Growth of silicene on Ag(111) studied with low energy electron microscopy

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Abstract

The discovery of graphene and its properties is of big importance in the realm of science. Graphene exhibits exotic physical properties like the integer quantum Hall effect, the Klein paradox and a linear dispersion relation. The fact that silicon has similar properties as carbon has motivated the growth and study of a graphene-like material called silicene. To date only scanning tunneling microscopy (STM), atomic force microscopy (AFM), low energy electron diffraction (LEED) and angle-resolved photoemission spectroscopy (ARPES) experiments have been performed on silicene on Ag(111). Real-time imaging of changes in surface topography through surface diffusion, growth and phase transitions were not performed yet. Here, low energy electron microscopy (LEEM) has been used as a technique to study changes in surface topography. We find that a phase transition from silicene to sp^3 hybridized silicon inhibits the growth of a second silicene layer. Furthermore, we conclude that it is not possible to cover a Ag(111) surface entirely with silicene.

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Introduction

Two dimensional materials like graphene exhibit exotic physical properties. For example, the integer quantum Hall effect was observed as well as the Klein paradox. Massless Dirac fermions in graphene obey the relativistic Dirac equation leading to a linear dispersion relation with relativistic Fermi velocities. Additionally, the very high mobility of electrons in graphene could be utilized in next-generation devices [1]. Graphene consists of carbon atoms in a honeycomb structure and therefore it is of interest to study if silicon atoms, that have the same valence electron configuration as carbon, can also form a similar two dimensional honeycomb structure called silicene. Recently theoretical, experimental and computational studies of silicene have been performed [1, 2, 3].

So far the evidence of silicene's existence has been provided by scanning tunneling microscopy (STM) [1, 4], atomic force microscopy (AFM) [5] and low energy electron diffraction (LEED) [2, 6]. While STM and AFM acquire atomic resolution, both techniques lack the ability to perform realtime imaging of changes in surface topography through surface diffusion, sublimation, growth, phase transitions, adsorption and chemical reactions. LEED experiments are always done in reciprocal space and do not provide any information on changes in surface topography except phase transitions. With a large field of view and the ability to perform real-time and real space imaging low energy electron microscopy (LEEM) can obtain the information that is not accessible by LEED, STM and AFM. Through the use of a field-limiting aperture, the low energy electron microscope also gives the possibility to perform localized LEED experiments, referred to as μ LEED, to confirm the growth of silicene. Therefore, the objective of the work described in this master thesis is to study the growth of silicene on Ag(111) using the low energy electron microscope enables a further understanding of silicene and its possible future implementations in high-tech industry.

Chapter 1 Background of silicene

1.1 What is silicene?

The electronic configuration of silicon, $[Ne]3s^23p^2$, is comparable to the electronic configuration of carbon, $[He]2s^22p^2$, hence silicon and carbon have similar valence electrons. Carbon is either sp^3 hybridized (diamond structure) or sp^2 hybridized (graphite and graphene). Therefore the expectation is that silicon should also have a sp^2 hybridized structure called silicene.

Although graphene exhibits a planar structure, theoretical [3, 7] and experimental [1, 4, 7] work has shown that silicene exists in a buckled structure. A graphic representation is given in Fig. 1.1.



Figure 1.1: Topview of a 4×4 silicene overlayer structure on Ag(111) (a), and the sideview where the buckled structure is visible (b). Image reproduced from Ref. [1].

Ag(111) was chosen as the substrate. The tendency to form an Ag-Si alloy is low and makes the Ag(111) substrate ideal for the growth of silicene. Due to a low segregation energy, several overlayer structures may exist for silicene on Ag(111) surfaces. Other possible substrates are ZrB_2 and Ir[8]. The most common overlayer structure of silicene on Ag(111) is 4×4 [9]. Other phases that have been observed and reproduced are $\sqrt{3} \times \sqrt{3}$ [4], $\sqrt{13} \times \sqrt{13} R 13.9^{\circ}$ [1], $3.5 \times 3.5 R 26^{\circ}$ [2] and $2\sqrt{3} \times 2\sqrt{3} R 30^{\circ}$ [6]. Even more phases are reported as Figs. 1.2 and 1.3 show. There is still debate on whether or not the structure of some phases was determined correctly [1]. Furthermore, multiple phases may exist simultaneously depending on the substrate temperature and deposition time as Figs. 1.2 and 1.3 show [2, 6].



Figure 1.2: Different superstructures occur in the LEED patterns as a function of deposition time and substrate temperature. Image reproduced from Ref. [2].



Figure 1.3: LEED patterns as a function of substrate temperature: at $150 \,^{\circ}\text{C}$ (a), $210 \,^{\circ}\text{C}$ (b), $270 \,^{\circ}\text{C}$ (c) and $300 \,^{\circ}\text{C}$ (d). Image reproduced from Ref. [6].

1.2 Fermi-Dirac equation and Dirac cones

The electrons in silicene behave as relativistic massless Dirac fermions [3]. Therefore, a quantum mechanical description would not satisfy and should be combined with Einstein's special theory of relativity. One possible way to describe relativistic quantum mechanical phenomena is by using the Klein-Gordon equation. However, in this case the Klein-Gordon equation will fail, because it is only applicable to particles with zero spin and therefore impossible to apply to fermions with spin $\pm \frac{1}{2}$. Another way of describing the physics is by using the Fermi-Dirac equation.

The quantum mechanical part is given by the time-dependent Schrödinger equation:

$$\left[\imath\hbar\frac{\partial}{\partial t} - \hat{H}\right]\psi(x,t) = 0 \tag{1.1}$$

Here \hbar is the constant of Planck, \hat{H} is the Hamiltonian operator and $\psi(x, t)$ is the one dimensional

time dependent wave function. The relativistic dispersion relation is written as:

$$E^2 = p^2 c^2 + m^2 c^4$$

or

$$E^2 - p^2 c^2 - m^2 c^4 = 0 (1.2)$$

E denotes the energy, whereas p denotes the momentum, m the mass and c the speed of light. Dirac's approach was to factorize Eq. 1.2 into

$$E^{2} - p^{2}c^{2} - m^{2}c^{4} = (E + \alpha pc + \beta mc^{2})(E - \alpha pc - \beta mc^{2})$$
(1.3)

The right-hand side of Eq. 1.3 should be equal to zero. Because E, αpc and βmc^2 are positive terms, only the last factor on the right-hand side can give a possible zero outcome i.e.

