrt{3}$	$ b_1 \sqrt{2}$
Diagonal	$3.27 \text{ \AA}^{-1}$	$3.45 \text{ \AA}^{-1}$	$2.36 \text{ \AA}^{-1}$

The lattice constants of the films are assumed to be identical to those of the corresponding bulk crystals, i.e., the films are considered to be fully relaxed. In Figure 4.18, the radius of the ring should be $1.99 \text{ \AA}^{-1}$, but the Si reflection is located outside the ring, which cannot be true. So, the hypothesis of having two 30° rotated hexagonal FeSe domains is incorrect.

Since the LEED pattern shows 12 spots, it is logical to consider both 3-fold and 4-fold rotational symmetries. Since the substrate has threefold rotational symmetry, we attribute the fourfold symmetry to the overlayer, which would be tetragonal FeSe. We thus consider the presence of three 120° rotated domains of tetragonal FeSe. Figure 4.19 is the cartoon showing three tetragonal FeSe domains in reciprocal space with rotational angles of 0° , 120° , 240° . The red horizontal line represents the shadow edge of the RHEED screen. Accordingly, we identify the half-order RHEED streak ‘1’ in Figure 4.16 as the $|b_1| = 1.67 \text{ \AA}^{-1}$ reciprocal lattice vector of tetragonal FeSe, which is indeed very close to the half-way distance between the (00) and (11) reflections in the Si(111) plane ($= 1.64 \text{ \AA}^{-1}$). This is the (1,0) reflection labeled in the cartoon, Figure 4.19. Also labeled are the (1.37,0) and (2.24,0) coordinates. Those are not the actual coordinates in reciprocal space, but their momentum transfer along the shadow edge matches the positions of the streaks in 4.16. These reflections originate from the rotated domains. Because they have a small momentum transfer perpendicular to the shadow edge (or plane of the film), the streaks show a small vertical offset, consistent with the experimental RHEED pattern. Both RHEED and LEED provide strong evidence for the existence of tetragonal FeSe.

We also observed the tetragonal phase on a 1 UC thick FeSe film on Si(111):GaSe. The corresponding RHEED pattern and STM image are shown in Figure 4.20. The streaks corresponding to the three domains of tetragonal FeSe discussed above are faint but visible on the monolayer FeSe film. The same sample’s atomic-scale STM topography image is also shown, measured with the tunneling bias of 0.5 V. The STM image indicates the square lattice as expected. It is not known at this point whether the film is superconducting.

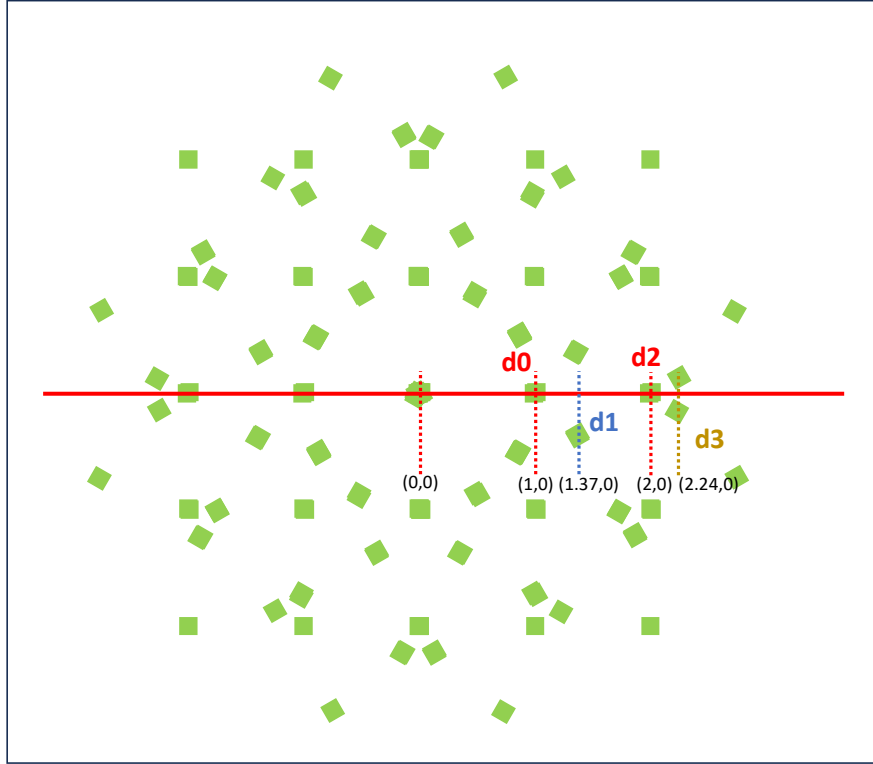


Figure 4.19: Cartoon showing three tetragonal FeSe domains in reciprocal space with rotational angles of 0° , 120° , 240° . d0, d1, d2 and d3 corresponds to streaks on the RHEED pattern of Figure 4.16.

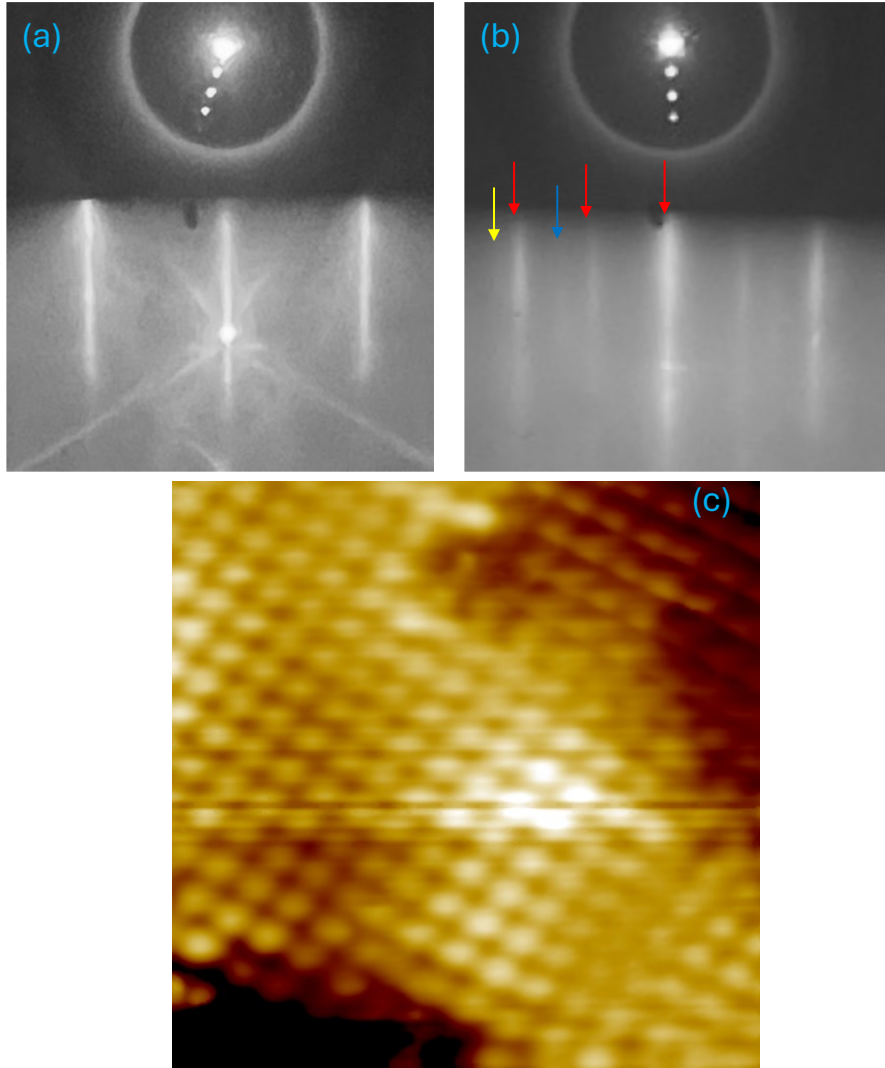


Figure 4.20: (a) RHEED pattern of Si(111):GaSe. (b) RHEED pattern of a 1 UC thick FeSe film on Si(111):GaSe. Notice that the streaks corresponding to the tetragonal domains are faint but visible. (c) STM image of the same sample, measured with a tunneling bias of 0.5V.

4.5 Multilayer FeSe films on passivated Si(111)

We also attempted to grow 5-UC thick FeSe films on n-type GaSe passivated Si(111), employing the same growth conditions as before. Figure 4.21 shows the corresponding LEED and RHEED patterns of the substrate and film. The LEED pattern of the film, shown in Figure 4.21(f), is rather faint. The corresponding RHEED pattern in Figure 4.21(c) clearly reveals the presence of transmission spots along the vertical direction. This indicates that the growth front has become quite rough. In addition to the transmission spots in RHEED, we also see streaks halfway in between the integer order streaks, which indicates the formation of a superstructure with a doubled lattice constant or perhaps the formation of tetragonal FeSe. The vertical spacing between the diffraction maxima indicates a c lattice parameter of 5.3 Å, which is slightly less than the reported lattice parameters of hexagonal and tetragonal FeSe.

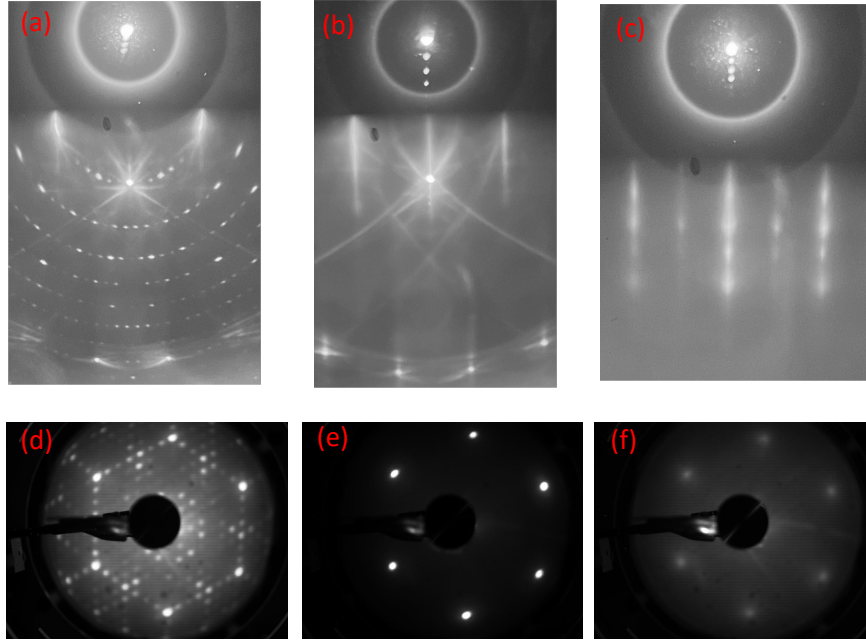


Figure 4.21: LEED and RHEED [(a, d), (b, e), (c, f)] patterns of Si (111), GaSe passivated Si(111) surface and 5-UC thick FeSe film grown on top of the passivated surface, respectively.

