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Abstract

We successfully produced amorphous carbon (a-C) samples of nm and Å thickness by magnetron sputtering. Atomically resolved annular dark-field (ADF) imaging of monolayer patches of the Å-thin sample shows random polygons and suggests layered growth which would lead to predominantly sp^2 bonding. We performed fluctuation electron microscopy (FEM) on a-C samples with both thicknesses. The results suggest a significantly shorter correlation length scale in the Å-thin sample compared to the nm-thin sample and a graphite-like structure without a high proportion of hexagonal rings. We also compared our results to results obtained on nm-thin a-C found in commercial "Quantifoil" transmission electron microscopy (TEM) grids and to simulated data on recent structural models of a-C formed with different deposition energies. While we found reasonable correspondence with the experimental data, the correspondence with any of the models was at best mediocre. Additionally, combining FEM and ptychography for gaining both global statistical and local atomically resolved information was begun to be explored as a first step showing the robustness of FEM against oversampling.

Kurzzusammenfassung

Wir haben erfolgreich amorphe Kohlenstoff (a-C)-Proben mit Dicken im Bereich von nm und Å durch Magnetron-Sputtern hergestellt. Atomar aufgelöste annular dark-field (ADF) Abbildungen von Monolagen-Patches der Å-dünnen Probe zeigen zufällige Polygone und legen nahe, dass schichtweises Wachstum stattgefunden hat, was auf ein Vorwiegen von sp^2 -Bindungen hindeutet. Wir führten Fluktuationselektronenmikroskopie (FEM) an a-C-Proben beider Dicken durch. Die Ergebnisse deuten auf eine deutlich kürzere Korrelationslängenskala in der Å-dünnen Probe im Vergleich zur nm-dünnen Probe hin und auf eine graphitähnliche Struktur ohne einen hohen Anteil an hexagonalen Ringen. Wir verglichen unsere Ergebnisse auch mit Ergebnissen, die an Å-dünnen a-C-Proben in kommerziellen "Quantifoil" Transmissionselektronenmikroskop (TEM)-Gittern gefunden wurden, sowie mit simulierten Daten zu aktuellen Strukturmodellen von a-C, die mit unterschiedlichen Depositionsenergien gebildet wurden. Während wir eine näherungsweise Übereinstimmung mit den experimentellen Daten fanden, war die Übereinstimmung mit den Modellen gering. Darüber hinaus wurde begonnen, die Möglichkeit einer Kombination von FEM und Ptychographie zu erforschen, um sowohl globale statistische als auch lokal atomar aufgelöste Informationen zu erhalten, indem als erster Schritt die Robustheit von FEM gegenüber Oversampling gezeigt wurde.

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EM electron microscopy

- TEM transmission electron microscopy
- **STEM** scanning transmission electron microscopy
- **EELS** electron energy loss spectroscopy
- FEM fluctuation electron microscopy
- AFM atomic force microscopy
- **PDF** pair distribution function
- **RDF** radial distribution function
- **DP** diffraction pattern
- SRO short-range order
- MRO medium-range order
- LRO long-range order
- 1D one-dimensional
- 2D two-dimensional
- 3D three-dimensional
- 4D four-dimensional
- vdW van-der-Waals
- C carbon
- **a-C** amorphous carbon
- Si silicon
- a-Si amorphous silicon
- NaCl sodium chloride
- **IPA** isopropanol
- UHV ultra-high vacuum

- c-FEG cold field-emission gun
- VOA virtual objective aperture
- OL objective lens
- BF bright-field
- DF dark-field
- ADF annular dark-field
- MAADF medium-angle annular dark field
- HAADF high-angle annular dark field
- CCD charge-coupled device
- **APS** monolithic active pixel sensors
- **PAD** hybrid pixel array detector
- **PVD** physical vapor deposition
- MFC mass flow controller
- DC direct current
- FOV field of view
- SNR signal-to-noise ratio
- ML machine learning

Chapter 1

Introduction

1.1 Structure of amorphous materials

"Amorphous" means "without form". However, amorphous materials are not completely without form or order. In crystals, defects result in many of their interesting properties. Likewise, in amorphous materials, it is their order or structure [1].

Per definition, there exists no long-range order in amorphous materials. Still, in solids atom positions cannot be truly random, as two atoms cannot be much closer than a typical bonding distance. Due to these constraints significant short-range order (SRO), i.e., order within a distance of a few bond lengths, occurs [2, 3]. Amorphous materials can also possess medium-range order (MRO), which occurs on length scales of 0.5 - 3 nm [4, 5].

The structure of an amorphous material can vary massively depending on preparation parameters. This is especially true for a-C [6], which is the main material of interest in this thesis. For tuning properties to specific demands it would be very useful to understand the structure and how it is correlated with the properties.

1.2 Challenges in direct imaging of amorphous materials

Imaging of thin crystalline materials at atomic resolution via aberration-corrected scanning transmission electron microscopy (STEM) has become a straightforward task and hence crystalline materials are well studied. However, imaging thin amorphous materials is not as straight-forward. In trying to extract information about the structure of amorphous materials from images, one encounters several obstacles. For example, the signal of the atoms may be hardly distinguishable from that of the background because the coherent diffraction signal is weak and easily lost in the background [2]. One might even be tricked by pattern recognition artifacts to interpret structure where there is no structural information [2]. Another problem is that TEM and STEM images are two-dimensional (2D) projections, so information concerning the *z*-coordinates of the atoms is lost. Therefore, for amorphous materials with more than one atomic layer and without the regularity of atomic columns, projection images leave considerable ambiguity concerning the three-dimensional (3D) structure [4]. Additionally, amorphous allotropes are prone to electron beam-induced structural changes or even crystallization under the beam [7].

1.3 Study of the structure of amorphous materials

With state-of-the-art aberration-corrected STEM and for monolayer amorphous materials, it is possible to perform direct imaging and subsequently analyze the ring size distribution [8]. This is however not possible for multiple atomic layers. For acquiring information about the structure of thicker amorphous 2D materials the two main methods are pair distribution function (PDF) analysis and FEM.

PDF analysis can be based on electron-, X-ray- or neutron-diffraction data and gives statistical information on coordination number and average bond length [9]. It allows quantifying SRO because in the PDF the nearest-neighbor peak typically appears sharp and well-defined. The other peaks however quickly broaden out, so that beyond atom pair separations of 1 nm there is little correlation detectable, rendering the detection of MRO infeasible [2].

FEM is a hybrid diffraction-imaging technique that extracts information about the MRO in amorphous materials by statistical analysis of intensity variations in images or diffraction patterns. It is sensitive to not only pair-correlations but also pair-pair correlations. Also FEM can be performed in electron microscopes, X-ray, or light microscopes [2].

1.4 What is contributed to the topic by this work

This project is aimed at exploring how much and which information can be obtained from the structure of few- and mono-layer amorphous samples, specifically amorphous carbon and amorphous silicon, by FEM in a STEM. For the study of both materials FEM has been used in the past [10, 11]. However, to my knowledge at the time of writing no Å-thin samples of a-C or a-Si have been studied via FEM.