$$E - \alpha pc - \beta mc^2 = 0$$

Rewriting

$$E = \alpha pc + \beta mc^2$$

The latter is then transformed into a quantum mechanical operator

$$E = \alpha pc + \beta mc^2 \iff \hat{H} = \alpha \hat{p}c + \beta mc^2$$

where $\hat{p} = -i\hbar \frac{\partial}{\partial x}$

By substituting this new quantum mechanical operator into Eq. 1.1 one gets

$$\left[\imath\hbar\frac{\partial}{\partial t} - \left(\alpha c(-\imath\hbar\frac{\partial}{\partial x}) + \beta mc^2\right)\right]\psi(x,t) = 0$$
(1.4)

Now to find the parameters α and β the right-hand side of Eq. 1.3 is defactorized

$$(E + \alpha pc + \beta mc^2)(E - \alpha pc - \beta mc^2) = E^2 - \alpha^2 p^2 c^2 - \beta^2 m^2 c^4 - (\alpha \beta + \beta \alpha) pmc^3$$

To equalize the right-hand side of the equation above with the left-hand side of Eq. 1.3, the following needs to be satisfied:

$$\begin{aligned} \alpha^2 &= 1\\ \beta^2 &= 1\\ \alpha\beta + \beta\alpha &= 0 \end{aligned}$$

The solutions of α and β are 2x2-matrices

$$\alpha = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \sigma_x \text{ and } \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \sigma_z$$

Now that the Pauli matrices are introduced, a spinor $\Psi(x,t)$ will be defined as

$$\Psi(x,t) = \left(\begin{array}{c} \psi_1(x,t) \\ \psi_2(x,t) \end{array}\right)$$

Substituting the Pauli matrices and the spinor in Eq. 1.4 gives the Fermi-Dirac equation

$$\left[\imath\hbar\frac{\partial}{\partial t} - \left(c\sigma_x(-\imath\hbar\frac{\partial}{\partial x}) + mc^2\sigma_z\right)\right] \left(\begin{array}{c}\psi_1(x,t)\\\psi_2(x,t)\end{array}\right) = 0$$
(1.5)

Equation 1.5 holds only for one-dimensional systems, whereas silicene is two dimensional. It is extended fairly simple to 2D.

$$\left[i\hbar\frac{\partial}{\partial t} + i\hbar c \left(\sigma_x \frac{\partial}{\partial x} + \sigma_y \frac{\partial}{\partial y}\right) - mc^2 \sigma_z\right] \left(\begin{array}{c} \psi_1(x, y, t) \\ \psi_2(x, y, t) \end{array}\right) = 0$$
(1.6)

Equation 1.6 is the two dimensional Fermi-Dirac equation which is applicable to silicene. A solution to the two dimensional Fermi-Dirac equation is given in Eq. 1.7.

$$\Psi(x, y, t) = e^{-\frac{i}{\hbar}Et}\Phi(x, y) \tag{1.7}$$

Here $\Phi(x, y)$ is the solution to the time-independent Schrödinger equation. As a result of this, one can derive that

$$c = v_F$$
$$m = 0$$

And this shows that the electrons of silicene indeed behave as massless Dirac fermions.

An interesting property of graphene is that it exhibits a linear dispersion relation, called Dirac cones. The question that naturally arises is whether or not silicene also has a linear dispersion relation. ARPES experiments confirmed that silicene on Ag(111) exhibits a linear dispersion relation [7]. Studies with scanning tunneling spectroscopy (STS) also gave similar results [10]. From the former experiment a Fermi velocity of $1.3 \cdot 10^6 \,\mathrm{m\,s^{-1}}$ was found. The latter experiment resulted in a Fermi velocity of $1.2 \cdot 10^6 \,\mathrm{m\,s^{-1}}$. Although there is a minute discrepancy between these two results, both do correspond roughly with the theoretical Fermi velocity of $\sim 10^6 \,\mathrm{m\,s^{-1}}$ [3].

Wang et. al stated without clear evidence that the linear dispersion relation does not occur due to silicene, but rather from the Ag(111) substrate [7]. Density functional theory calculations were run and resulted in a linear dispersion relation for standalone silicene only while interactions between silicene and Ag(111) cause the Dirac cone to disappear [8], which is in contradiction with the experimental work. A plausible explanation might be that the *sp* electrons in Ag behave like free electrons and thus the *sp* band may be considered parabolic. Then a linear function could be fitted for a finite energy interval away from the minimum energy of Ag(111). This finite energy range coincided with the experimental studies [7, 8].

Chapter 2

Experimental methods

Two techniques have been used to characterize silicene on Ag(111): low energy electron microscopy (LEEM) and low energy electron diffraction (LEED). While real space images were recorded *in situ* on LEEM, LEED acquired reciprocal space images *in situ*. While real space images gave insight in growth, nucleation and other surface effects, the reciprocal space images were used to identify the various phases of silicene on Ag(111).

2.1 LEEM

2.1.1 Basics

While surfaces and thin films are becoming more important, so, too, does surface imaging with electrons. On the one hand scanning tunneling microscopy (STM) provides info on the atomic scale topography, whilst on the other hand electron microscopy yields a multitude of contrast mechanisms to disciriminate between surface features. Electron microscopy has two principal imaging modes: scanning and true imaging. In scanning mode an electron beam is focused onto the surface where interaction between the electron beam and sample produces secondary, backscattered, Auger electrons as well as other particles. These electrons, particles and their corresponding energies are detected and they carry physical and chemical information from the focal point of the beam on the sample. The beam is then scanned throughout an area of which a scanning surface image is recorded. This mode is in contrast to the true imaging mode where all pixels of the surface image are retrieved simultaneously from the area of the surface that is illuminated by the beam.

Two techniques that function in true imaging mode were used: low energy electron microscopy (LEEM) [11] and photoemission electron microscopy (PEEM). In the former case a low energy electron beam illuminates the sample and elastically backscattered electrons are detected. The latter (PEEM) involves photons that interact with the sample, from which photoelectrons are emitted and detected. Since PEEM has no significance for the experiment besides optical alignment, it will not be discussed in what follows.

Interaction between low energy electrons and matter

Low energy electrons form the foundation of the LEEM, hence the technique is called low energy electron microscopy. LEEM involves low energy electrons. Electrons are generated at a cathode and an electron beam is emitted towards the sample at a voltage of exactly 20 kV. Just before the electrons interact with the sample, the electron velocity is reduced dramatically until the electrons have an energy of the order of 1 to 10 eV. At these low energies the first Born approximation is not valid anymore. Therefore, inelastic scattering and elastic backscattering become more important, while the dominance of forward scattering decreases. Furthermore, at very low energies light atoms backscatter stronger than heavier atoms over a wide energy range. At low energies the dependence of elastic backscattering on nuclear charge is strongly non-monotonic, which is advantageous because this makes it possible to observe light atoms on heavy substrates. Although backscattered electrons in a LEEM are generally scattered elastically, this does not hold for all electrons. There are several mechanisms for inelastic scattering of these electrons. An incident electron still penetrates a finite distance into the solid and therefore may lose some of its energy. Also, at the interface of the sample there are surface states which are different from bulk states. Furthermore, impurities and defects on the surface may also lead to inelastic scattering.