A different result is observed on a 2 UC thick FeSe on p-type Si(111):GaSe. The growth of the FeSe film proceeded in several steps. Initially, a 1 UC thick FeSe film is grown and subsequently cooled to room temperature. Then, an additional 1 UC thick layer of FeSe is grown after several hours. The atomic resolution STM image, acquired at 0.5 V bias voltage, shows a tetragonal phase of FeSe coexisting with the hexagonal phase. Figure 4.22 shows the STM image of the tetragonal phase. The wiggling of the columns in the STM image is caused by the drifting of the tip during the scanning of the surface. This sample differs in two aspects: a) the substrate is p-type Si(111) compared to the n-type Si(111) mentioned above, and b) the growth condition is slightly different. These experiments show that the formation of the hexagonal and tetragonal phases is sensitive to precise growth conditions. We did not obtain an atomic resolution of the hexagonal phase.

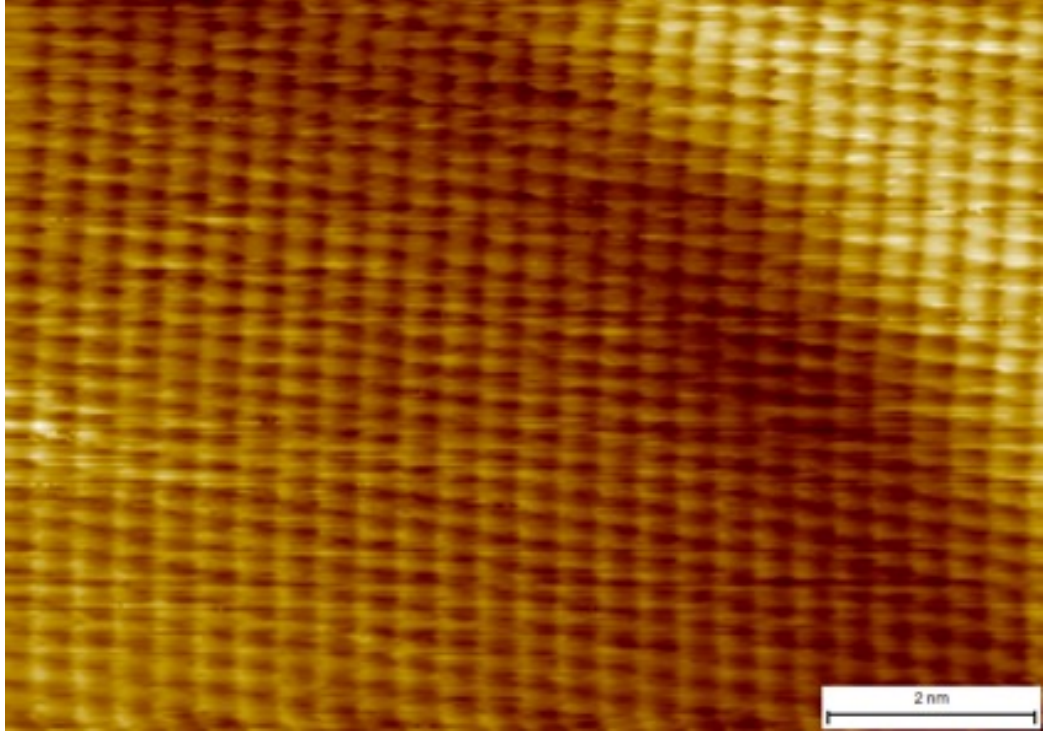


Figure 4.22: Smaller scale STM image with an atomic resolution for a 2 UC FeSe grown on GaSe passivated p-type Si(111). The image was acquired at a bias voltage of 0.5 V.

4.6 Conclusions

Both hexagonal and tetragonal FeSe films can be grown on the GaSe passivated Si(111) surface. The observed layer thicknesses indicate that the hexagonal FeSe films grow in multiples of $c/2$, though we observe various other layer heights during the early stages of growth. The observed growth modes suggest that the Fe layer nucleates on top of the GaSe layer, meaning that there is no intermediate Se layer that would indicate van der Waals growth. Indeed, the in-plane lattice parameters of the hexagonal FeSe films match those of Si(111), *i.e.*, the films are under tensile strain. On the other hand, the tetragonal FeSe films appear fully relaxed, see, *e.g.*, Figure 4.17. The evolution of the layer heights on n-type and p-type Si(111):GaSe appears to be different, for reasons that are yet to be understood.

Chapter 5

Core level and Auger Spectroscopy

In this chapter, we explore the nature of the FeSe/Si(111):GaSe interface using X-ray photoelectron spectroscopy (XPS). We will demonstrate that the interface is chemically abrupt, and there is little charge transfer across the interface. The Fe $2p$ core level spectra of the FeSe thin films show striking similarities to those of FeSe/STO interfaces, despite the significant differences in the local environment of the Fe atoms. This suggests that the mechanism of the core hole decay is dictated by the nature of the hetero-polar Fe–Se bond.

5.1 Si $2p$ core level spectrum

Passivation of n-type and p-type Si(111) is achieved by depositing a half-sheet of GaSe onto Si(111)7 $\times$ 7 at a substrate temperature of 550 °C. The Si $2p$ spectra of the GaSe passivated n-type and p-type Si(111) surfaces are shown in Figure 5.1 (a) and (c), respectively. The spin-orbit split $2p_{1/2}$ and $2p_{3/2}$ spectra were fitted with Voigt functions, which constitute a Lorentzian line shape (due to the lifetime broadening of the core hole) that is convoluted with a Gaussian (to account for instrumental broadening). Figure 5.1 (b) and (d) show the Si $2p$ spectra after deposition of a 1 UC thick FeSe. From the fits, we obtain branching ratios that are very close to the theoretical value of 0.50 and an expected spin-orbit splitting

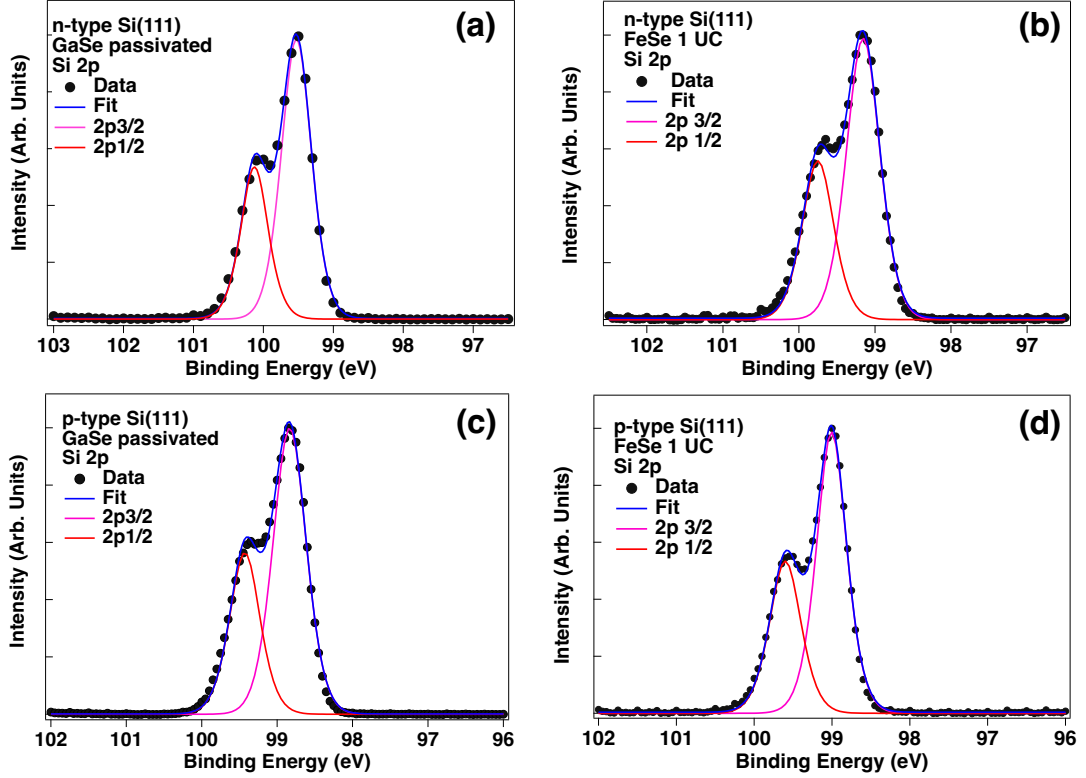


Figure 5.1: Si 2p core level fits of (a,c) Si(111):GaSe, and (b,d) Si(111):GaSe covered with a 1 UC thick FeSe film. Panels (a) and (b) correspond to n-type Si; panels (c) and (d) correspond to p-type Si. The spectrum consists of two spin-orbit split components, namely the $2p_{1/2}$ and $2p_{3/2}$ spectrum. They are fitted using a Voigt function after subtracting a Shirley background.

of 0.60 eV. This indicates that there is no need to incorporate additional (unresolved) core levels arising from possibly inequivalent Si sites. In other words, all Si atoms below the GaSe layer are very close to their bulk environment, and there is no sign of chemical intermixing at the FeSe/Si(111):GaSe interface. Note that this is not true for Si(111)7 $\times$ 7, where there are several inequivalent sites within the unit cell. The 7 $\times$ 7 spectrum can be fitted with two components, but the branching ratio is severely off. Fitting parameters are summarized in Table 5.1.

The Si $2p_{3/2}$ binding energy of the n-type and p-type Si(111) substrates was 99.53 eV and 98.83 eV, respectively, suggesting that the Fermi level at the surface differs by as much as 0.7 eV.