Chapter 2

Materials

2.1 Amorphous carbon (a-C)

To understand the possible atomic structures of a-C, it is helpful to review the possible bonding configurations of carbon (C). C has four valence electrons, assigned in the ground state one *s* and three *p* orbitals. Those orbitals can however hybridize in different ways, giving rise to different bonding geometries, as schematically depicted in fig. 2.1. In the *sp*³ configuration, all four valence orbitals hybridize and the valence electrons occupy one of the resulting equivalent hybrid orbitals each. The *sp*³ orbitals are oriented in tetrahedral symmetry and so are the σ -bonds that can be formed with neighboring atoms. The *sp*² configuration is formed by hybridization of the *s* and two of the *p* orbitals. Three of the four valence electrons occupy the resulting *sp*² orbitals, which are oriented trigonally in the xy-plane, forming a σ -bonding plane. The remaining valence electron occupies the non-hybridized *p_z* orbital and forms weaker π -bonds with adjacent *p_z* orbitals. The *sp*¹ configuration results from the hybridization of one *s* and one *p* orbital and allows the two valence electrons in the resulting *sp*¹ orbitals to form σ -bonds, while the remaining two electrons occupy the *p_y* and *p_z* orbitals. This leads to the formation of linear molecules like alkanes [6].

Those different possible bonding configurations allow carbon to form different allotropes. Most notable and well-studied are the crystalline allotropes diamond with sp^3 bonding and bond length of 1.54 Å and graphite and graphene with sp^2 bonding and σ -bond length of 1.42 Å. The different graphene layers making up graphite are held together by weaker van-der-Waals (vdW) forces and the distance between them is 3.35 Å [6, 12].



Figure 2.1: Schematic representation of sp^3 , sp^2 and sp^1 hybridized orbitals, based on [6].

However, carbon does not only occur in the form of crystalline allotropes but also in more disordered configurations. In amorphous carbon allotropes, not every atom necessarily has the same bonding configuration. This means that there are not merely one or a few amorphous carbon allotropes, but a continuum of possible structures with different ratios of sp^3 -, sp^2 -, and sp^1 -bonded atoms as well as different degrees of order. Also, amorphous carbons need not be homogenous but can contain microcrystallites. Additionally, amorphous carbon need not be pure but can contain other atoms, most frequently hydrogen atoms [6].

Carbon bonding configuration and hydrogen content are the two parameters that define the SRO in amorphous carbon. However, the structure is not fully defined by the SRO, as there still exist a variety of possibilities for the degree and type of MRO. The MRO of amorphous carbon is of particular interest because it influences many of its properties, e.g., notably presents the source of the material's optical band gap [6]. For more details on the properties of amorphous carbon allotropes, especially on their electronic structure, the interested reader is referred to Ref. [6].

2.2 Amorphous silicon (a-Si)

Similar to C, a silicon (Si) atom has four valence electrons, two in an s-orbital and two in porbitals [13]. Like in carbon, those orbitals can hybridize, however, in Si, the sp^3 hybridization is significantly more favorable than sp^2 or sp hybridization [14]. Followingly, silicon atoms preferably crystallize in the diamond structure [13]. Nevertheless, silicene - the Si analog of graphene, featuring a buckled honeycomb structure - has been predicted and synthesized [15, 16].

A-Si lacks the long-range order (LRO) of the crystalline forms [17]. However, FEM measurements find MRO regardless of deposition method [10]. Nearest-neighbor distance, mean coordination

number, and bond angle distribution closely resemble crystalline Si [10]. Those properties are described well by a paracrystalline model consisting of small ordered grains in an amorphous matrix [10].

A-Si is an amorphous semiconductor and as such used in thin-film transistors or solar cells [17].

Chapter 3

Methods

Electron microscopy (EM) is an important tool for gaining information about structures on atomic length scales. While diffraction techniques gather merely statistical information, microscopy allows gaining spatially resolved information. The diffraction limit renders visible light with wavelengths of a few hundred nanometers useless as a probe. In contrast, electrons accelerated to a few tens of keV have wavelengths on the order of picometers. However, for EM it is to date not the diffraction limit that restricts resolution, but the aberrations inherent to electron lenses. The development of aberration correctors has allowed for mitigating this problem in state-ofthe-art devices [18]. There exist various types of electron microscopes. The main data for this work is obtained via an aberration-corrected scanning transmission electron microscopy (STEM), therefore the following section will introduce this technique.

3.1 STEM

The STEM instrument used for our experiments, a Nion UltraSTEM 100, is shown in fig. 3.1. The components from the bottom to the top (in the direction the electrons travel) are: A cold field-emission gun (c-FEG) and a pair of deflectors steering the beam up from the gun, three round condenser lenses and the virtual objective aperture (VOA), followed by a quadrupole–octupole C3/C5 corrector for aberration correction and quadrupole triplet (QLM) for coupling to the objective lens (OL) and the scan-coils which are integrated into the OL system. The OL consists of two modules, in the middle of which the sample is inserted. Then follow four round projector lenses and the detector volume containing various detectors and other devices: A beam stop, a high-



Figure 3.1: Photograph of Nion UltraSTEM 100 in our lab (a). Schematic depiction showing the components of a Nion UltraSTEM 100 (b), based on [18, 19].

angle annular dark field (HAADF) detector, medium-angle annular dark field (MAADF) detector, and a charge-coupled device (CCD) camera sitting on the optical axis. Lastly, there is an electron energy loss spectrometer with a quadrupole/octupole coupling module (QOCM) and an aperture, a drift tube and another CCD detector [18]. The most important of those components in this thesis and their role in STEM will be described in the following.

3.1.1 Probe formation

Electron gun

The electrons are produced by an electron gun. In the case of the Nion UltraSTEM 100 the gun is a cold field emission gun (c-FEG) by VG [18].

The most important component of a c-FEG is a very sharp tungsten tip. The principle behind field emission is that the strength of electric fields produced by a voltage applied to a body is considerably increased at sharp tips. This only works if the surface is pristine, so the c-FEG must be kept in ultra-high vacuum (UHV). The c-FEG is brought to a high voltage so that it is the cathode with respect to two anodes. The first anode provides the extraction voltage to pull electrons out of the tip, the second one accelerates those electrons [4]. Our device can accelerate electrons to 55 - 100 keV. For all experiments conducted during this project 60 keV is used.

Probe-forming system and aberration correctors

The resolution of a STEM is limited by the size of the electron probe. Therefore, to enable direct atomic-resolution imaging, the electrons coming from the gun's tip, which has a spatial extent of a few nanometers, have to be formed into a probe focused on few Å or less. The resulting electron wave shape should be as spherical as possible so that it converges on a small spot of the specimen. This is achieved by the probe-forming system consisting of electron lenses [4]. Electron lenses can be realized by strong electrostatic or magnetic fields, that change the electrons' trajectories [4]. In the Nion UltraSTEM 100 magnetic lenses are used for focusing and shaping the beam. Because the practically reachable probe size is limited by aberrations inflicted on the probe by the electron lenses, aberration correctors consisting of complex systems of multi-pole lenses are employed. The aberration-corrector of the Nion UltraSTEM 100 uses 12 rotatable quadrupole and three combined quadrupole-octupole lenses and is able to correct up to fifth-order aberrations

and help to produce a probe of ≈ 1 Å size [18].