Many inelastic scattering processes involve inner electron shells. However, due to the low energy of the incident electrons it is assumed that incident electrons do not have sufficient energy to interact with the electrons from the inner electron shells of the sample. If there is any inelastic scattering, then it should occur through interaction with the outer shells. Therefore, valence electron excitations determine attenuation by inelastic scattering. At low energies inelastically scattered attenuation is weaker than elastically backscattered attenuation up to a certain threshold energy which is directly related to plasmon excitations. The regime where elastic backscattering dominates over inelastic scattering, typically electron energies up to $20 - 30 \,\mathrm{eV}$, is therefore crucial for doing LEEM experiments.

Instrumentation

What makes a low energy electron microscope special is that it uses a cathode lens as an objective lens and that the incident and imaging beams are separated by a beam separator. In an ideal situation the objective lens and the beam separator would be enough to image samples. However, in reality aberrations and astigmatism affect the quality of the results. The quest to optimize resolution and image quality leads to different setups of the low energy electron microscope. Only the type of low energy electron microscope that has been used in our experiments to study silicene is discussed in this section.

The beam separator of the LEEM operates with 60° deflection as can be seen in Fig. 2.1. Astigmatism and aberrations caused by deflectors are eliminated by realizing equal path lengths in the field and by increasing focusing in the plane normal to the magnetic field. The latter is done by shaping of the magnetic field with inner and outer magnets in the beam separator. Another important component of the LEEM is the objective lens. It produces a virtual image behind the object by a homogeneous electric accelerating field and the magnetic lens produces a real image of the virtual object. Although the aberration of the electric accelerating field has the largest influence on the resolution, the total potential configuration of the lens affects the resolution as well. The optical system is shown in Fig. 2.2. A LaB₆ electron gun generates electrons which travel through the illumination column consisting of three condenser lenses. While the first condenser lens demagnifies the cross-over, the other two condenser lenses and the beam separator





image the cross-over into the back-focal plane of the objective. In the imaging column the transfer lens images the back-focal plane into the center of the field lens, whereas the field lens in turn images the primary image plane into the object plane of the intermediate lens. The intermediate and projective lenses either image the center of the separator or the back-focal plane. From here the electrons move to the channel plates and are targeted at a fluorescent screen.



Figure 2.2: A schematic view of the low energy electron microscope. Image reproduced from Ref. [13]

2.1.2 LEEM experiments on silicene

Bright field low energy electron microscopy (BF-LEEM) is achieved by selecting the specular diffraction spot with the contrast aperture to form a real space image. All real space images in this thesis were recorded in bright field mode.

Image corrections

Images are recorded at the screen of the LEEM which consists of microchannel plates, a fluorescent screen, and a camera. Some microchannel plates differ in thickness from other microchannel plates producing differences in amplification factors. Consequently, contrast gradients occur in the real space images. If the horizontal position of a pixel is given by x and the vertical position of a pixel by y, then the image intensity of a pixel is Im(x, y). This is the intensity that is recorded after an amplification A(x, y) is factorized at the given pixel. Thus the unamplified intensity of a pixel is F(x, y) = Im(x, y)/A(x, y). The image intensity of a featureless image recorded in mirror mode, i.e. electron energy of 0 eV or lower, is equal to A(x, y). This mirror image is used as a reference image and the image intensities of the real space images that are to be corrected, are divided by the intensity of the mirror image. A drawback of this correction is that the visibility of the image noise increases slightly. However, the advantages outweigh the disadvantages. An example of the image correction is shown in Fig. 2.3. One can observe that the intensity gradient has diminished and even the microchannel plate defect (the black area at the bottom of the image) is less prominently present as well.



Figure 2.3: The left image shows an original LEEM image which needs to be corrected. Notice the intensity gradient in the image that is also visible in the mirror image (middle). By dividing the left image by the mirror image a corrected image is retrieved. These images are recorded with a field of view of $4 \,\mu\text{m}$.

Vibrations and thermal drift during LEEM experiments translate the image in the horizontal plane which makes data analysis hard to perform. If the vibrations and thermal drift are however not too large, a correction can be done by automatically finding and tracking correlations between images throughout the whole stack.

Data analysis

Real space images offer physical and chemical information which are also accompanied with different analysis approaches. Area, time, pixel intensity, distance, temperature and electron energy are the quantities that can be measured in low energy electron microscopy. *ImageJ* has been used to analyze data.

2.2 µLEED experiments

2.2.1 Basics

Diffracted electrons leaving the sample are focused on the back-focal plane of the objective, forming a diffraction pattern. This makes it possible to relate real space images recorded in LEEM mode to crystal structure information acquired in LEED mode. An even more advantageous feature is the insertion of an illumination aperture that reduces the diameter of the incident electron beam diameter to $1.4 \,\mu\text{m}$, hence the name μLEED . A great advantage of inserting such an illumination aperture is that, rather than averaging the LEED patterns of many different structures, one measures only on the desired part of the surface where one or two crystalline domains of interest exist, which immediately yields the desired information on that region's crystal structure.

2.2.2 Cumulative µLEED experiments on silicene

 μ LEED has been used to determine the superstructure of silicene on Ag(111). When recording diffraction patterns at one certain start voltage (or electron energy), not all spots are visible simultaneously which causes difficulties in analyzing the diffraction pattern and establishing the symmetry of the superstructures. This was solved by recording LEED patterns at several start voltages and by summing them into one single image via *ImageJ*. A drawback of this approach is that the information in the intensities of the spots is lost and, consequently, a structure factor determination of the superstructures becomes impossible. Luckily, in the experiments performed here, the exact intensity of a spot was not required.

Corrections to reciprocal space images

Most of the diffraction patterns contain backscattered electrons as well as secondary electrons. Secondary electrons are undesired in reciprocal space images. By duplicating the image, applying minimum, maximum and Gaussian filters and dividing the original image by the filtered duplicated image the secondary electron contribution is significantly reduced. After adjusting the contrast and inverting the pixel intensities, a corrected LEED pattern looks like what is shown in Fig. 2.4. Inverting pixel intensities was only performed when it made the information in the image better visible.