Table 5.1: Fitting parameters of the Si 2*p* spectrum for Si(111)7×7, Si(111):GaSe, and Si(111):GaSe covered with a 1 UC thick FeSe film. The Gaussian broadening was kept at 0.3 eV in all cases. The 2*p*_{3/2} core level is located 98.74 eV below the VBM (Himpsel et al. (1983))

	Parameters	Si(111)7×7	GaSe passivated Si(111)	FeSe film
n-type Si(111)	2 <i>p</i> _{1/2} (eV)	99.90	100.13	99.75
	2 <i>p</i> _{3/2} (eV)	99.32	99.53	99.16
	$\Delta_{s.o.}$ (eV)	0.59	0.60	0.59
	Area Ratio	0.73	0.50	0.53
p-type Si(111)	2 <i>p</i> _{1/2} (eV)	99.74	99.43	99.60
	2 <i>p</i> _{3/2} (eV)	99.15	98.83	99.00
	$\Delta_{s.o.}$ (eV)	0.59	0.60	0.60
	Area Ratio	0.69	0.52	0.53

Deep inside the bulk, we expect that Fermi levels to differ by approximately 1 eV, as the Fermi level of the n-type (p-type) sample is close to the conduction band minimum or CBM (valence band maximum or VBM). Similar passivation techniques employed by Fritsche et al. resulted in a Fermi level difference of 0.5 - 0.6 eV, slightly smaller than ours (Fritsche et al. (2002)).

The large change in Fermi level location at the surface for n- and p-type Si is indicative of weak pinning, due to the absence of surface states inside the Si band gap. To understand this phenomenon, we first consider the case of strong Fermi level pinning, namely Si(111)7×7, which has metallic surface states. For moderate doping, the Fermi level is located at 0.63 eV above the VBM, regardless of whether the bulk is n-type or p-type. According to Himpsel et al. (Himpsel et al. (1983)), the $2p_{3/2}$ core level is located 98.74 eV below the VBM. For our heavily doped n-type Si(111)7×7 sample, we find that the Fermi level is located 0.6 eV above the VBM, consistent with Himpsel et al. (Himpsel et al. (1983)). From Table 5.1, we find that the Fermi level is 0.8 eV above the VBM after GaSe passivation; see Figure 5.2. Completely flat band conditions would have required that the Fermi level be located at 1.0 eV above the VBM. Such a scenario is rarely realized as defect levels inside the gap can trap some donor charges originating from bulk As dopants, resulting in some small upward band bending.

Equation (5.1) provides a simple relation between the density of trapped surface charge n_s and the band bending V_B in the abrupt depletion layer approximation:

$$n_s = \sqrt{2\epsilon\epsilon_0 e V_B N_D} \quad (5.1)$$

where ϵ is the static dielectric constant of the semiconductor (11.7 for Si); N_D is the donor concentration (Hansson and Uhrberg (1988)). The band bending V_B corresponds to the difference between the Fermi level locations at the surface and deep inside the bulk, as measured relative to the VBM.

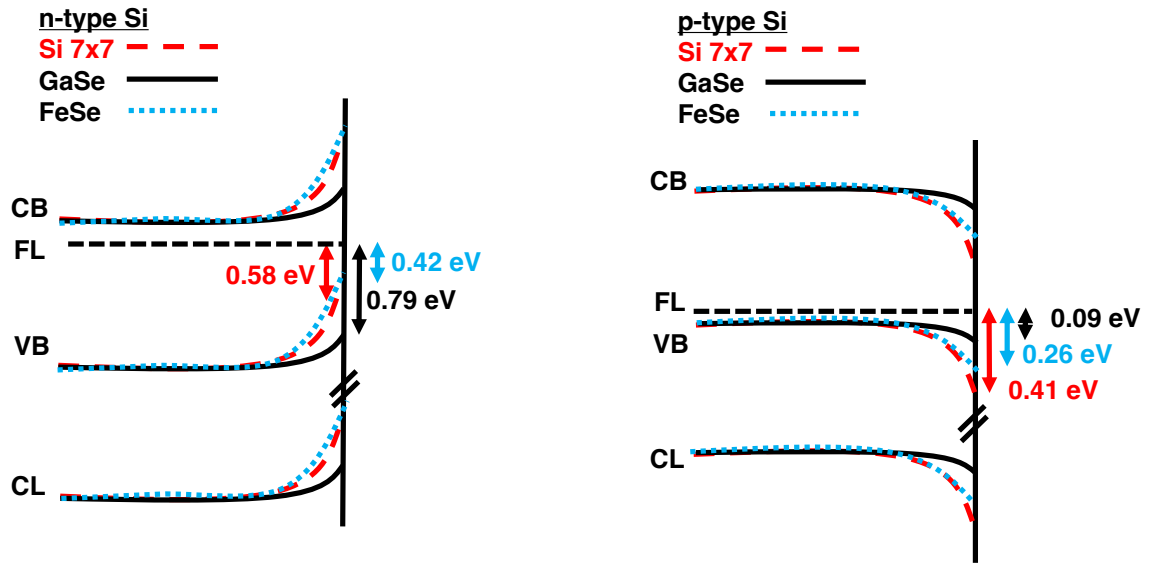


Figure 5.2: Fermi level position for Si(111)7 $\times$ 7, Si(111):GaSe, and 1 UC thick FeSe on Si(111):GaSe for (a) n-type and (b) p-type Si. The large difference in Fermi level position between the n-type and p-type Si(111):GaSe substrates suggests the absence of intrinsic surface states inside the Si band gap, as expected for a chemically passivated surface.

For our n-type Si sample, the dopant is As, and the corresponding donor level is located 54 meV below the CBM. So the band bending of our n-type Si(111):GaSe sample is $(1.12 - 0.80 - 0.05) = 0.27$ eV, resulting in a surface charge density of 1.9×10^{-2} C/m², or 1.2×10^{13} electrons/cm². Here, we used a donor concentration of 4×10^{25} m⁻³, which is estimated from the nominal resistivity of the Si wafer (0.002 Ω cm). Repeating the calculation for p-type Si(111):GaSe, we find that $V_B = 0.05$ eV and an excess hole concentration $p_s = 1.4 \times 10^{12}$ holes/cm². Here, we used an acceptor concentration of 3×10^{24} m⁻³. The boron acceptor level is located at 45 meV above the VBM. Considering the areal density of atoms in the Si(111) plane (7.83×10^{14} atoms/cm²), the excess charge per surface atom is 0.015 electron and 0.002 holes for the n-type and p-type substrates, respectively. These electrons and holes would be located at defect sites with levels that are located inside the band gap of Si.

The situation is somewhat different after we grow the FeSe monolayer. From Table 5.1, we infer that the Fermi level is located 0.42 eV above the VBM, implying a band bending of $(1.12 - 0.42 - 0.05) = 0.65$ eV. Plugging the values in the above equation, the surface charge density for n-type Si is 2.9×10^{-2} C/m², which corresponds to 1.8×10^{13} electrons/cm². For p-type, it becomes 2.9×10^{12} holes/cm². For a 1 UC thick FeSe film, the areal density of Fe is 1.78×10^{15} atoms/cm². For the n-type substrate, the amount of surface charge thus equals $1.8 \times 10^{13} / (1.8 \times 10^{15}) = 0.01$ electrons per Fe atom (or 0.02 electrons per unit cell). Similarly, for p-type Si, the charge transfer would be about 0.002 holes per Fe atom, indicating minimal charge transfer.

The depletion layer width (z) can be calculated using $z = n_s / eN$, N being the donor or acceptor concentration. For n-type (p-type) substrates, we find that $z = 45$ Å (98 Å). These values should be compared to the inelastic mean free path of the Si 2p photoelectrons, which is of the order of 20 Å. This means the core level shift averages the band bending over some limited depth, which is a sizable fraction of the depletion layer width. Accordingly, the band bending shifts and surface carrier densities might be slightly underestimated.

The n-type Schottky barrier height for the Si/FeSe contact matches the distance between the Fermi level and CBM at the interface, which amounts to $1.12 - 0.42 = 0.7$ eV. Likewise, the p-type Schottky barrier height equals the distance between the Fermi level and VBM at the interface, which is 0.26 eV. The sum of the n-type and p-type Schottky barriers (0.96 eV) should ideally be equal to the band gap of Si (1.12 eV). In our case, the sum is slightly less. This is expected as our bend bending values are slightly underestimated.

The valence band spectrum for the GaSe passivated n-type and p-type Si (111) surface is shown in Figure 5.3, where the valence band edge is separated by exactly 0.7 eV. This is expected since the same distance separates the corresponding Si 2p core level spectra (see 5.1(a, c)). Figure 5.3 (d) shows that the valence band spectra perfectly overlap after shifting the valence band spectrum of n-type Si by -0.7 eV. The peak at 10 eV corresponds to Si 3s (Hunger et al. (2005)), whereas a peak at 7 eV is hybridized 3s and 3d-like states of Si (Blase et al. (2008)). The peak at 3 eV is the contribution from GaSe and Si 3p level (Blase et al. (2008), Hunger et al. (2005), Adams et al. (2005)).

Figure 5.4 shows the valence band spectra of 1 UC FeSe grown on n-type and p-type GaSe:Si(111) surface. No alignment shift was needed here since the film is metallic. The two spectra essentially overlap, showing that the films on n-type and p-type Si are essentially the same. The shoulder at ~ 0.4 eV is the contribution from Fe 3d orbitals (Yoshida et al. (2009)). They also contribute to the spectral intensity at about 3 eV binding energy (Parker (2017)).

5.2 Fe 2p core level and CVV Auger spectrum

The Si 2p core level spectra showed that the FeSe/Si(111):GaSe is chemically abrupt. The Fe 2p and CVV Auger spectra, on the other hand, provide information about the chemical nature, composition and screening response of the FeSe thin film to core hole ionization.