3.1.2 Scanning the beam or moving the sample

In STEM an image is formed by scanning the probe across the sample while for every probe position, the respective signal is collected by detectors. During scanning the beam must be kept parallel to the optical axis. This can be accomplished by two pairs of scan coils [4].

For movements across longer distances as needed in finding a suitable sample area, the sample is moved relative to the beam via a specialized sample stage with nanometer precision [18].

3.1.3 Image formation

Origins of contrast in STEM

In STEM, contrast arises from the scattering of the incident electrons off atoms in the sample. Electrons can be scattered elastically or inelastically. For inelastic scattering the electron's energy is changed. The resulting signal is used, e.g., in electron energy loss spectroscopy (EELS) to identify atomic species. For elastic scattering, the electron's energy remains (nearly) unchanged, but its is altered. Elastic scattering is the main source of contrast in TEM and STEM. Elastic scattering between electrons and atoms is mediated via the Coulomb interaction. Interaction with the negatively charged electron cloud leads to scattering angles of a few degrees, while interaction with the positively charged nucleus leads to much higher scattering angles, the higher the closer the electron passes by the nucleus (up to backscattering). One important property of the scattering process is its coherency, referring to the maintenance of the electron's phase relationship during scattering. While inelastic scattering angle. Low-angle coherent scattering depends on the relative positions of the atoms the interfering electron waves are scattered from and leads to phase-contrast. High-angle coherent scattering is mostly Rutherford scattering which depends on the atomic number and is hence termed Z-contrast [4].

Coherency is not only a property of scattering, but also of the detection, i.e. the detection can add incoherency even for coherent scattering (the opposite cannot occur, if coherence is lost it cannot be restored). This imaging coherency depends not on the absolute scattering angle, but on the angular range over which the detector integrates the signal. A point detector theoretically allows for perfect coherent imaging, while an infinite detector would record no coherent scattering signal, but only signal from inelastic scattering [20].

For completeness, it should be mentioned that other factors can also contribute to STEM contrast, e.g., changes in the thermal vibration amplitude and contrast due to static strains [20]. Those contributions however are not significant in our experiments.

ADF imaging

In STEM, the image is not magnified and projected by lenses. Instead at every probe position signals from various detectors can be recorded synchronized with the scanning and subsequently be correlated to the probe positions. The choice of detector allows the operator to choose which electrons contribute to the image [4]. For example, annular detectors collect all electrons scattered to a specific angular range over the detector area, leading to an intensity value for every probe position [20]. The annular detectors in our setup are a MAADF detector with an angular range of 40 to 600 mrad half-angle and a HAADF detector with an angular range of 80 to 240 mrad half-angle [18]. Due to the coherency of scattering depending on the scattering angle those detectors record contrast stemming from different mechanisms: For MAADF phase-contrast and Z-contrast contribute, while HAADF records mostly Z-contrast.

STEM nanodiffraction and 4D-STEM

Electron diffraction is a typical method for gaining structural information from materials in EM as the interference in the scattered beam which determines the angles to which scattering predominantly occurs is representative of structural characteristics of the sample [4, 21].

Acquiring diffraction patterns in STEM is quite straightforward. In fact, electron-optically a STEM can be seen as a TEM operating in diffraction mode with a camera positioned in the diffraction plane. While for typical STEM ADF imaging, the diffracted intensity is summed over the detectors' angular range, one can in principle also record the full diffraction pattern using pixellated detectors. This is called STEM-nanodiffraction [20].

The resulting dataset will be four-dimensional, hence the term 4D-STEM for this acquisition technique [22]. One way to analyze 4D-STEM data is to implement arbitrary "virtual " detectors by picking which subsets of pixels of the diffraction patterns are used during analysis. In this way, virtual bright-field (BF) or ADF images with arbitrary angular ranges (up to the maximum

collection angle) can be calculated. Also more sophisticated virtual detector geometries can be implemented or more sophisticated other analysis methods performed on the datasets [22].

For pixellated detectors currently, the technology most commonly found in TEMs and STEMs is CCD. CCD detectors offer decent electron sensitivity, but low readout speeds and limited dynamic range, which makes them ill-suited for most 4D-STEM applications [22]. There are two main alternative detector technologies, namely monolithic active pixel sensors (APS) and hybrid pixel array detector (PAD). Both offer good electron sensitivity and fast readout speeds, PADs additionally offer a high dynamic range [22] and thus are superior to CCDs for 4D-STEM data acquisition. However, the pixellated detector currently available in our setup is a CCD.

3.2 FEM

FEM is an analysis method performed on a particular type of 4D-STEM datasets of amorphous samples [22] that was originally proposed by Treacy and Gibson in 1996 [23]. Because this technique is central to this work it will be described in detail in this dedicated chapter.

3.2.1 The fluctuations in FEM

The "fluctuations" in fluctuation electron microscopy refer to differences in scattering between neighboring sample regions [24] and appear in images or diffraction patterns as "speckles" [2]. For disordered atomic structures, always some particles will coincidentally be aligned to allow coherent scattering. If the particle distribution is truly random, the speckle pattern will be nearly uniform (except for shot noise which becomes more significant with larger scattering angles). If there exist ordered regions with structural correlations within the probed sample volume, there will be a non-random coherent scattering contribution, creating speckles [5]. Treacy and Gibson confirmed by examining simulated electron microdiffraction data (from amorphous silicon) that intensity fluctuations increase monotonically with the percentage of crystalline grains in the material [25].

3.2.2 FEM data acquisition

FEM data can be collected by two main methods, which in principle lead to equivalent 4D-STEM datasets. One method is dark-field (DF) microscopy in a TEM, the other is micro- or nanod-iffraction in a STEM [3]. For our experiments STEM nanodiffraction is used, thus the following description will focus on this method.



Figure 3.2: Schematic depiction of FEM acquisition in a STEM. A focused, but not atomically sharp probe is scanned over the sample and a diffraction pattern is collected for every probe position. Based on [2]

STEM micro- or nanodiffraction requires a probe focused on a small region of the sample. For each probe position r_i a speckle pattern $I(r_i, Q)$ in the diffraction plane is recorded. Each diffraction pattern contains the full range of diffraction vectors $Q = Q_i$ [24]. It is important to note that the probe is not atomically sharp as is typically desirable in STEM, but has a size of a few nanometers. The size of the probe defines the specimen volume that contributes to a specific speckle pattern [26]. The speckles will be strongest when this roughly matches the length scales of the structural correlations [22]. Variable resolution FEM, where multiple datasets with different probe sizes are acquired, makes use of this relationship [3]. STEM is especially suited for variable resolution FEM because its probe-forming optics allow varying the probe width flexibly [24]. There also exists variable coherence FEM, for which not the probe size, but the probe coherence is varied [23]. However, as in our experiments variable resolution FEM is used following explanations will focus on this variant. Also note that for FEM typically probe positions are picked in a manner that the illuminated sample volumes do not overlap to ensure statistic independence of the data from different sample volumes.