2.3 Experimental and sample preparation

2.3.1 Setup

The experimental setup and all crucial parts are depicted in Fig. 2.5. The low energy electron microscope is an ELMITEC LEEM III model. The system is separated into three parts by gate valves: preparation chamber, main chamber and column. All three compartments operate under ultrahigh vacuum conditions to ensure that atomically clean surfaces can be maintained for the duration of an experiment. Also, the lifetime of the microchannel plates and the LaB₆ cathode can be compromised if vacuum levels become too high. The alignment of the complex



Figure 2.4: The left image shows the original image and secondary electrons and on the right hand the corrected and esthetically better image is given. The secondary electrons are strongly visible on the left side of the (0,0) spot.

electron-optical system was done by optimizing the optical system as discussed in Section 2.1.1 under instrumentation.



Figure 2.5: The ELMITEC LEEM III: electron gun (1), beam splitter (2), phosphor screen and camera (3), main chamber (4), preparation chamber (5), illumination aperture (6) and the contrast aperture (7). The silicon evaporator is located beneath the main chamber and it is not visible.

In the preparation chamber the sample is sputtered and annealed. In the main chamber interaction of the sample with the low energy electrons takes place. Several evaporators (of which one for silicon) are present in the main chamber, ready for deposition experiments. The main chamber also allows for control over sample temperature. Finally, the column is the part where the optics manipulate take place.

In PEEM mode light coming in from a mercury discharge UV-lamp generates electrons through photoemission. Silver has a low work function and is therefore an excellent material for photoemission electron microscopy making alignment more convenient since it does not involve an incident electron beam.

2.3.2 Sample preparation

The Ag(111) substrate was purchased from Surface Preparation Laboratory and mounted on a sample holder. The sample was put in the preparation chamber where it was sputtered and annealed took place. Sputtering was performed at 10^{-5} mbar with 1000 eV Ar^+ ions for 30 min. The sample was then annealed for eight minutes at $650 \,^{\circ}\text{C}$ immediately after sputtering. These cycles were repeated until a clean Ag(111) substrate was observed as depicted in Figs. 2.4 and 2.6. The real space image shows large terraces without defects and thus it is regarded as clean.



Figure 2.6: A clean Ag(111) surface as viewed by LEEM within a field of view of 4 µm. Terraces are large and no significantly defects are observed on the surface.

The sample is then transferred into the main chamber where a silicon evaporator (operated at approximately 1100 °C) is mounted. After the deposition experiments the sample was sputtered and annealed as preparation for consecutive experiments.

Chapter 3

Results and Discussion

3.1 Coverage

To get a general impression of how the growth dynamics of silicene proceeds, a long run of silicon evaporation was performed to measure how the area fraction of silicene develops with time and visualize the various phases that form. Our observations are summarized by a serie of LEEM images that is shown in Fig. 3.1. The Si evaporator reaches its deposition temperature at t = 0 s, marking the beginning of Si deposition on the Ag(111). Initially, the LEEM images show only a flat surface with steps, but no other structural features, see Fig. 3.1(a). The only measurable change that occurs in this early stage of the deposition is a slow, but gradual decrease in the reflected intensity from the Ag surface, hinting at the formation of a dilute background density of silicon adatoms that act as diffuse scatterers. After 70 s an initial layer of Si starts, as shown in panel (b). We presume this layer to be one of the various forms of silicene that was observed in other experiments [2, 6]. Islands nucleate randomly on the surface, both on terraces and at steps. Over time the islands expand and coalesce, as is shown in panels (c)-(e). In contrast to a conventional nucleation and growth type experiment, where a second layer of the deposited material nucleates on top of the first layer, something surprising happens. There is no nucleation of a second layer, but instead, the almost closed initial layer converts into a different structure that covers a much smaller fraction of the surface than the initial layer. The conversion is imaged in panels (f-h) of Fig. 3.1. The same bright intensity level that was previously observed for the bare Ag(111) reappears in the areas around the nuclei of the newly formed structure and expands outwards until a relatively small fraction of the surface is covered with domains consisting of the second phase. The latter observation hints that this second structural phase of Si on Ag(111)is of a three-dimensional nature since the material that was deposited to form the initial layer is now confined to a much smaller projected area of the surface. Field distortions that occur around these features and that can be made visible when the current of the objective lens of the instrument is varied also hint that the second phase that forms has a three-dimensional character. A similar series of observations is plotted in Fig. 3.2, albeit that the LEEM images were recorded using a smaller field of view to allow for a more detailed observation of the nucleation and growth process.

LEEM images like those shown in Figs. 3.1 and 3.2 were analyzed and the area fraction covered by the Si phases was measured. This was achieved with a simple thresholding analysis using *ImageJ*. First, the grey levels of the Ag substrate and the initial layer were determined. A threshold that is approximately equal to the mean of these two values was used to segment the



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Figure 3.1: Snapshots of silicon deposition on Ag(111). FOV = 10 µm. t = 0 s (a), 178 s (b), 564 s (c), 838 s (d), 1018 s (e), 1092 s (f), 1202 s (g) and 1382 s (h). A defect is to be found in the lower left corner. The deposition starts off with a clean Ag(111) substrate (a). Deposition starts and small islands of silicene form on the surface (b,c,d). These islands are sp^2 hybridized. The area percentage of silicene increases as the deposition continues and it reaches a maximum at $86 \pm 1.5\%$ (e). Beyond this point silicon atoms tend to agglomerate on top of the silicene monolayer, thereby initiating a clustering of silicon atoms to form three dimensional structures.



Figure 3.2: Snapshots of silicon deposition on Ag(111). FOV = $2 \mu m$. t = 0 s (a), 76 s (b), 256 s (c), 376 s (d), 460 s (e) and 628 s (f). For a detailed description of the observation, please refer to Fig. 3.1. The area percentages in panels b and d are 96.5% and 12.7% respectively.

recorded images into a binary image. The fraction of the image occupied by the Ag and Si phases was then measured as a function of time. The measured area fraction is plotted in Fig. 3.3.



Figure 3.3: Area percentage versus time. The area percentage of silicene does not reach 100% which demonstrates it is not possible to entirely cover a surface with silicene. Silicene islands start to appear after approximately 70 seconds. Afterwards a linear increase of $1.025 \cdot 10^{-3} s^{-1}$ is observed until the maximum of 95.7% is reached.

It shows an initial amount of dead time, where nothing apparent happens, corresponding to the period in which the diffusely scattered intensity from the surface increases. After this period a linear increase in area fraction is observed. This is the period in which the domains of the initial layer nucleate and grow out towards a full coverage. Full coverage is however never reached. We observe that the graph peaks at a value of 95.7% and then continues with a steady and rapid decline, corresponding to the conversion of the initial layer into the second phase. The maximum and final value of another deposition experiment with a smaller field of view shown in Fig. 3.2 were measured to be 96.7% and 12.7% respectively. The ratio between this value and the peak value of 96.5/12.7 = 7.6 provides a solid indication of the three-dimensional nature of the second phase.