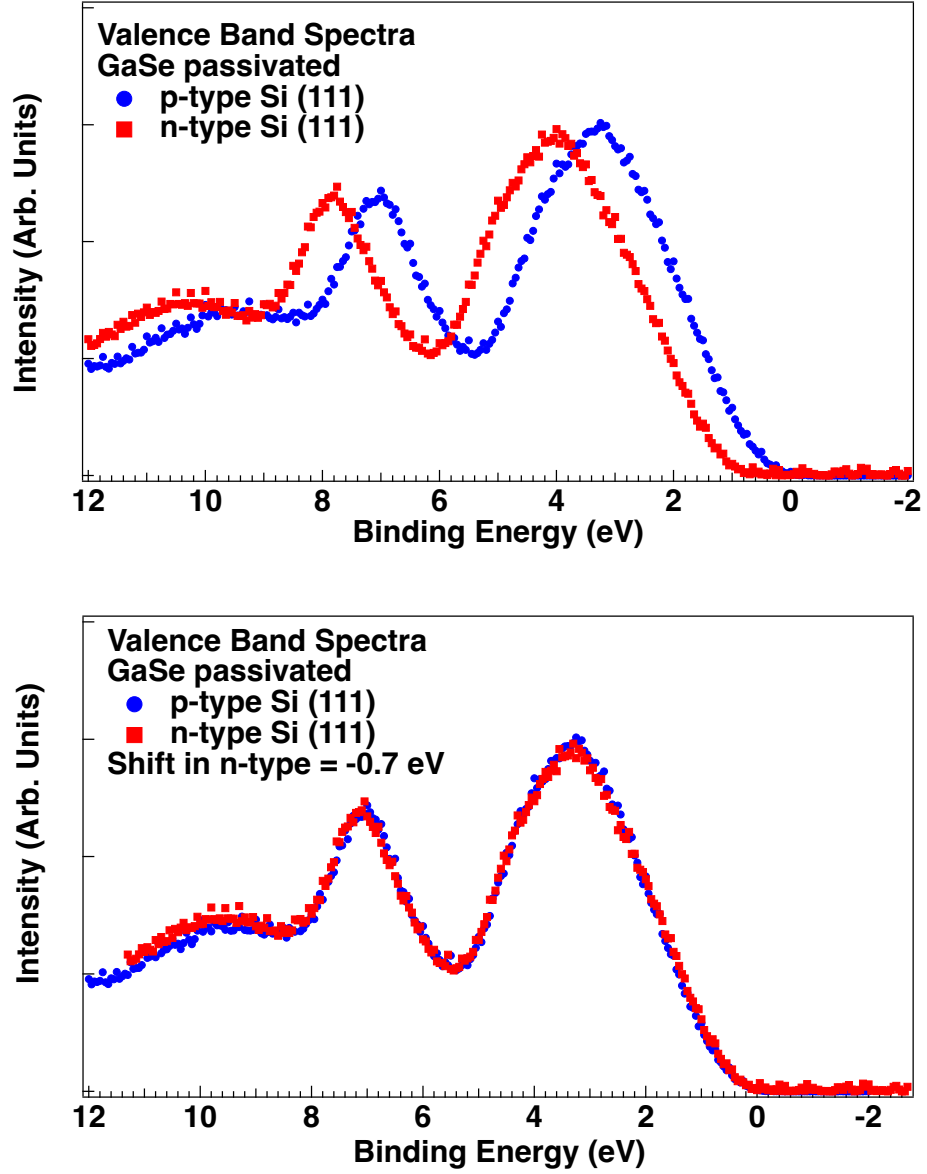


Figure 5.3: Top: Valence band spectra of n-type and p-type GaSe passivated Si (111). Bottom: The n-type valence band is shifted by -0.7 eV to match the p-type spectrum.

Figure 5.5(a) shows the Fe $2p_{3/2}$ core level spectrum of a 1 UC thick FeSe film grown on n-type and p-type Si(111):GaSe substrates. The spectrum clearly consists of multiple components. More analysis must be done to pinpoint the peak locations and their nature.

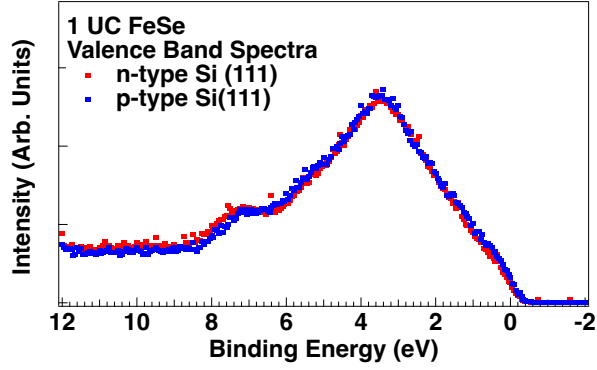


Figure 5.4: Valence band spectra of 1 UC FeSe grown on n-type and p-type GaSe passivated Si(111) surface.

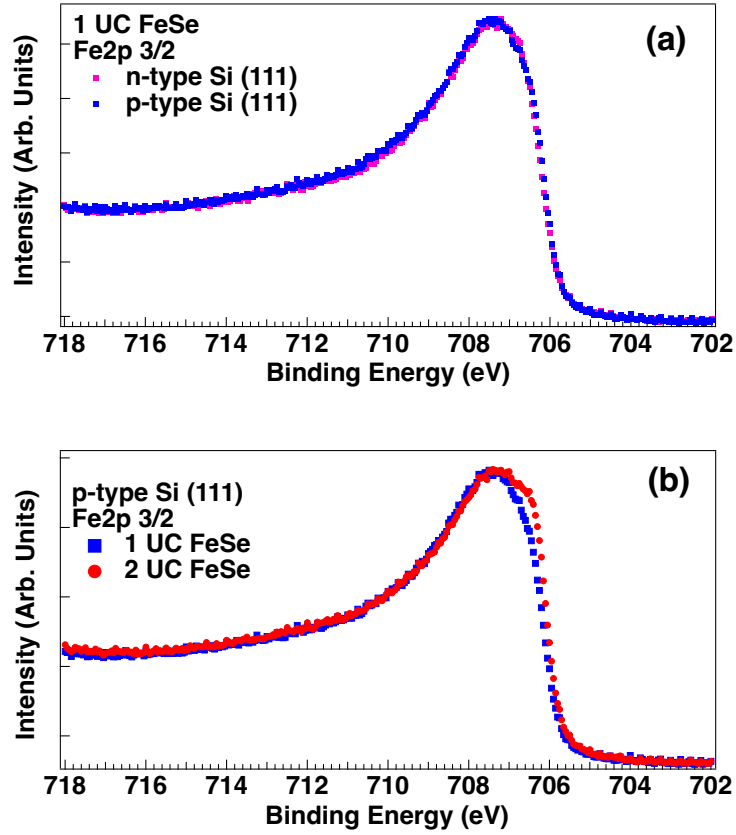


Figure 5.5: (a) Fe $2p_{3/2}$ core level spectrum of 1 UC thick FeSe film grown on n-type and p-type Si(111):GaSe surfaces. (b) Fe $2p_{3/2}$ core level spectra of 1 UC and 2 UC thick FeSe films grown on p-type Si(111):GaSe.

The Fe $2p_{3/2}$ core level spectra of 1 UC and 2 UC thick FeSe films grown on the p-type Si(111):GaSe surface are shown in Figure 5.5(b). For 2 UC thick FeSe, the shoulder at lower binding ~ 706.5 eV is stronger than for the 1 UC thick film.

The presence of the two peaks suggests that there are two inequivalent Fe sites in the unit cell, or they could represent two different screening channels in the FeSe film, whereby the peak at the lowest (highest) binding energy corresponds to the well-screened (poorly screened) final state (Hüfner (2013)). In addition, the spectrum has a very long tail, which likely originates from electron-hole excitations near the Fermi energy. To further analyze these spectra and to determine the stoichiometry of the sample, we need a better understanding of what part of the spectrum constitutes background and what part constitutes the real signal. This is a work in progress.

Figure 5.6 compares Fe $2p_{3/2}$ spectrum measured at grazing geometry for 1 UC thick FeSe film grown on Si and STO substrates. The films on STO, an unannealed and annealed sample, were grown and measured by Mr. Xiyu Peng and Mr. Kaleb G. McClure using a different MBE chamber. Unannealed refers to the as-grown sample, whereas annealed refers to the post-anneal of the sample after the growth. It has been reported that the post-growth anneal is necessary to achieve superconductivity in those FeSe films (He et al. (2013), Liu et al. (2012)). All the samples grown on the Si substrate are as-grown, and no treatment is performed after the growth. The samples grown on the STO substrate are tetragonal, and those grown on the Si substrate are hexagonal. The spectra for unannealed FeSe films on STO and Si look very similar. The post-annealed FeSe sample differs from the other two. On the other hand, the spectrum of the 2 UC thick FeSe film grown on Si (Figure 5.5(b)) resembles that of the postannealed 1 UC FeSe film on STO. These Fe $2p_{3/2}$ core level spectra consist of at least two peaks. In summary, the Fe $2p_{3/2}$ spectra of the hexagonal and tetragonal phases are quite similar. Considering the fact that the local environment of the Fe atom and the nature of the supporting substrate is very different, it is unlikely that the presence of the two Fe $2p$ core levels is simply due to an initial state effect (i.e., different Fe sites). Furthermore, considering the fact that a FeSi spectrum looks

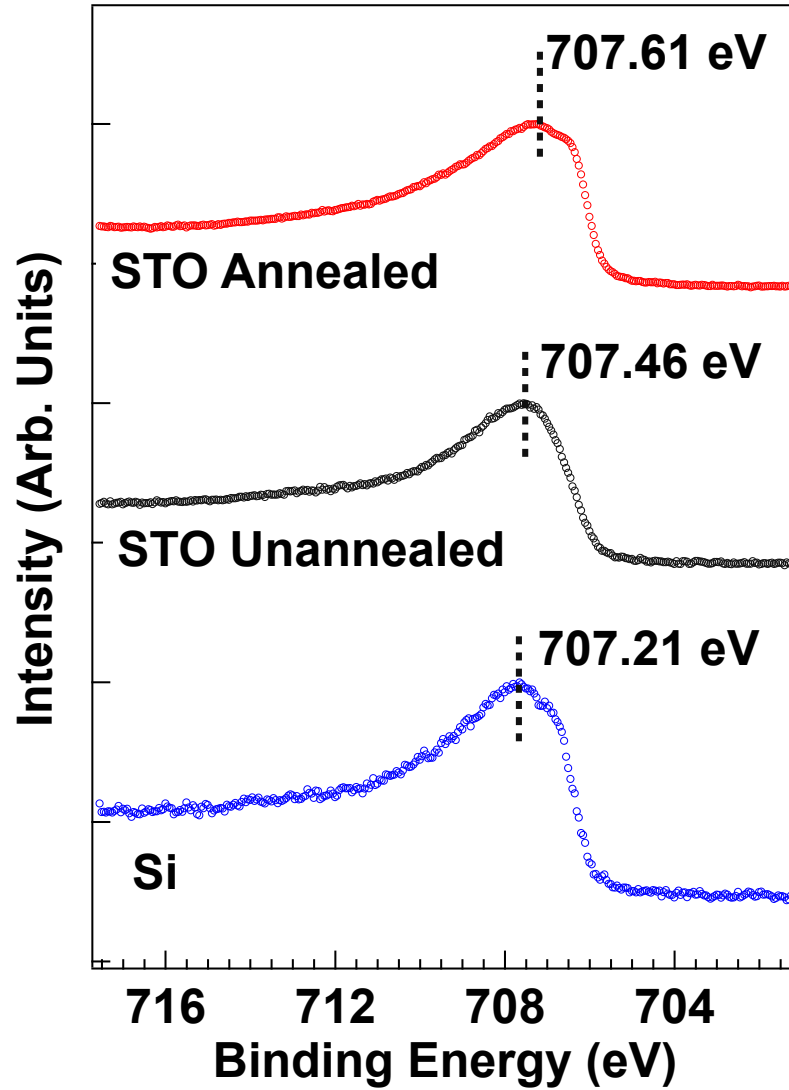


Figure 5.6: Fe $2p_{3/2}$ core level spectra of the 1 UC thick FeSe film grown on Si(111):GaSe surface, and those of the as-grown and postannealed 1 UC thick FeSe film grown on STO. The spectra were taken at grazing emission. A vertical offset has been added for comparison purposes. The dotted vertical lines show the peak positions.

dramatically different, as shown in Chapter 3, it is likely that the core level spectrum is closely related to the nature of the Fe-Se bond.