3.2.3 Sensitivity to MRO

The sensitivity of FEM to the MRO structural correlations stems from the information contained in the FEM signal: While pure diffraction data contains only two-body correlations between the atoms (pair-correlations), FEM data contains up to four-body correlations (= pair-pair correlations). This surplus of information stems from the spatially resolved nature of the FEM acquisition. While pure diffraction data is acquired with a plane wave probe with no spatial resolution, FEM is acquired with a convergent probe, making it a spatially resolved diffraction technique. The higher-order correlations then arise from statistics between different sample volumes probed at different probe positions [24].

3.2.4 FEM data analysis

The simplest statistical parameters available are the mean and the variance of the intensity in the speckle patterns [24]. While the mean of the speckle intensity depends on two-body correlations, the speckle intensity variance depends on two-, tree- and four-body correlations, which are more sensitive to MRO [27].

In order to compensate for the scattering falling off with increasing scattering angle , the normalized intensity variance is typically used [5]. The normalization is done by dividing by the square of the mean intensity [24]

$$V_N(\vec{q}) = \frac{\langle I^2(\vec{r}, \vec{q}) \rangle_{\vec{r}}}{\langle I(\vec{r}, \vec{q}) \rangle_{\vec{r}}^2} - 1, \qquad (3.1)$$

where, I is the scattered intensity, q is the reciprocal coordinate corresponding to the scattering angle and r is the real space coordinate corresponding to the probe position, over which the averaging is done.

A truly random distribution of point scatters would lead to absence of peaks in the normalized variance $V_N(q)$ plots. Peaks in the reciprocal coordinate only appear if the sample structure contains local ordering [2, 24]. Treacy and Gibson found the reduced normalized variance of diffracted intensity to vary approximately linearly with the volume fraction of crystalline grains [25]. Also, the scattered intensity varies with the square of the number of aligned atoms, therefore speckles from small ordered regions can be relatively pronounced [5]. The q-values of peaks in the normalized variance plots can be identified with different structural features in different allotropes of a material [5].

So far FEM on itself is not yet a quantitative technique, but relies on the comparison of the normalized variance data with predictions calculated from models like done in Ref. [5]. Typically simple models with as few atoms as possible are used because the computation of the normalized variance is rather time-consuming. The V(q) curves obtained in this way typically show accurate correspondence of peak locations, but not of peak heights [5]. However, also the possibility to obtain structural models directly from FEM data via reverse Monte Carlo methods has been explored in the literature [28].

3.2.5 Specifics of our FEM setup

The acquisition of variable resolution FEM datasets requires the possibility of changing the probe size in a controlled manner. In our setup, this is implemented via a custom-built mode of the condenser settings that allows us to adjust the electron probe size while compensating for unwanted side effects. The probe size is changed by changing the strength of the C2 lens, then the probe is refocused via the C1 lens. Note that these steps potentially change the beam current. Accordingly, the beam current is expected to vary with probe size. Additional parameters are varied in order to compensate for the most relevant unwanted side effects like a shift of the beam on the sample or on the CCD camera or newly introduced astigmatism. The bulk of those adjustments is done automatically within the FEM mode control, fine adjustments are done by the user via a FEM controls window.

The projector settings are left untouched in reference mode because once the probe is focused on the sample the position of the CCD is already in the diffraction plane, ready for 4D-STEM acquisition.

The 4D-STEM dataset is acquired by scanning the probe and acquiring the CCD data for every probe position via the dedicated 4D-STEM acquisition functionality "Acquisition" provided by the microscope operation software Nionswift. (Nionswift stable version 16.8 was used for all experiments.)

Before the start of an acquisition the desired probe size is chosen and the necessary adjustments are made. Then a region from where the data is to be acquired, the desired number of speckle

patterns to be acquired, and the dwell time for the acquisition of each pattern are chosen.

In the following, the implementation of the home-built FEM mode is described. The hardware of the Nion Ultrastem 100 is controlled by the "AS2" software, which includes controls that act on the various hardware elements. Additionally to the direct hardware drives, virtual drives can be built by combining them. This can be done in a nested manner. The relevant drives for the FEM mode are those acting on the condenser lenses, because the condenser system controls the probe formation. In order not to mess up the global settings of the respective controls, a first layer of virtual drives is introduced (containing a control "FEM_x" for every control "x" to be targeted). Those new controls simply forward their parameters directly passed to the corresponding direct controls, but only when the FEM mode is active. Low-level FEM controls are acted upon by the master control "FEM ProbeSize". This takes the desired probe size value from the user input in the FEM control window and applies the necessary changes to the controls of the C1 lens for changing the probe size, but also to all the other controls for refocusing compensating the unwanted side effects and aberrations introduced. The action on the different hardware-close controls is determined by empirical mathematical expressions. Those were worked out by Murray Gibson by recording data on the side effects and the parameters necessary to counteract them for many probe positions and performing fits on the data points. In a perfect world without imprecision, hysteresis, and drift in parameters this would suffice, however in practice manual fine adjustments of the individual controls by the user are required. These adjustments are enabled in the FEM control window via the additional controls "FEM_Focus", "FEM_AstigA", "FEM_AstigB", "FEM_CenterA", "FEM_CenterB", "FEM_ShiftA", "FEM_ShiftB". Those act as variables passing the user input to the respective lower-level FEM controls after adjusting the units and purifying the effects by compensating for unwanted side effects via mathematical expressions.

3.3 Physical vapor deposition (PVD)

PVD is an umbrella term for methods for producing thin films that involve the physical removal of atoms or small clusters of atoms from a sputtering target. Those atoms then pass through a low-pressure chamber and form a thin film on a substrate. The most common ways of removing atoms from the target are thermal evaporation and sputtering [29]. Those methods also are the ones we used for sample production. For thermal evaporation, a material is heated until atoms transition into the gas phase [29]. In our setup, the heating is accomplished by passing high

electrical currents through a tungsten boat holding the material [30].

Sputtering is the physical vaporization of atoms from a target by momentum transfer from bombardment with small particles, usually, electrons or ions accelerated in an electric field [31]. The setup we use is a direct current (DC) magnetron sputtering configuration, and the particles are Ar ions, and the carbon target consists of graphite. The Ar ions are produced from Ar gas and kept close to the graphite target via a magnetron. From there they are accelerated towards the target by an electrical potential which results in carbon atoms or clusters of carbon atoms being sputtered off the graphite surface. After traversing the vacuum chamber some of them eventually impinge on the sample substrate [29, 30].

Chapter 4

Results and Discussion

4.1 Sample preparation

4.1.1 Deposition

The samples were produced by PVD on NaCl single crystals as substrate. The crystals come as 1 cm by 1 cm cubes and were cleaved to 5 mm by 5 mm by 2 mm cuboids using a scalpel. The cleaved crystals were either used immediately or kept in a clean Petri dish until they were used. Additionally, for a-C batches 7 to 10 and for all a-Si batches the crystals were ultrasound cleaned in an isopropanol (IPA) bath of 99.5 % purity for 5 min before deposition. The deposition was done in a vacuum chamber (HEX deposition system from Korvus technology) that is shown in fig. 4.1. The system is equipped with a Pfeiffer MVP 040-2 dry backing pump and a Pfeiffer HiPace 80 Turbomolecular pump and can reach vacuum levels in the range of 10 \times 10^{-6} mbar. The pressure is measured by a Pfeiffer PKR251 Pirani/Cold cathode combination pressure gauge. The system is equipped with a CUSP magnetron sputter source featuring a FISSION magnetron sputter head for classical DC magnetron sputtering and a TES thermal boat source for thermal evaporation of materials by applying DC current directly through a tungsten boat containing the evaporant. The magnetron source uses Ar as a sputter gas and is fitted with an Ar gas line with flow regulated by a mass flow controller (MFC). Dry N2 is used as a vent gas for the deposition chamber. Additionally, the system is equipped with a quartz crystal microbalance enabling approximate measurement of the thickness of deposited material. All devices as well as the sample table can be blocked via moveable shields to avoid unwanted deposition [30].