3.2 Structure determination

3.2.1 Structure of the initial silicene layer at 280 °C

To analyze the structure of the initial silicene layer that forms, a deposition of silicon was performed and the deposition was aborted prior to the conversion to the second phase. The sample temperature was held constant at a temperature of approximately $280 \,^{\circ}$ C. µLEED images on the initial layer were recorded by ramping the electron energy from 1 eV to 42 eV in steps of 0.1 eV. These images were accumulated into the pattern that is shown in Fig. 3.4. Recording these types of cumulative LEED patterns rather than recording an individual pattern at one fixed energy gives us the certainty that we have visualized all spots and can establish the symmetry and structure of the phase that is being investigated.



Figure 3.4: Approximately 300 images were accumulated to one LEED pattern to visualize every spot. A $2\sqrt{3} \times 2\sqrt{3} R 30^{\circ}$ superstructure. Spot splitting is observed for several spots due to scattering by silver atoms that are exposed in the center of the silicene rings, and which are at a lower level than the silicene [14].

To define the superstructure *LEEDpat30* simulations were performed. The results are shown in Fig. 3.5. The measured structure corresponds to the commensurate $2\sqrt{3} \times 2\sqrt{3} R 30^{\circ}$ phase, which is written in matrix notation as

$$\left(\begin{array}{cc}4&2\\2&4\end{array}\right)$$

Thus, the initial layer is an sp^2 hybridized form of silicon, or silicene. Although the measured LEED image shows similarities with the calculated LEED pattern, double spots do not appear in the simulated LEED pattern. Figure 3.4 is the sum of many reciprocal space images recorded at different energies. The energy dependence of the LEED patterns contains the explanation for



Figure 3.5: On the left a simulation of the real space unit cell is given. Red dots visualize silicon atoms and red lines form the unit vectors of the silicene unit cell. The gray lines are the unit vectors of the Ag(111) unit cell. On the right a simulated reciprocal space image of the $2\sqrt{3} \times 2\sqrt{3} R 30^{\circ}$ superstructure on Ag(111) is given.

the double spots. When the electron energy is ramped, one spot of a spot pair is dominant over the other, as is shown in Fig. 3.6. The real space lattice of the $2\sqrt{3} \times 2\sqrt{3} R 30^{\circ}$ superstructure



Figure 3.6: Two examples of LEED patterns are given. The yellow lines are pointing out the dominant spots whereas the red lines point out the weakest spot. These images were recorded at electron energies of $16.0 \,\mathrm{eV}$ (a) and $18.1 \,\mathrm{eV}$ (b). This image has not been corrected to avoid the intensities from becoming corrupted.

on Ag(111) is given in Fig. 3.7, indicating the positions of all the individual atoms that make up the structure. Jamgotchian et al. found a -10.9° rotation of a flat silicene layer relative to the silver substrate [6]. If the occurrence of double spots was caused by different rotational domains, the further one would move away from the specular reflection, the more the spots pairs would be split. The splitting remains identical in the cumulative LEED pattern, indicating that the rotation does not contribute (significantly) to the splitting of the spots. Silver atoms are stronger scatterers than silicon and from Fig. 3.7 one can see comparatively large open areas where silver atoms are exposed to incident electrons. Consequently, reflected beams from the silver and silicene can interfere with each other. This results in constructive and destructive interferences at certain energies and an alternating on-off behaviour of the spots that make up a spot pair [14]. The relaxed lattice parameter is deduced from Fig. 3.8 as

$$a = \frac{4}{3} \cdot \frac{4.09}{\sqrt{2}} = 3.856 \text{\AA}$$

This is in agreement with the results of Behera et al. [15]. Furthermore, most of the silicon atoms are not on top of high-symmetry Ag positions, which hints at a weak coupling between silicene and the Ag(111) substrate (see Figs. 3.7 and 3.8).



Figure 3.7: Model of a $2\sqrt{3} \times 2\sqrt{3} R 30^{\circ}$ silicene superstructure on Ag(111). Image reproduced from [6].



Figure 3.8: Real space model of one of the six domains of a $2\sqrt{3} \times 2\sqrt{3} R 30^{\circ}$ overlayer structure.

3.2.2 sp^2 hybridized silicene at 256 °C

In another experiment the deposition of Si was again aborted prior to the conversion of the initial sp^2 hybridized silicene layer and LEED patterns were recorded at a constant temperature of 256 °C. Unfortunately, during this experiment no cumulative LEED patterns could be recorded, leading to a less reliable structure determination. The measured LEED pattern is shown in Fig. 3.9 and includes domains of the following phases: 4×4 , $2\sqrt{3} \times 2\sqrt{3}R 30^{\circ}$ and $\sqrt{13} \times \sqrt{13}R 13.9^{\circ}$. Comparing Figs. 3.4 and 3.9 with Figs. 1.3 (c) and (d), the temperature dependence of the structure of silicene found by Jamgotchian et al. [6] is confirmed.



Figure 3.9: a LEED image recorded at 256.6 °C with an electron energy of 30.6 V. A mix of the phases 4×4 , $2\sqrt{3} \times 2\sqrt{3} R 30^{\circ}$ and $\sqrt{13} \times \sqrt{13} R 13.9^{\circ}$ is observed.

3.2.3 Structure of the converted layer

The conversion of the silicene layer that is visible in the later stages of Figs. 3.1 and 3.2 can be induced by depositing Si in excess of 1 ML, but can also be induced by annealing the silicene to a higher temperature. This was done in another experiment where the surface was first approximately half covered with silicene. Temperature was then increased to a value of 356 °C and the evolution of the silicene domain pattern was monitored with LEEM. Figure 3.10 shows the image sequence that was recorded. In the initial structure, the nucleus of a new phase forms. Around this new nucleus the silicene domains disappear rapidly, whilst the new nucleus expands at a very modest rate, remaining relatively small in the process. Figure 3.10(f) shows that eventually the surface is depleted from all silicene domains, and only the small nuclei that formed during the conversion process are left. After the conversion has completed, a slow decay of the new structure with time is observed. The first impression one gets is a phase transition from sp^2 to a three dimensional silicon structure. To analyze the structure of these features, a nucleus of silicon that is similar to the one that is seen in Fig. 3.10(f) was analyzed with µLEED to determine its structure. The analyzed region is shown in Fig. 3.11. To perform the LEED measurement the temperature of the sample was reduced to room temperature, otherwise the three dimensional silicon structure would evaporate and/or intercalate. The µLEED pattern is given in Fig. 3.12 where the double spots that are visible in the pattern are now due to a rotation of the silicon overlayer structure relative to the substrate. The rotation angle is approximately 10.9°. A $\frac{1}{2}\sqrt{21} \times \frac{1}{2}\sqrt{21} R 10.9^\circ$ was found and confirmed by simulations as given in Fig. 3.13. In matrix notation the structure is approximately given by

$$\left(\begin{array}{cc} 2.00 & 0.500 \\ -0.500 & 2.50 \end{array}\right)$$



Figure 3.10: Conversion of the sp² hybridized layer at $T = 356 \pm 4$ °C. FOV = 4 µm. t = 0 s (a), 20 s (b), 38 s (c), 58 s (d), 78 s (e) and 88 s (f). Darker domains in panel (a) are sp^2 hybridized silicene. The silicene layer converts into another phase that first forms at a point at the center of the region that is highlighted by a yellow line. A similar region develops in the left of the image, with the nucleus being just outside the field of view.