Figure 5.7 shows the Fe $2p$ core level and CVV Auger spectra of a 1 UC thick FeSe film grown on n-type and p-type Si(111):GaSe. Once again, the spectra look

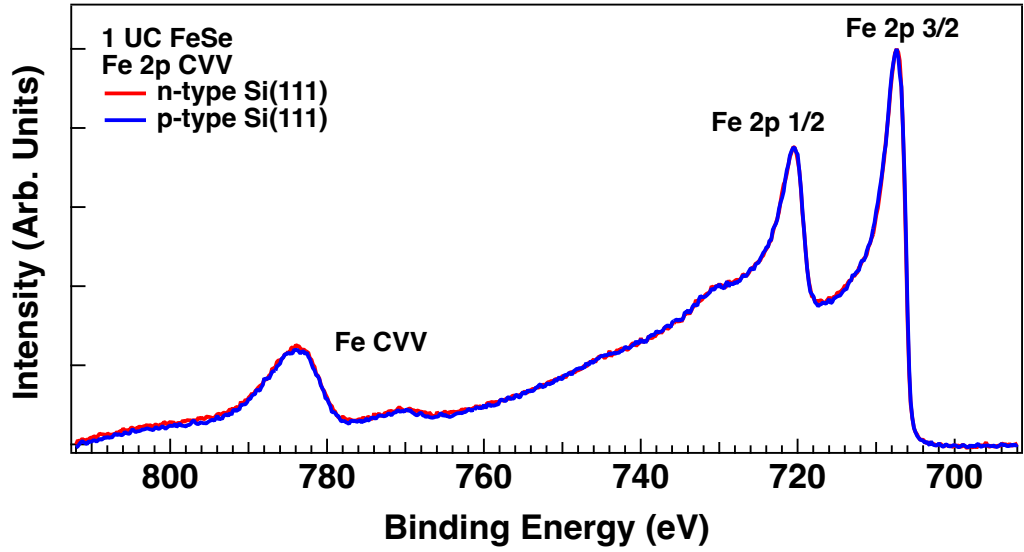


Figure 5.7: Fe 2p core level and CVV Auger spectra of a 1 UC thick FeSe film grown on n-type and p-type Si(111):GaSe.

identical. Figure 5.8 shows the comparison between the 1 UC thick films on STO and Si(111). The spectrum of the FeSe/STO sample rides on an inclined background due to the losses associated with the STO core levels appearing at lower binding energy.

Figure 5.9 provides a closer look at the CVV Auger spectra of a 1 UC thick FeSe film grown on Si(111) surface and on STO. The spectra look similar, but the low kinetic energy tail of the FeSe/STO samples seems longer than that of FeSe on Si. Figure 5.9(b) is the plot of the CVV Auger spectra on the two-hole energy scale. The spectra are offset vertically for clarity. The dotted vertical lines give the averaged weighted energies (referred to as centroids) of the spectrum. The centroid is slightly at lower energy for FeSe film grown on Si(111):GaSe substrate. Comparing those values with the density functional theory calculations of the single-particle density of states, the electron correlations in the corresponding systems can be extracted. A more detailed analysis is needed. A similar but detailed analysis in iron pnictide superconductors can be found in (Vilmercati et al. (2012)).

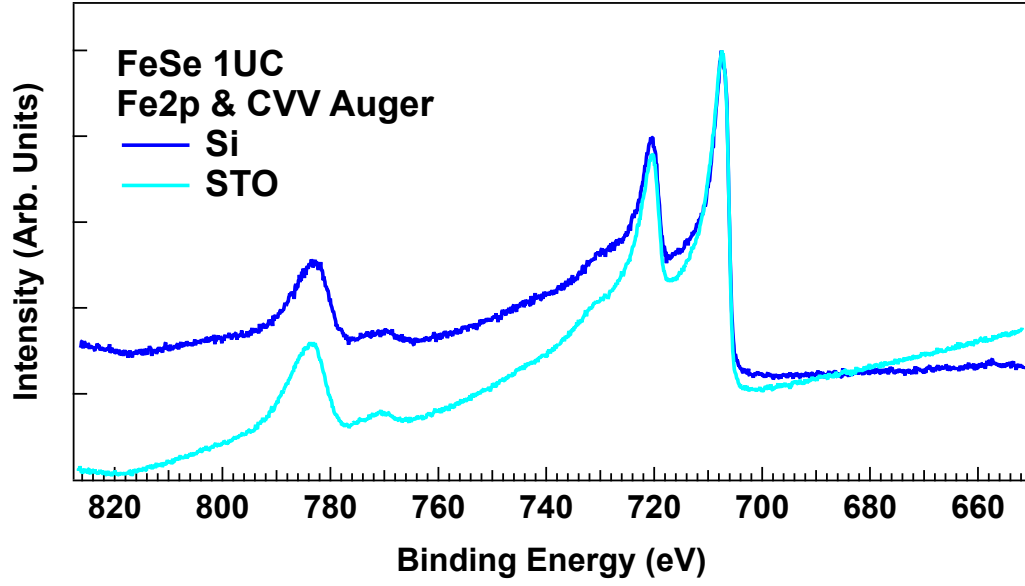


Figure 5.8: Fe $2p$ core level and CVV Auger spectra of a 1 UC thick FeSe film grown on Si(111):GaSe and on STO

5.3 Conclusions

This chapter provides a more in-depth discussion of the core-level and valence band spectra. We showed that the FeSe/Si(111):GaSe interface is chemically abrupt and that there is little charge transfer across the interface. The Fe $2p$ core level and CVV Auger spectra are qualitatively similar to those of FeSe films on STO, suggesting that the line shape is primarily determined by the nature of the Fe-Se bond. More detailed analysis is needed to evaluate the stoichiometry of the films and the role of screening and electron correlations in the photoemission and Auger spectra.

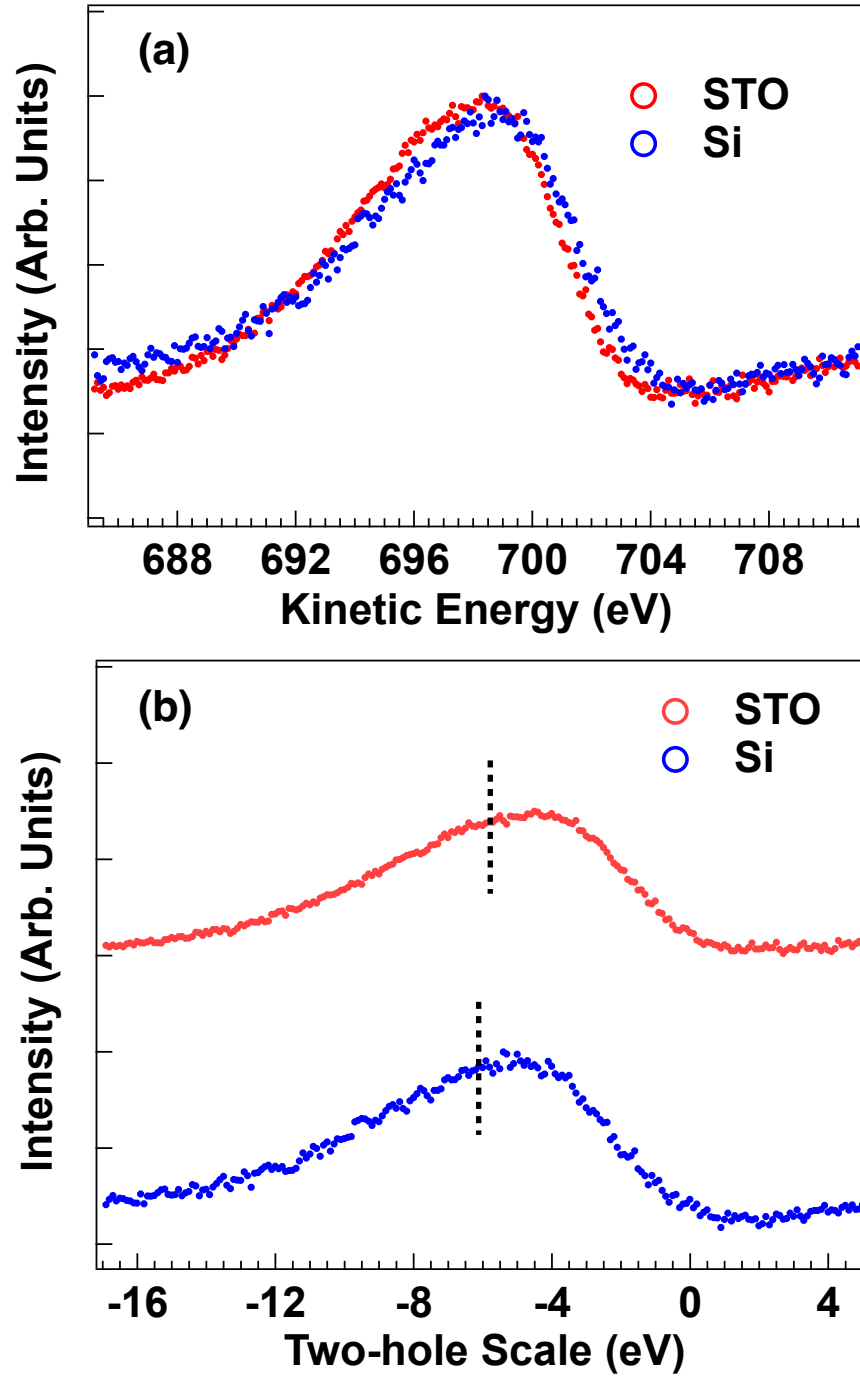


Figure 5.9: CVV Auger spectra of a 1 UC thick FeSe film grown on Si(111) and on STO shown in (a) kinetic energy scale and (b) two-hole scale. The spectra were taken at grazing emission. A vertical offset has been added in plot (b) for comparison purposes. The dotted vertical lines give the averaged weighted energies (referred to as centroids) of the spectrum.