Figure 4.1: a) Photograph of the deposition chamber with turbomolecular pump (mounted on the bottom), magnetron sputter (mounted on the left side), and thermal evaporator (mounted on the right side). b) Photograph from the inside of the vacuum chamber with magnetron sputter (on the right side) and thermal evaporator (on the left side). The samples are mounted on the top, behind the moveable shield. c) Photograph of the sample table with sodium chloride (NaCl) crystals mounted and ready for deposition.

The samples are mounted via small clips and screws on the sample table as shown in fig. 4.1. The sample table is then mounted at the top of the chamber and the sputter target or thermal evaporation material is put in the respective device. Then the chamber is sealed and pumped down. After reaching a sufficient vacuum level the deposition of the respective material is executed as described in the following.

a-C deposition

The a-C deposition was done via DC magnetron sputtering. A graphite target of 99.999 % purity was used as a carbon source and Ar as sputtering gas. The Ar flow could be regulated via a MFC, and the DC current via a high voltage supply. For igniting the Ar plasma, relatively high Ar flows (approx. 40 to 45 $\text{cm}^3 \text{min}^{-1}$) and low currents (0.01-0.02 A) were used. Once the plasma was ignited and stable, the Ar flow was slowly reduced to approx. 10 or 20 cm³ min⁻¹ (depending on the desired deposition rate, for the thinner samples $10 \text{ cm}^3 \text{min}^{-1}$, for the thicker samples 20 $\text{cm}^3 \text{min}^{-1}$), and the current increased to approx. 0.04 A. The decrease of the Ar flow is a slightly tricky step. On the one hand, it should be done as soon and fast as possible in order not to burden the turbo pump for too long, on the other hand, care has to be taken to keep the plasma stable. Once a stable state with the desired parameters was reached, the parameters were kept for 10 to 15 min to allow surface contamination to evaporate from the graphite target before starting the actual deposition. Then, the shield at the sample was opened simultaneously with resetting the quartz balance and closed again once the desired thickness had been deposited according to the quartz balance. After this, the current and Ar flow were reduced to zero, the devices turned off, the vacuum chamber vented with N₂, and the samples retrieved. Special care was taken to not touch the sample side with the tweezers or anything else. The crystals are stored with the sample side up in cleaned Petri dishes. To identify the individual samples in one batch, a number was written on the non-sample side with a waterproof pen while the samples were held at the sides with tweezers.

There were ten batches of a-C samples produced, the respective deposition parameters and additional information are listed in table 4.1. Unfortunately for batches 7 to 9 the residual atmospheric pressure could not be recorded due to a broken sensor.

Batch	Nominal thickness	Residual atmospheric gases	Ar flow rate	Current supplied
1	10.0 Å	$1.2 \times 10^{-5} \mathrm{mbar}$	$10.1 {\rm cm}^3 {\rm min}^{-1}$	0.040 A
2	5.1 Å	$4.6 \times 10^{-6} \text{mbar}$	$10.1 {\rm cm}^3 {\rm min}^{-1}$	0.040 A
3	10.0 Å	$5.6 \times 10^{-6} \text{mbar}$	$10.1 {\rm cm}^3 {\rm min}^{-1}$	0.040 A
4	20.0 Å	$5.4 \times 10^{-6} \text{mbar}$	$10\mathrm{cm}^3\mathrm{min}^{-1}$	0.040 A
5	30.2 Å	$6.3 \times 10^{-6} \mathrm{mbar}$	$10\mathrm{cm}^3\mathrm{min}^{-1}$	0.040 A
6	20.0 Å	$5.4 \times 10^{-6} \mathrm{mbar}$	$20\mathrm{cm}^3\mathrm{min}^{-1}$	0.040 A
7	3.0 Å	Not recorded	$10\mathrm{cm}^3\mathrm{min}^{-1}$	0.040 A
8	1.0 Å	Not recorded	$20\mathrm{cm}^3\mathrm{min}^{-1}$	0.084 A
9	2.0 Å	Not recorded	$32\mathrm{cm}^3\mathrm{min}^{-1}$	0.060 A
10	50.0 Å	$2.2 \times 10^{-6} \mathrm{mbar}$	$30.1 {\rm cm}^3 {\rm min}^{-1}$	0.037 A

Table 4.1: Deposition parameters for different sample batches of a-C.

a-Si deposition

The a-Si evaporation deposition was done by thermal evaporation of Si. Elemental Si of purity 99.95 % was placed in a tungsten boat that was heated to evaporation temperature by applying current via a TDK Lambda Genesys GEN6-100 power supply. The exact procedure was the following: In order not to break the tungsten boat by fast thermal expansion the current was slowly increased over the course of approx. 15 min until the Si would melt, then the current was decreased so the Si was slightly below the melting point. At this stage, the current was kept constant in order to allow surface contamination to evaporate for another approx. 10 min until the quartz balance showed no or a very small deposition rate. Then the current was increased until the Si would melt and the quartz balance again showed a significant deposition rate. At this point, the shield at the sample was opened simultaneously with resetting the Quartz balance and the material deposited while checking the thickness via the quartz balance. As soon as the desired thickness was reached, the shield at the sample was closed again and the current slowly (over the course of approx. 10 min) reduced to zero. Then the chamber was vented with N₂. After an additional cool-down phase to enable safe handling, the samples were retrieved. The crystals were afterward handled similar to those used for a-C.

There were three batches of a-Si samples produced, the respective deposition parameters are listed in table 4.2

Batch	Nominal thickness	Residual atmospheric gases	Max. temperature at sample
1	2.0 Å	low 10 ⁻⁶ mbar	44 °C
2	10.0 Å	$6.3 \times 10^{-6} \mathrm{mbar}$	56 °C
3	5.0 Å	$4.6 \times 10^{-6} \mathrm{mbar}$	55 °C

Table 4.2: Deposition parameters for different sample batches of a-Si.

4.1.2 Transfer to TEM grids



Figure 4.2: Transfer of sample to TEM grid. a) NaCl crystal with deposited sample facing downward on TEM grid ready for transfer. b) The dissolution of the NaCl substrate in deionized water is visible via observing the schlieren.