The area of the unit cell is calculated by evaluating the determinant of the superstructure matrix, which is 5.25 ML. If the number of atoms in a unit cell is defined as M, the unit cell area of the three dimensional silicon structure is 5.25/M. In case M is equal to three, as it is in Fig. 3.14, the area of the unit cell is computed as 1.75. This value is very close to

$$\left(\frac{a_{Si}}{a_{Ag}}\right)^2 = \left(\frac{5.431}{4.090}\right)^2 = 1.763$$

where a_{Si} and a_{Ag} are the bulk lattice parameters of silicon and silver. The area of the unit



Figure 3.11: The aperture for μ LEED measurements was placed on the yellow circle containing a three dimensional silicon structure.



Figure 3.12: A LEED pattern of the three dimensional silicon structure. A $\frac{1}{2}\sqrt{21} \times \frac{1}{2}\sqrt{21} R 10.9^{\circ}$ phase with double spots was observed.

cell deviates only 0.74% from 1.763 which we take as evidence for the formation of a bulk silicon structure that is sp^3 hybridized on top of silver. Even more evidence of this transition from sp^2 to sp^3 hybridized silicene can be provided by comparing the fraction of substrate that is covered by silicon in Figs. 3.2(b) and (f), as was already done in Section 3.1. There we calculated that the ratio of these areas was 7.6, indicating that the sp^3 hybridized silicon consists of at least 7.6 layers. In literature, we found Arafune et al. [2] claiming that the converted layer exhibits



Figure 3.13: Simulated real space lattice (left) and reciprocal space lattice (right) of a $\frac{1}{2}\sqrt{21} \times \frac{1}{2}\sqrt{21}$ phase rotated 11° relative to the substrate. In the left picture the red dots are silicon atoms and the red lines visualize the unit vectors of the silicon structure. The gray lines represent the unit vectors vectors of the substrate. On the right the two possible rotational domains are indicated with different colors.

a $4/\sqrt{3} \times 4/\sqrt{3}$ phase corresponding to a bilayer of silicene. Although, a $4/\sqrt{3} \times 4/\sqrt{3}$ phase indeed resembles a $\frac{1}{2}\sqrt{21} \times \frac{1}{2}\sqrt{21} R 10.9^{\circ}$ phase, they are definitely not the same. Furthermore, we did not find a bilayer of silicene, but rather a sp^3 hybridized structure.

Finally, the last variable that we have not investigated is the positioning of the superstructure with respect to the substrate. Fig. 3.14 shows that two out of three atoms in the unit cell can be positioned in a threefold coordinated on-top site, while the other atom is located on a twofold coordinated bridge site. This arrangement of the atoms is not a coincidence since it gives strong coupling with the substrate, which is needed to saturate the otherwise dangling bonds of the silicon structure. In conclusion, the three dimensional structure that has been found corresponds to sp^3 hybridized silicon and thus a transition from sp^2 hybridized silicon (silicene) to sp^3 hybridized silicon was observed.

3.3 Nucleation and growth

3.3.1 Deposition rate

A quantitative evaluation of the growth process requires knowledge of the amount of silicon that is present on the surface at any moment in time. The deposition rate of silicon was determined by finding the superstructure symmetry and coverage using µLEED, and using this information to express the area percentage increase over time in a Si coverage. The latter was found in a similar way as in Section 3.1. The area fraction increases $1.025 \cdot 10^{-3} s^{-1}$. This value was found by least-squares fitting a line to the data shown in Fig. 3.3. The superstructure phase exhibiting on top of the substrate was $2\sqrt{3} \times 2\sqrt{3}R 30^{\circ}$ as stated in Section 3.2.1. The overlayer structure is given by

$$\left(\begin{array}{cc}4&2\\2&4\end{array}\right)$$



Figure 3.14: A $\frac{1}{2}\sqrt{21} \times \frac{1}{2}\sqrt{21}$ superstructure rotated 10.9 ° relative to the substrate. Red dots are the centers of silicon unit cells and the red lines visualize the bases of the silicon structure. The blue lines represent the base vectors of the substrate.

The deposition rate is then calculated by

$$d = \frac{N\tau}{\Pi A_{Si}} = \frac{14 \cdot 1.025 \cdot 10^{-3} \, (s^{-1})}{12 \cdot 2.007 \, (nm^2)} = 5.96 \cdot 10^{-4} nm^{-2} s^{-1} \tag{3.1}$$

Here, d is the deposition rate (number of adatoms / nm²), τ is the increase in area percentage in time obtained from Fig. 3.3. N is the number of atoms in one unit cell of silicene, which is 14 as found in Section 3.2.1. The determinant of the overlayer structure matrix is given by Π . A_{Si} is the area of a silicene unit cell, which is $(2\sqrt{3})^2$ times the unit cell area of Ag(111) with a lattice parameter of 4.090 Å.

3.3.2 Chemical potential

With the deposition rate determined the chemical potential of silicene was evaluated via intensity versus time measurements. When the first deposition of silicon started, no silicene islands were visible until after approximately 70 seconds of deposition. During this time period the intensity of the Ag(111) substrate changes due to diffuse scattering. The intensity versus time measurement is depicted in Fig. 3.15(a). By multiplying Eq. 3.1 with time, the intensity is plotted versus the density of silicon adatoms per square nanometer as shown in Fig. 3.15(b). The intensity is then calibrated with respect to the density of adatoms by a simple linear fit as done in Fig. 3.15(b). Combining this calibration with data from Fig. 3.15(a) enables plotting density versus time as in Fig. 3.15(c). From this plot the maximum chemical potential difference during nucleation can be evaluated by using Eq. 3.2.