Chapter 6

Surface Reconstruction

6.1 Introduction

The reduced coordination of atoms at the surface of a metal or semiconductor often leads to a restructuring of the surface and the formation of new periodic superstructures. The atoms compensate for the loss of bonding at the surface via a lattice distortion or a complete restructuring, modifying existing bonds and/or creating new bonds. The distortion pattern typically penetrates several atom layers into the bulk. One of the best-known surface reconstructions is the Si(111) 7×7 surface, where the unit cell area increases by a factor of 49. The driving force for such a dramatic restructuring is the reduction of the number of energetically unfavorable half-filled bonds from 49 to 19 per 7×7 unit cell. The structure is metallic and stable below 800 °C. Often, restructuring is accomplished via a band Jahn-Teller deformation or charge ordering transition at low temperatures that opens up a (partial) band gap near the Fermi level. This tends to be the leading instability for most semiconductor surfaces, as well as for many quasi two-dimensional materials. Both are inherently low-dimensional and prone to electronic instabilities. In this chapter, we will present evidence for a structural distortion in 1 UC thick FeSe films on GaSe passivated Si(111). These strictly 2D films are metallic at room temperature but undergo a

(4x1) restructuring below 180 K. The restructuring is likely electronically driven, but the unusual temperature dependence of the (4x1) order parameter suggests the possibility that there may be a competing order that has yet to be identified.

6.2 Evidence of Surface Reconstruction

A UC thick FeSe was grown on a GaSe passivated Si(111) surface. During growth, the film was monitored by RHEED and later checked with LEED. Both RHEED and LEED patterns indicate a high-quality FeSe film. The film was then loaded into a vacuum suitcase and transported to the low temperature STM chamber for topographic imaging and STM spectroscopy. The images were acquired at 77 K. Figure 6.1 shows two atomically-resolved STM images. The images (a) and (b) were taken at different sample positions with a bias voltage of +0.5 V (empty states) and -0.5 V (filled states), respectively. The scanned area is $4.94 \text{ nm} \times 6.42 \text{ nm}$ and $4.90 \text{ nm} \times 6.38 \text{ nm}$, respectively. Since the films are likely Se terminated, the protrusions in these images are likely Se atoms. Both images reveal the presence of a 4x1 supercell. Figure 6.2 replicates the image of Figure 6.1(a), this time showing the line profiles along the major hexagonal axes. Those clearly reveal a quadrupling of the periodicity along one of the axes where all four Se atoms within the 4x1 unit cell have a different height. This indicates that the reconstruction is primarily a 4x1 buckling distortion of the Se atoms. There is no buckling distortion along the other hexagonal axis. It should be kept in mind that the height differences may be part structural and part electronic, since the STM probes the LDOS. While there may also be some in-plane atomic displacement, the calibration of the STM piezo elements is not accurate enough to make that determination.

Figure 6.3 shows the high-resolution STM images for the same sample acquired at a bias voltage of (a) + 1.0 V, (b) 0.8 V, (c) 0.6 V, and (d) -0.6 V, respectively. The scanned area is $3.60 \text{ nm} \times 4.68 \text{ nm}$. A 2×1 reconstruction was observed in some parts of the sample, as shown in panels (a) and (b). Panels (c) and (d) show no

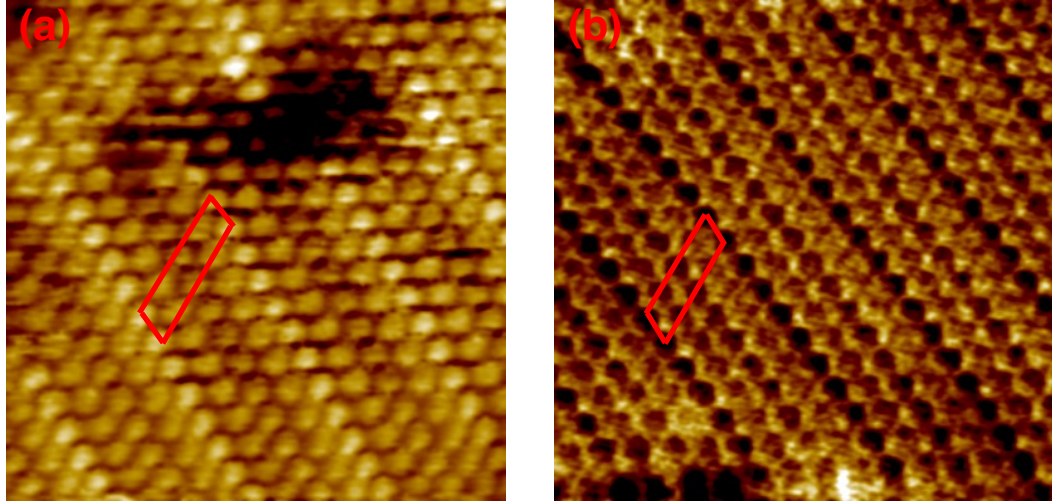


Figure 6.1: Atomically-resolved STM images of a 1 UC thick FeSe film grown on GaSe passivated Si(111). Panels (a) and (b) were acquired at a bias voltage of + 0.5 V and -0.5 V, respectively. A 4×1 reconstruction is observed in both images. The unit cells are indicated in red.

clear evidence of either a 4×1 or 2×1 superlattice, and thus we conclude that the (2×1) and (4×1) domains coexist with unreconstructed (1×1) domains. Figure 6.4 shows atomically-resolved dual-bias STM images, recorded with a bias voltage of ± 1 V. Panel (a) suggests that the FeSe film has a 2×1 superstructure, but the change in bias polarity in panel (b) clearly reveals the 4×1 periodicity. The bright rows at positive bias correspond to the dark rows at negative bias, indicated by arrows. This could be due to some charge disproportionation between neighboring sites, which would be indicative of a charge ordered state.

Charge ordering is often accompanied by a lattice distortion due to the coupling between the charge density and the lattice (Peierls (1996), Gruner (2018)). Indeed, we observed half-order superlattice reflections in LEED but never observed the 4th-order diffraction spots, in contrast to STM, where we observed both (2×1) and (4×1) reconstructions, even within a single dual-bias image set. This suggests that the 4×1 reconstruction might be a purely electronic contrast and that the lattice periodicity is (2×1) .

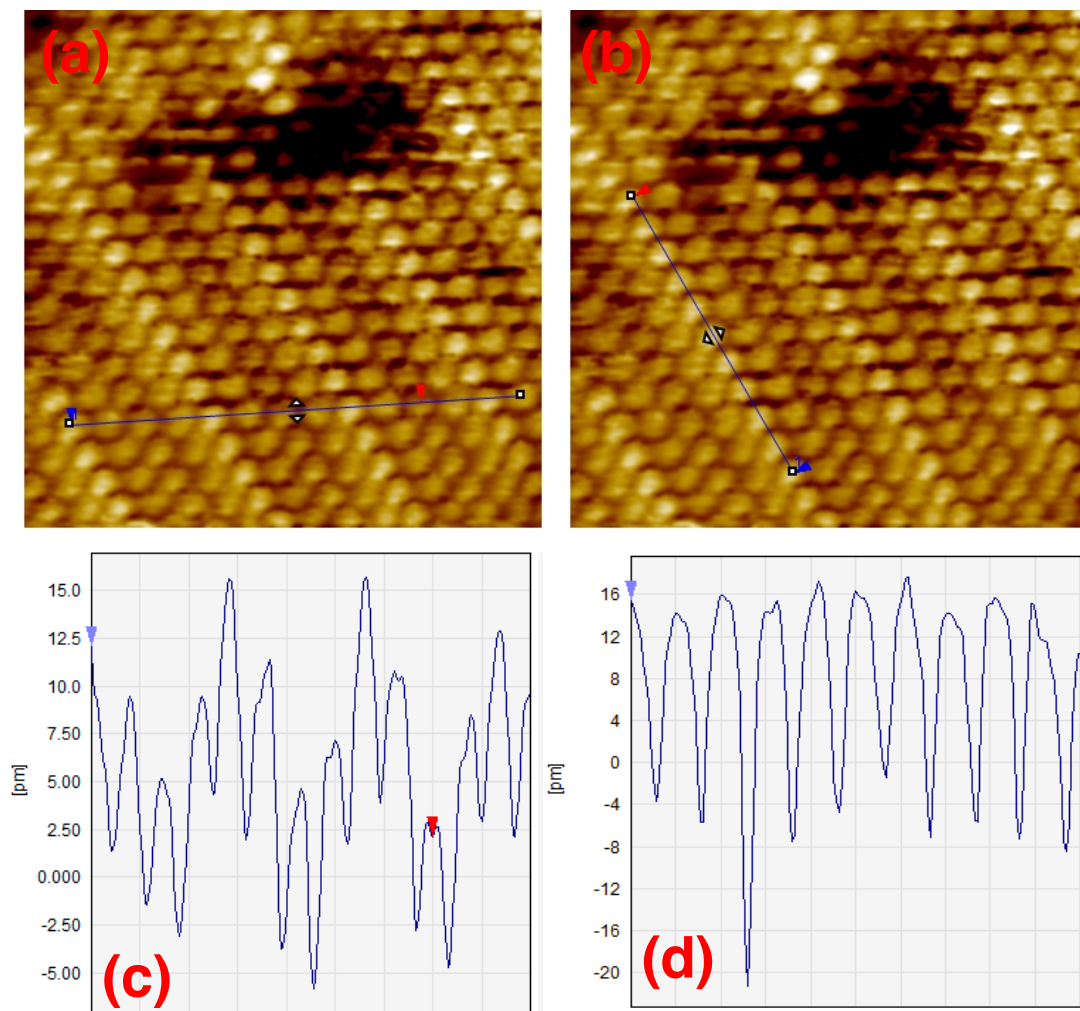


Figure 6.2: Line profiles taken along the major hexagonal axes of the image in Figure 6.1. The blue lines in panels (a) and (b) indicate the location of the line profiles shown in panels (c) and (d), respectively. Notice the quadrupling of the periodicity in panel (c), as well as the height variation of the individual atoms.