For electron microscopy, the samples have to be transferred to TEM grids. Quantifoil Au 2/2 grids were used. They consist of a 3.05 mm gold mesh with a 10 to 12 nm thick a-C layer featuring holes of 2.0 μ m diameter and 2.0 μ m spacing between the holes [32]. The use of this type of grid allows microscopy of free-standing sample areas suspended over the holes. The sample transfer onto TEM grids was carried out by dissolving the NaCl substrates in deionized water

as shown in fig. 4.2. In a small metal wire box fabricated for this purpose was placed the TEM grid with the sample side facing up and on it the NaCl crystal with the deposited sample facing down. The metal box was held by inverse tweezers which were held by "helping hands" on a height-adjustable platform. Using the height-adjustable platform the sample was lowered into an empty beaker. Then the beaker was carefully filled with deionized water until the TEM grid and sample were covered and the NaCl was allowed to dissolve. The waterproof pen traces from marking the samples that were floating up on the surface of the water were fished out using tweezers to make sure they would not end up contaminating the sample. The dissolution of the NaCl crystal could be followed by observing the schlieren resulting from the different density refractive index of NaCl saturated water. Some minutes after no schlieren were visible anymore the metal box containing the TEM grid now holding the sample was carefully lifted out of the deionized water and allowed to dry in air for a few minutes. The TEM grids with the samples underwent a coverage check in a DeLong Instruments LVEM5 Mini-TEM and were subsequently stored in membrane boxes until they were eventually loaded into the UHV system of our Nion microscope.

4.1.3 Sample washing, and cleaning attempts

In order to clean the samples from residues of NaCl and other contamination, different approaches were explored. In order to dissolve residual NaCl, the TEM grids were once again bathed in deionized water after being fished out from the deionized water where the NaCl was dissolved. Various variants of performing this second bath were explored, including submerging the TEM grid with or without the metal basket and letting it sit on the surface of the deionized water with the sample side facing up or down. Washing durations from one hour to one weekend were tried out. However, there was no significant difference in the amount of contamination noticed neither in the Mini-TEM nor in ADF imaging.

In order to clean the samples from possible organic residues an attempt of acetone-vapour cleaning was made on an a-C sample of 1 Å nominal thickness (sample 8_3_b). Fig. 4.3 shows the setup of the acetone vapor cleaning attempt. The TEM grid was held by inverse tweezers at an inclination of 45° with the sample-side facing down and placed over acetone vapor produced from acetone of 99.5 % purity overnight. Examination in the Mini-TEM showed nearly no coverage, while it showed good coverage for the control sample (sample 8_3_a) that was produced in the exact same way without this additional cleaning step. This hints at the chemical cleaning proce-



Figure 4.3: Setup for acetone vapor cleaning attempt. The sample is held by inverse tweezers over an acetone bath heated to 60°C on a heating plate, the beaker is covered with Parafilm to minimize acetone evaporation.

dure resulting in the etching of the sample. As any modification of the atomic structure of the sample is unwanted, no further acetone vapor cleaning attempts were made.

4.1.4 Attempts at thickness measurement via AFM

Initial attempts were made at measuring the thicknesses of the samples via AFM. For this purpose with every batch, one or two dedicated samples were produced with a striped mask as shown in Fig. 4.1, that would allow to measure the thickness via an AFM line-scan perpendicular to the sample stripes. AFM measurements were conducted with an WITec alpha 300A environmental AFM. A variety of different AFM tips were tested. Unfortunately, however, no sufficient height resolution was reached with either tip. There are several factors limiting height resolution. On the one hand, the limit of the device itself is in the Å range, on the same order as the thin samples. Also, in environmental AFM there is always a nm-thick layer of water from the atmosphere adsorbed on the sample. This can lead to significant deviations of the apparent from the actual sample height [33]. Additionally, even though different tips were tested, the a-C might have required still another tip. Because environmental AFM seemed little promising for our thin samples, the method was abandoned and the thickness was instead roughly estimated by measuring

the deposited material thickness via the Quartz microbalance in the PVD system.

4.2 STEM precharacterization

Samples a-C_8_3_a (nominal thickness 1 Å, henceforth referred to as "Å-thin a-C sample"), a-C_10_2 (nominal thickness 50 Å, henceforth referred to as "nm-thin a-C sample"), and a-Si_2_1 (nominal thickness 10 Å, henceforth referred to as "Å-thin a-Si sample") were introduced to the UHV system of the Nion via a load-lock where the samples were baked up to 180°C in vacuum overnight in order to avoid introducing atmospheric moisture or contamination into the system.

4.2.1 ADF imaging of a-C



Figure 4.4: MAADF images of Å-thin a-C sample: a) Quantifoil hole covered with a very thin and porous layer of a-C. The darkest regions are pores, on the bottom left is a less porous area where the subsequent images were taken. b) Sample area featuring patches of different thicknesses and a pore (at the top right corner). c) monolayer patches (big patch in the middle right, two smaller patches left) surrounded by multilayer patches and possibly contaminant atoms of higher atomic number.

Imaging was performed using the MAADF detector. Figure 4.4 show MAADF images of sample a-C 8_3_a with increasing magnification. The Å-thin a-C layer features many pores but also continuous regions where one and few-atom-thick patches can be found, as exemplified in fig. 4.4. A thickness of the quasi-continuous a-C layer in the region marked "ROI" in fig. 4.4 of 13 to 17 Å was measured via comparison of the relative average contrast of the region to vacuum vs quantifoil to vacuum. The patches of different thicknesses in the images suggest that the growth happens



Figure 4.5: Å-thin a-C sample: ADF image series showing structural changes under the electron beam.

predominantly in layers. Layered growth would imply sp^2 bonding, this hypothesis has to be underpinned by FEM analysis in section 4.3.4.

It is difficult to tell the atomic structure from the ADF images since atoms are barely discernible and only in the monolayer patches. Those patches however contain a big proportion of nonhexagonal rings. This confirms the sample's amorphousness at least in some regions. More representative conclusions about the structure can only be made from FEM analysis following in section 4.3.4.

The random polygon structure and apparent sp^2 -bonding found in our ADF images corresponds well to the random polygon structure featuring tetragons, pentagons, hexagons, heptagons, and octagons) imaged by Kotakoski et al. via high-resolution-TEM on monolayer a-C produced from graphene by amorphization under continuous electron irradiation just above the knockon threshold [8]. Also, more recent studies imaging a-C monolayers produced by CVD found sp^2 -bonded layers containing random polygon structures (with pentagons, hexagons, heptagons, and octagons) as well as graphene-like nanocrystallites [34, 35]. In Ref. [34] samples were produced at different substrate temperatures. While low substrate temperatures (300 °C) resulted in large graphene-like regions, MRO and electrical conductivity, higher substrate temperatures (\geq 300 °C) resulted in smaller graphene-like nanocrystalline and a loss of MRO and electrical conductivity. For even higher substrate temperatures (\geq 500 °C) bilayer regions were found [34].

It should be noted that the atomic structure of our samples appears not fully stable under the electron beam. This is indicated by horizontal stripes in the quasi-atomically resolved images and can be seen more directly in figure 4.5. The movement affects predominantly edges of layers and atoms on top of layers, which are possibly even contamination of another atomic species.

4.2.2 ADF imaging of a-Si



Figure 4.6: MAADF images of different Quantifoil holes of Å-thin a-Si sample featuring homogenous clean sample areas, but also folds, ripped areas and contamination.