$$\Delta \mu = kT \ln \frac{\Theta_{max}}{\Theta_{eq}} \tag{3.2}$$

Here k is the Boltzmann constant which is $8.617 \cdot 10^{-2} \text{ meV K}^{-1}$. T is the temperature (273 °C or 546 K). The quantities $\Theta_{max} (0.0347 \,\mathrm{nm}^{-2})$ and $\Theta_{eq} (0.0258 \,\mathrm{nm}^{-2})$ correspond with the maximum density Θ_{max} and the saturation/equilibrium density Θ_{eq} found in Fig. 3.15(c). Equation 3.2 is applicable if the dilute phase is assumed to be an ideal two dimensional monatomic gas [16]. Using these values in Eq. 3.2 leads to a chemical potential $\Delta \mu$ of 13.9 meV. To compare, in another experiment performed with the same LEEM used in our experiment, 4,4'biphenyldicarboxylic acid (BDA) molecules were deposited on Cu(001) and a supersaturation of 6 meV was found for nucleation [16]. The supersaturation that is needed to achieve nucleation roughly provides a measure for the energetic stability of the structure that forms. The higher the supersaturation, the lower the energetic stability of the phase that forms. Silicene is a relatively unfavorable configuration of silicon. Therefore, because of its lower coordination in the sp^2 hybridized states, the fact that the required supersaturation is twice as high need not be surprising. Repeating the experiment at different temperatures would open the doors to a rich field of thermodynamical analysis. According to Eq. 3.2 decreasing the temperature results in a linearly decreasing chemical potential difference i.e. supersaturation and thus, in principle, reduces the time needed to form silicene. An interesting analysis would then be to compute supersaturation levels versus the superstructure symmetries in a phase diagram.

3.4 sp^2 to sp^3 kinetics and energetics

3.4.1 Origin of kinetics

Figure 3.10 shows that the conversion from sp^2 to sp^3 hybridized silicon on Ag(111) occurs in a very peculiar fashion. Once the conversion temperature has been reached, silicene islands $(sp^2$ hybridized) shrink in area at the expense of a three dimensional silicon object as can be seen in Fig. 3.10. The growth in area of a denuded zone around the sp^3 hybridized silicon was measured by drawing manually a circumference around the zone using *ImageJ* resulting in an area versus time plot given in Fig. 3.16. Circumference examples are shown in Figs. 3.10(b,c). Figure 3.16 shows that the area of the denuded zone increases linearly in time. Analogously one may say that the silicene area decreases linearly in time indicating interface limited kinetics [17]. Another analysis that has been performed concerning the kinetics of the system is an intensity versus distance measurement as shown in Fig. 3.17. Clearly a concentration gradient is observed even if the microchannel plate inaccuracy is included in the analysis. At first sight the presence of a concentration gradient, i.e. diffusion limited kinetics, would contradict the observation of interface limited kinetics. Experimentally we were not able to determine the type of kinetics. Therefore, arguments in favor of each case are discussed.

Interface limited kinetics

In order to understand this contradiction Ostwald ripening of islands must be considered. Ostwald ripening occurs when different sized particles exhibit different Gibbs-Thomson chemical potentials. The Gibbs-Thomson equation is given in Eq. 3.3.

$$\rho = \rho_{\infty} e^{2\Omega\gamma/R} \tag{3.3}$$

Here, R is the curvature radius, where Ω is the atomic size and γ is the line tension. Different islands in Fig. 3.10 with different line tensions result in different Gibbs-Thomson equations. The two other quantities stand for vapor pressures at a curved interface of radius R (ρ) and at a flat interface (ρ_{∞}). If assumed the three dimensional object is sp^3 hybridized, then the sp^3 hybridized silicon structure has one more chemical bond than sp^2 hybridized silicon (silicene)



Figure 3.15: From t = 0 s to 46 s the system is as a lattice gas. In between t = 46 s and 70 s supersaturation and nucleation take place. From t = 70 s and on the system is in equilibrium (a,c). From the calibration of intensity with the density of adatoms (b) a density of adatoms vs time graph was plotted containing the Θ_{max} (0.0347 nm⁻²) and Θ_{eq} (0.0258 nm⁻²) (c).



Figure 3.16: The area of a denuded zone plotted versus time.

and therefore, the sp^3 hybridized silicon structures will coarsen at the expense of silicene islands. Now different islands have different ρ_{∞} and, consequently, will have different Gibbs-Thomson equations. Eventually, the Gibbs-Thomson equation varies in two ways, namely through ρ_{∞} and γ . The variation causes a huge mass flow of silicon occurs during the conversion, leading to a concentration gradient. The observation of a concentration gradient implies that the system is far out of thermal equilibrium and makes the claim of having interface limited kinetics valid.

Diffusion limited kinetics

In the diffusion limited case the graph would show a $A \propto t^{2/3}$ characteristic. From Fig. 3.10 it can be seen that the denuded zone was rapidly growing too large. Already in Fig. 3.10d it was not possible anymore to measure the area of the denuded zone, while at that time silicene islands were still significantly present on the surface, leading to a lack in area measurements during the last phases of the disappearance of silicene islands. Figure 3.18 gives an example of a (A,t)-diagram from another diffusion limited system, Cu on Cu(111). If the last phase of the experiment is not measured, one might interpret it as a linear function. The concentration gradient as seen in Fig. 3.17 provides evidence for diffusion limited kinetics, thus a $A \propto t^{2/3}$ should be present in the (A,t) diagram after an extrapolation.

3.4.2 Activation energy

Calculating an activation energy from a decay curve is strictly speaking only valid in a diffusion limited case [17]. The area of the denuded zones versus time was measured as a function of temperature (Fig. 3.19). Unlike the experiment performed in the previous section, the temperature



Figure 3.17: Intensity versus distance measurements on the given arrows were recorded (a). Panel (b) shows that the intensity of the lines increase towards the center of the denuded zones. The intensity change indicates the presence of a concentration gradient, which substantiates the evidence of having diffusion limited kinetics.



Figure 3.18: An example of a (A,t)-diagram from a diffusion limited system. Image reproduced from [18].

was ramped. During this experiment the initial temperature was 301.0 °C whereas the final temperature was 338.8 °C. The results of the area versus time measurements and fitting are given in Fig. 3.20(a). We assume thermally activated diffusion and hence an exponential fit has been used.

$$A(t) = c_1 e^{c_2 t}$$

After finding the parameters c_1 and c_2 this equation was differentiated with respect to time to measure the rate of change of the area of the denuded zone.

$$\frac{dA(t)}{dt} = c_1 c_2 e^{c_2 t}$$

Since the temperature is known at each specific time a (dA(t)/dt, 1/T)-diagram was created with a logarithmic vertical axis as shown in Fig. 3.20(b). The activation energy E is found by evaluating the slope of Fig. 3.20(b):

$$\frac{dA(t)}{dt} \propto D_0 e^{-\frac{E}{kT}} \Longleftrightarrow \ln \frac{dA(t)}{dt} \propto \ln D_0 - \frac{E}{kT}$$

The slope is found to be $-9.38 \cdot 10^3$ and with

$$-9.38 \cdot 10^3 = -\frac{E}{k}$$

the activation energy was found as 0.81 ± 0.10 eV. The error margin is high due to the non-zero curvature in Fig. 3.20(b). Large thermal drifts are present in the system and together with the microchannel plate inaccuracy defining the denuded zone border is difficult. Diffusion of single (heavy metal) atoms on (111) surfaces exhibit higher activation energies than diffusion of single atoms on lower indexed surfaces [19]. The activation energy for Si on W(110) was found to be 0.70 eV [20], which is close to our result. Silicon has four valence electrons that are eager to form bindings with the substrate. In a (111) substrate, such as our Ag(111) substrate, three valence

electrons can strongly bind to the substrate at the three-fold sites on the substrate. Therefore, the activation energy for diffusion of silicon on Ag(111) is expected to be higher than for Si on W(110).