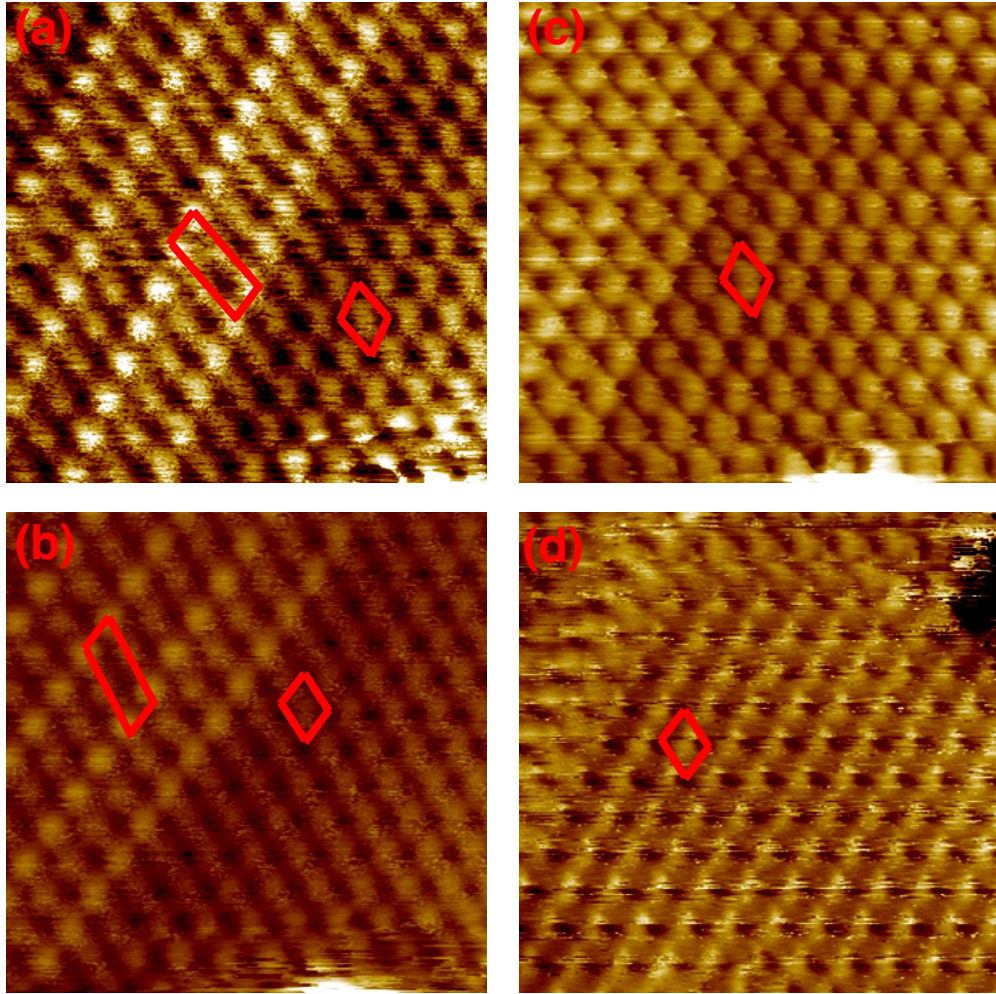


Figure 6.3: Atomically-resolved STM images of a 1 UC thick FeSe film grown on the GaSe passivated Si(111) surface, acquired at a bias voltage of (a) + 1.0 V, (b) 0.8V, (c) 0.6 V, and (d) -0.6 V, respectively. A (2 $\times$ 1) structure coexists with unreconstructed (1 $\times$ 1) regions. The unit cells are indicated in red.

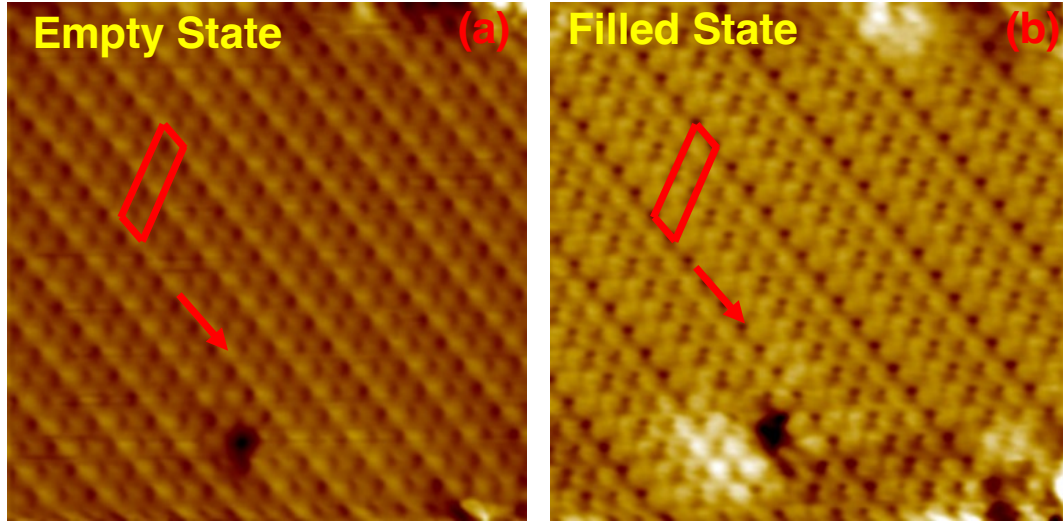


Figure 6.4: (a) Atomically-resolved registry-aligned STM images of a 1 UC thick FeSe film grown on GaSe passivated Si(111). Images were acquired at 77 K with a bias voltage of (a) 1.0 V and (b) -1.0 V.

Figure 6.5 shows the tunneling spectra of a 1 UC thick FeSe grown on GaSe passivated Si(111). The spectra were recorded at 77 K. Panel (a) contains five-point spectra acquired at the same lattice location in forward and backward scans. The spectra are nearly identical, indicating that the tip and temperature were very stable. Panel (b) shows the average of all five STS spectra. The spectrum in panel (c), is the dI/dV spectrum, which is proportional to the LDOS. It suggests the presence of a tiny gap. However, the $\log |I|$ versus V spectrum in panel (d) indicates that the film is metallic. The current minimum appears at a small negative bias, suggesting the the minimum in the LDOS is located below the Fermi level.

Figure 6.6 shows the LEED patterns of a 1 UC thick FeSe film grown on the GaSe passivated Si(111) surface, at temperatures ranging from 10 K to 200 K. The LEED pattern does not change between 200 K and room temperature. The integer order spots are intentionally saturated in the LEED pattern so as to better visualize the fractional order spots. However, another set of LEED patterns was taken to analyze the integer order spots without saturating those spots. To determine the intensity of the fractional order spots, we selected a region of interest around those spots and

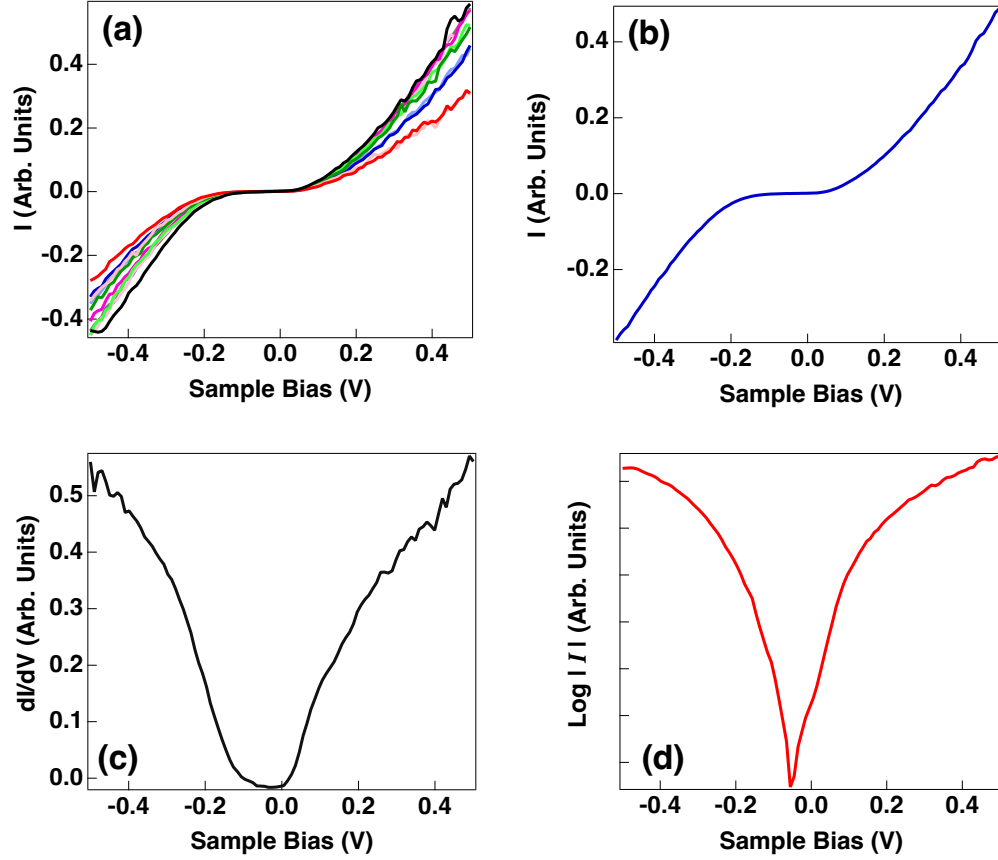


Figure 6.5: STS spectra of a 1 UC thick FeSe film grown on GaSe passivated Si(111). (a) The I-V spectrum was recorded five time during forward and backward scans. (b) Average of the I-V spectra in (a). (c) Averaged dI/dV spectrum with possibly a tiny gap at or below the Fermi level. (d) $\log |I|$ spectrum, indicating the absence of a tunneling gap.

integrated the intensity pixel by pixel. To estimate the background intensity, we selected four adjacent areas for each spot and averaged their integrated intensities. The averaged background intensities were then subtracted from the spot intensity in the region of interest.

The half-order spots are clearly seen at 10 K. Interestingly, their intensity increases up to about 70 K and then decreases until they are no longer visible above 160 K. This behavior is fully reversible. Figure 6.7 compares the LEED intensity of two half-order diffraction spots as a function of temperature. The inset shows the selection of those spots. Their temperature dependence is identical, as expected.