Figure 4.7: MAADF images of Å-thin a-Si sample: a) Quantifoil hole covered with a thin and porous layer of a-Si. The small dark spots are pores, the broad bright stripe is a fold in the material, subsequent MAADF images were taken in the area at the bottom left between the fold and the rim of the hole. b) Sample area with contamination of higher atomic number (near center). c) Small monolayer patches (bottom left), surrounded by bilayer patches (around center), multilayer patches and possibly contaminant atoms of higher atomic number.



Figure 4.8: MAADF image series of the Å-thin a-Si sample showing structural changes under the electron beam.

Imaging was performed using the MAADF detector. Figure 4.6 show different a-Si covered quantifoil holes. Figure 4.7 show MAADF images of the Å-thin a-Si sample with increasing magnification. The a-Si layer features small pores and some bigger folds. In some areas, there is visible contamination. Small sample patches of seeming monolayer or bilayer thickness can be found. For a-Si it seems there are fewer or only smaller regions of monolayer thickness compared to a-C. This aligns with the expectation that Si forms sp^3 bonds rather than sp^2 bonds. However, the nominal thickness of the a-Si sample is 10 Å (which is the thinnest thickness with which a sample with significant coverage could be produced). This is an order of magnitude higher compared to the 1 Å nominal thickness of the a-C sample.

Also for the a-Si sample, the atomic structure does not appear fully stable under the electron beam, as indicated by horizontal stripes in the images. Again, the movement affects predominantly the edges of layers and atoms on top of layers, which are possibly contamination. The qualitative effects of the electron beam on the atomic structure are exemplified by fig. 4.8.



4.2.3 EELS of a-Si revealing oxygen contamination

Figure 4.9: Å-thin sample a-Si_2_10: EELS spectrum showing a pronounced oxygen peak with K-edge at an energy loss of 532 eV

Because we suspected oxygen contamination in the a-Si sample due to its production by thermal evaporation in a suboptimal vacuum, the oxygen content of the a-Si sample was checked via EELS. The EELS measurement was performed on a sample area of 512 by 512 nm. Figure 4.9 shows the result of averaging 1024 EELS spectra acquired over a grid of 32 by 32 probe positions

in this area. The spectrum features a strong peak with onset at an energy loss of ≈ 532 eV. This corresponds to the literature value for the oxygen K-edge [36], indicating a significant oxygen content in the sample, to a degree that it is most probably not correct to speak of amorphous silicon, but rather of some form of amorphous silicon oxide. As the vacuum conditions in our PVD system cannot be significantly improved, the quest for producing and analyzing atomically thin a-Si was abandoned.

4.3 4D-STEM acquisition and FEM analysis



4.3.1 4D-STEM data acquisition

Figure 4.10: a) CCD overview of area and b) MAADF image of quantifoil hole covered with sample where variable resolution FEM dataset was taken for the nm-thin a-C sample.

Variable resolution FEM datasets were taken exclusively on a-C samples, specifically on the nmthin sample and the Å-thin sample. The respective sample areas and quantifoil holes where the datasets were acquired are shown in figs. 4.10 and 4.11. 4D-STEM datasets were taken with FEM probe sizes of 3, 5, 7, 10, 15, 25, 40, and 60 Å. In order to avoid beam damage, datasets for different probe sizes were acquired in different areas within the same quantifoil hole or in neighboring holes. Each dataset contains nanodiffraction patterns acquired at 1024 probe positions distributed in a 32 by 32 grid over a field of view (FOV) of 128 nm. For the normalized variance calculation of the Å-thin sample two such datasets were combined to increase the signal-to-noise ratio (SNR). Those two datasets were acquired in three neighboring quantifoil holes, only two of which are



Figure 4.11: a) CCD overview of area and b) MAADF images of quantifoil holes covered with sample where variable resolution FEM dataset was taken for the Å-thin a-C sample.

shown in the ADF images fig. 4.11, because one of the holes was not found again during the acquisition of the variable resolution dataset when switching to larger probe sizes, so the data acquisition had to be continued in another quantifoil hole in the same area.

4.3.2 Code used for FEM analysis

The datasets were analyzed using python code in jupyter notebooks. The processing of the 4D-STEM datasets and the calculation of the normalized variance from them was done via code written by Tom Pekin and optimized for the task at hand by Toma Susi and myself. The resulting normalized variance data from datasets acquired at different was then loaded into another jupyter notebook written by me for that task in order to combine it for producing 3D plots of normalized variance versus reciprocal coordinate and probe size.

For reciprocal scale calibration a graphene dataset is used. The calibration is performed by detecting the 1st and 2nd diffraction peaks, corresponding to the lattice vector and the nearest neighbor distance in graphene respectively, and then finding the calibration factor in inverse Å per pixel by comparing to the literature values of those distances. This calibration step only needs to be redone in case there are major changes to microscope alignment, e.g., after service.

For FEM analysis, the relevant datasets are loaded and their metadata is extracted directly from the h5 files as saved by Nionswift. Those files contain the acquired 4D-STEM data plus relevant metadata, including nominal probe size, exposure time, and acquisition timestamp. To speed up the calculations the 4D-STEM data is binned in reciprocal space by summing the values of neighboring pixels resulting in reduced spatial resolution with accordingly increased dynamic resolution per pixel. The original reciprocal dimensions recorded by our Orca CCD camera are 2048 by 2048 pixels, and after binning by a factor of four the reciprocal dimensions 512 by 512 pixels. Optionally, multiple 4D-STEM datasets from different areas can be combined to increase SNR and statistical significance. If this is done the speckle patterns have to be centered before. Removal of streaking background noise is performed via a py4DSTEM function. The expected positions of the amorphous rings are calculated from the real space atom distance and the detected reciprocal space range. Then the relevant part of the diffraction pattern is selected by masking off both the central beam and the range of high scattering angles with insufficient SNR. Optionally, ellipse fitting can be performed to amend the effects of astigmatism. This, however, was not done in our case because there was very little astigmatism and the ellipse fitting code would have induced distortions rather than fixing them. Correction for drift or beam sway can be performed. Also, this was not done for our data, because we did not have significant drift or beam sway. The masked range of the data is transformed from cartesian to polar-elliptical coordinates, after which the actual normalized variance calculation is done via a py4DSTEM function that can perform four different ways of calculating the normalized variance from the speckle patterns [37]. We used "annular mean of variance image", where first the variance of the diffracted intensity between speckle patterns from the set of speckle patterns is calculated on a pixel-by-pixel basis, resulting in a variance image. Then, of this variance image the annular mean is calculated. The normalized variance data together with the metadata of the respective dataset are saved as ison files for plotting, which is carried out in a separate jupyter notebook.

4.3.3 Diffracted intensity

As a first check before starting the actual FEM analysis, for both samples, the radially averaged scattered intensity I(q, Q) was calculated on the dataset acquired with the largest probe size (60 Å) and hence closest to a regular diffraction dataset. The results are shown in fig. 4.12. The peaks are more pronounced for the nm-thin sample, for the Å-thin sample both peaks are weaker with the first only faintly discernible. This is expected due to a weaker scattering signal from the thinner sample. Both radial intensity curves show peaks at scattering angles of ≈ 0.4 Å⁻¹ and ≈ 0.7 Å⁻¹, respectively. Those values correspond well to the reciprocal spacings in graphene of 0.41 Å⁻¹ corresponding to the lattice constant of graphene with 2.46 Å⁻¹ and 0.7 Å corresponding to the next-neighbor distance in graphene with 1.42 Å [6, 12]. This suggests graphite-like ordering or predominately sp^2 bonding, however, this conjecture has to be scrutinized in the following



Figure 4.12: Radially averaged scattered intensity I(q) for dataset taken with probe size 60 Å on nm-thin a-C sample.