Figure 3.19: Measuring the area of denuded zones at different times and temperatures within a field of view of 20 µm at t = 0 s, T = 308.3 °C (a), t = 66 s, T = 329.9 °C (b), t = 140 s, T = 344.7 °C (c) and t = 220 s, T = 353.8 °C (d). The area was not measured after the denuded zones merged with each other.



Figure 3.20: Area versus time at different temperatures (a) and the $(dA(t)/dt, \frac{1}{T})$ -diagram (b).

Chapter 4

Future work

4.1 Systematic and experimental improvements

After finishing the silicene experiment the vacuum system of the low energy electron microscope underwent a transformation which resulted in less vibrations and thus reduction of noise. Furthermore, during the silicene experiment intensity corrections of LEEM images were not optimized. By recording mirror images consistently, intensity measurements should become more accurate.

4.2 Silicon evaporation and/or intercalation?

In Fig. 3.10 silicene islands break up and get consumed by sp^3 hybridized silicon structures. Annealing the sp^3 hybridized silicon covered sample initiated the silicon structures to disappear. There are two possible processes that may occur during annealing of the sample. The silicon object may evaporate and/or it may penetrate into the bulk (intercalation). If the latter is true, this phenomenon might be observed by measuring IV curves (Intensity versus Voltage) to establish the local work function. After a new silver sample is ordered, i.e. there is no deposition history, the intensity on a clean Ag(111) should be measured at different electron energies ranging from -3 to 10 eV in steps of 0.1 eV. Up to a specific electron energy that corresponds to the work function, the intensity is high and constant. At this specific electron energy the intensity decreases dramatically and remains low with variations depending on the sample. The same process must be performed after a deposition and anneal cycle. A change in the IV curve would indicate silicon accumulation in the near-surface bulk. This experiment will be accompanied by a cumulative µLEED experiment before and after the cycle. Additional spots after the cycle would also indicate silicon accumulation in the near-surface bulk. At the moment we expect this effect to be present since we observed roughening of the clean Ag(111) surface after each deposition and anneal cycle.

4.3 Additional µLEED measurements

On three dimensional structures

Figures 3.1 and 3.2 show that after the maximum area percentage is reached sp^3 hybridized structures occur. Unlike the three dimensional structure appearing during annealing as in Fig. 3.10 no μ LEED measurements were performed on sp^3 hybridized structures during excessive deposition. We would like to see if the structures after excessive deposition are similar to the structures during annealing. While reproducing the experiment, the area percentage versus time analysis will be redone to determine if the maximum area fraction is constant.

On the $2\sqrt{3} \times 2\sqrt{3} R 30^{\circ}$ superstructure

In Section 3.2.1 Bragg's law concerning the double spots was mentioned implicitly. For reasons still unknown the data of electron energies got corrupted. In a future experiment emphasis on measuring the electron energy will be put in order to determine the height of silicene relative to the silver substrate.

4.4 Determination of the kinetics and activation energy

Repeating the experiment mentioned in Section 3.4 with a larger field of view and less temperature increment should result in a sufficient number of data points in order to determine the origin of kinetics by merely the (A,t)-diagram. If the experiment would result in a diffusion limited kinetic process, then we can conclude that the calculation of the activation energy is legit. Furthermore, the activation energy is expected to be more accurate.

4.5 Variable temperatures

The experiment will be performed at variable temperatures in order to observe different overlayer structures and to see how the overlayer structures affect surface topography quantitatively. During the experiment a phase transition from sp^2 to sp^3 hybridizations was observed. An interesting experiment would be to reproduce phase transitions at different temperatures and to measure the period of time until the phase transition occurs. Additionally, the temperature dependence of the maximum area percentage can be monitored. Furthermore, evaluating the chemical potential at different temperatures would lead to thermodynamical analysis of the system as mentioned in Section 3.3.2.

4.6 Far future work on LEEM

Silicene exhibits similar or exotic properties as graphene, but what makes silicene interesting and promising for the semiconductor industry is that silicene has a band gap. However, we have showed in Fig. 3.3 silicene is not able to entirely cover a surface and this would prevent the semiconductor industry from using silicene. Experiments with surface modifications of the Ag(111) substrate could be performed to see how the modification affects the maximum coverage. Furthermore, a methodical search for other substrates might also deliver a solution to this problem.

Chapter 5 Conclusion

The growth of two dimensional sp^2 hybridized silicon structures, called silicene, on Ag(111) was studied with the low energy electron microscope and complemented with low energy electron diffraction experiments. With the latter technique various structures of silicene on Ag(111) were observed, depending on the sample temperature and coverage. At 280 °C a $2\sqrt{3} \times 2\sqrt{3} R 30^{\circ}$ silicene superstructure was found and at 256 °C a mix of 4×4 , $2\sqrt{3} \times 2\sqrt{3} R 30^{\circ}$ and $\sqrt{13} \times \sqrt{13} R 13.9^{\circ}$ silicene superstructures were found. Combined LEEM and µLEED experiments showed that after annealing or excessive deposition a phase transition from sp^2 hybridized silicon to sp^3 hybridized silicon took place. The transition occurred before the surface was entirely covered with silicene. Furthermore, the chemical potential difference (13.9 meV) of silicene on Ag(111) was measured, indicating silicene is a relatively unfavorable configuration of silicon. The kinetics that occur during annealing of silicene islands could not be fully classified. Future experiments should reveal whether the kinetics are diffusion limited or interface limited. In general, since the conversion of silicene into sp^3 hybridized bulk silicon-like structures appears inevitable when attempting to form a fully closed layer of silicene, a wider adoption of silicene in the semiconductor industry seems rather unlikely, unless other silicene-substrates combinations can be found that yield more favorable nucleation and growth kinetics.

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