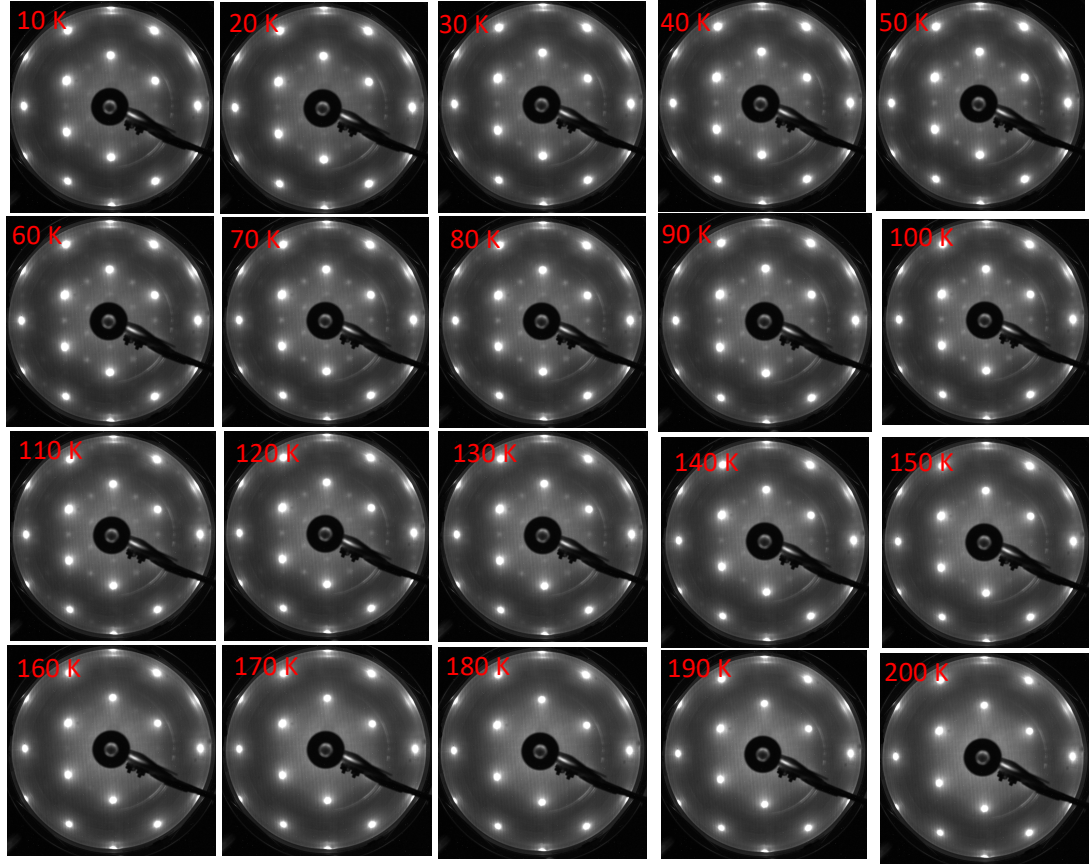


Figure 6.6: LEED pattern of 1 UC FeSe grown on GaSe passivated Si(111) for temperatures ranging from 10 K to 200 K.

The half-order spots are clearly seen at 10 K. Interestingly, their intensity increases up to about 70 K and then decreases until they are no longer visible above 160 K. This behavior is fully reversible. Figure 6.7 compares the LEED intensity of two half-order diffraction spots as a function of temperature. The inset shows the selection of those spots. Their temperature dependence is identical, as expected.

The decrease of the fractional order spot intensity below 70 K is unexpected. It suggests that the amplitude of the lattice distortion reduces below 70 K or that the area fraction of the (2×1) phase decreases. Both scenarios suggest that there might be a competing order that is not evident in LEED or STM. A possible competing order would be magnetism since bulk FeSe is an antiferromagnet or ferrimagnetic (see Chapter 1). Another, perhaps more mundane explanation is that the (2×1)

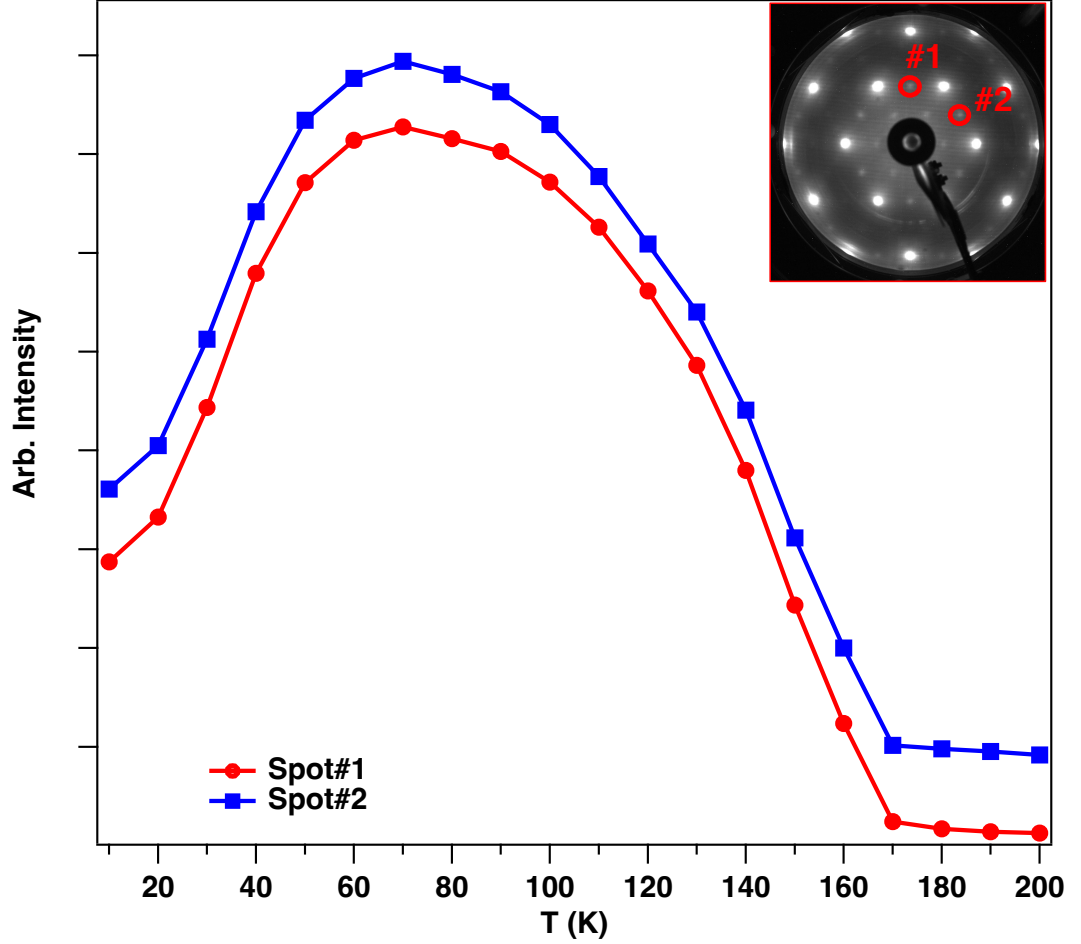


Figure 6.7: Comparison of the intensity of two half-order spots with respect to temperature. The spot selection is indicated in the LEED pattern. An offset is added to one graph for better visualization.

CDW nucleates below 180 K in isolated patches or domains. As the temperature decreases, the domains increase in size and begin to interfere. The decrease of the order parameter below 70 K could perhaps be explained by large-scale destructive interference between out-of-phase CDW domains that reduces the CDW amplitude.

While both scenarios are still speculative, we certainly can rule out the possibility that the (2×1) or (4×1) ordering is related to an ordering of Fe vacancies. While the hexagonal FeSe is prone to having vacancies (see Chapter 1), the observed temperature dependence of the LEED intensity would suggest that vacancies somehow become more disordered upon cooling below 70 K, in violation of the second law of

thermodynamics. Furthermore, an ordered vacancy pattern should be clearly visible in dual bias STM images as vacancies should show up as deep depressions at both positive and negative tunneling bias, which clearly is not the case.

Our observations call for several follow-up experiments. First, a detailed temperature dependent STM study should reveal the nucleation and spread of the CDW domains. In addition, since bulk hexagonal FeSe is antiferromagnetic, it is desirable to explore the possibility of magnetic ordering in the FeSe monolayer with spin-polarized STM. In particular, the observation of a CDW in a (possibly alter) magnetic system is intriguing in its own right. Finally, it would be interesting to monitor the LDOS as a function of temperature to see whether the temperature dependence of the LDOS is in any way related to the distortion amplitude detected with LEED.

6.3 Conclusions

We presented evidence for the existence of a (2×1) or (4×1) superstructure in a 1 UC thick FeSe film on GaSe passivated Si(111). The (2×1) superstructure is observed in both STM and LEED, indicating that the superstructure is associated with a periodic lattice distortion associated with a charge density wave (PLD/CDW). The (2×1) order parameter exhibits an unexpected non-monotonic temperature dependence, which might be attributed to a competing order parameter at low temperature or perhaps due to destructive interference between CDW domains. The observation of charge order in a system that is likely magnetic is intriguing and calls for further exploration.

Chapter 7

Summary and Outlook

Our studies primarily focused on the MBE synthesis of FeSe thin films on Si(111). Silicon is a particularly important materials platform because it has been -and still is- the main driver of technological innovation. It is also a relatively cheap and versatile template for growing and engineering hetero-structure materials and devices. The synthesis of superconducting FeSe thin films on a Si substrate would be a first step towards integrating unconventional superconductors into existing silicon technology. Unfortunately, FeSe deposition on silicon produces iron silicides. We demonstrated that silicide formation can be fully suppressed after the Si(111) surface is passivated with a GaSe monolayer. The passivated Si surface thus becomes a van der Waals surface that could facilitate the van der Waals growth of a series of transition metal chalcogenides. Our films are primarily hexagonal, though tetragonal films can also be stabilized, depending on the growth parameters. In this work, we not only explored the initial stages of growth but also studied the structure and electronic properties of these films.

Arguably, the most surprising outcome of these investigations is the discovery of a charge ordered state in the hexagonal FeSe monolayer, and particularly its unusual temperature dependence. Charge ordering likely competes with magnetic order

and possibly superconductivity. To better understand these intricacies, a detailed analysis of the stoichiometry is needed, as Fe vacancies strongly influence the magnetic properties of the films. Secondly, we do not know whether the charge ordering only appears in single layer FeSe or whether it survives in thicker films. The next series of experiments should focus on the temperature dependence of the CDW domains and CDW gap with STM in single layer and multilayer films. ARPES studies should be conducted to elucidate the connection between the periodic lattice distortion, band structure, and Fermi surface. Density Functional Theory calculations are currently underway to hopefully consolidate our understanding regarding the initial growth stages and elucidate the nature of the charge ordering in the monolayer film.

Finally, the observation of the tetragonal domain on Si offers a new possibility of controlling its superconducting T_c via modulation doping. Si is very easy to work with, and we envision that these studies will inspire new investigations into a wide variety of chalcogenide/silicon heterostructures and devices.

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Vita

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