FEM analysis. A peak at 0.35 Å⁻¹ would correspond to the distance of 2.84 Å between carbon atoms on opposite sides of the hexagonal rings in graphite or graphene. The absence of this peak implies a low portion of hexagonal rings in the structure [12] as would be expected from the ADF images on the monolayer patches of our Å-thin sample. Unfortunately, the scattering signal is too low compared to the direct beam to fully exclude the existence of a peak at 0.35 Å⁻¹. Except for the signal strength the I(q) curves from the two samples of different thicknesses are similar, suggesting similar ordering at least on the scale of SRO. A more detailed comparison of their structures requires the calculation of other statistical moments, e.g., the normalized variance as done in the following FEM analysis.

Comparison to electron diffraction literature on magnetron-sputtered a-C

Kulikovsky et al. produced a-C films of thicknesses in a range of 30 to 1500 nm by magnetron sputtering. As in our experiments also in theirs Ar was used as sputtering gas and sputtering took place in an Ar atmosphere at a pressure of 1.7×10^{-3} to 3.3×10^{-3} mbar. The residual concentration of atmospheric gases in the deposition chamber is not specified, however, they claim to have produced hydrogen-free a-C. The deposition happened either with no bias voltage applied, leading to samples with low hardness, or with an applied bias voltage of 100 to 150 V, leading to samples of high hardness [21]. The diffracted intensities they obtained from their magnetron-sputtered samples show three peaks. The first peak is at $q \approx 0.33$ to 0.34 Å⁻¹ for the sample deposited with high bias voltage and 0.26 to 0.28 Å⁻¹ for the sample deposited without bias voltage corresponds to

the spacing of (002) graphitic planes with a literature value of 0.30 Å⁻¹ in highly ordered pyrolytic graphite [12]. For the sample deposited at high bias voltage, the peak is significantly shifted to higher q, which Kulikovsky et al. ascribe to a compression of the interplanar spacing [21]. It is also close to 0.35 Å⁻¹ which would correspond to the distance of 2.84 Å between carbon atoms on opposite sides of the hexagonal rings [12]. It would however be surprising to find evidence of many hexagonal rings instead of evidence of the (002) spacing for the sample deposited at high bias voltage. The 2nd and 3rd peak appear at a q value of \approx 0.41 to 0.44 Å⁻¹ and \approx 0.87 to 0.90 Å⁻¹ respectively for both samples [21]. The 2nd peak aligns well with the peak at \approx 0.4 Å⁻¹ and the lattice spacing in graphene. The 3rd peak is located at significantly higher q than the peak at \approx 0.7 Å⁻¹ and the next-neighbor distance in graphene. This shift suggests a closer next-neighbor distance, which would be somewhat surprising.



4.3.4 FEM analysis

Figure 4.13: Normalized variance curves for all probe sizes a) for the nm-thin a-C sample, b) for the Å-thin a-C sample.

Figure 4.13 shows the normalized variance curves for all probe sizes for the Å-thin sample and the nm-thin sample, respectively. For the nm-thin sample, the first peak is at q = 0.2 to 0.25 Å⁻¹ and the 2nd peak at $q \approx 0.45$ Å⁻¹. A 3rd peak is very slightly discernible at q > 0.7 Å⁻¹ in the curves corresponding to smaller probe sizes up to 7 Å, but not visible in the curves corresponding to bigger probe sizes. For probe sizes up to 15 Å the first peak is higher than the 2nd peak. The peak height ratio of the first and 2nd peaks is maximal between 5 Å and 10 Å and then continuously decreases. The 3rd peak (where visible) has a height between those of the first and 2nd peaks. However, the continuous increase in $V_N(q, Q)$ with q should be noted, as it impairs a meaningful

comparison of peak heights at different q. More useful information can be gained by comparing the heights of a peak for different probe sizes. The height of the first peak increases when the probe size is increased from 3 Å to 5 Å, slightly declines for a probe size of 7 Å and reaches its pronounced maximum at a probe size of 10 Å, before monotonically declining with further increase in probe size. This suggests a correlation length of the structural features corresponding to the first peak of 10 Å. For the 2nd peak, the height undergoes qualitatively similar changes with changing probe size. Notably, it likewise features a slight decrease in peak height at a probe size of 7 Å. No meaningful conclusions about the peak heights can be made for the supposed 3rd peak because the signal is so low that the slight differences between the lower probe size curves that show peaks are lost in noise and the remaining curves show even stronger noise contributions. The q positions of the first peak show some variation with probe size, decreasing from 0.25 Å⁻¹ to ≈ 0.22 Å⁻¹ at 10 Å, at which point there is little change with further increase in probe size. A q dependence of peak positions could be connected to corrugations, which were recently shown to exist in graphene by Singh et al. [38]. Possibly the local curvature leads to small shifts of the peaks and different corrugation length scales existing simultaneously are probed by different probe sizes.

There is no peak discernible at a q of ≈ 0.35 Å, which would correspond to the distance of 2.84 Å between carbon atoms on opposite sides of the hexagonal rings in graphite or graphene [12]. The absence of this peak also in the normalized variance again implies a low portion of hexagonal rings in the structure. This corresponds well to what is seen in the ADF images on the monolayer patches of the Å-thin sample. Also, there is no peak discernible at a q of ≈ 0.30 Å, which would correspond to the spacing of (002) graphitic planes [12]. The interlayer-peak might have been expected from the ADF images on the monolayer patches of the Å-thin sample suggesting layered growth. However, in conjunction with a high proportion of non-hexagonal rings and considering that non-hexagonal rings can lead to strong local curvature (as exemplified by fullerenes) [12] it seems reasonable that there could be no graphite-like interlayer spacing even in case of layered growth.

For the Å-thin sample only the first peak at q = 0.2 to 0.28 Å⁻¹ is discernible and only for probe sizes up to 15 Å. Its height decreases with increasing probe size, with a clear maximum at the smallest probe size of 3 Å. The peak is quite broad compared to the first peak of the nm-thin sample. This and the weak signal make any meaningful statement about the peak positions difficult, it seems to show little dependency on probe size except for a slight shift to lower q for the 5 Å probe size. Also in the case of the thin sample with increasing q the curves show a decrease in SNR and a monotonous increase in $V_N(q, Q)$.

That the SNR decreases with increasing scattering angle q is expected, as there are less electrons scattered to higher scattering angles. The monotonous increase in $V_N(q, Q)$ however is unexpected. Notably, its contribution roughly increases with probe size, albeit for the thin sample with the exception of probe sizes 3 Å and 7 Å. We explored a number of possible sources for this artifact: One source could be shot noise, as its contribution gets more significant compared to the lower signal as is the case at higher q. It can even lead to spurious peaks [26]. However, if it was shot noise then its effect for the thicker sample should be significantly lower, while it is only slightly lower in our data.

It should be noted that due to the low dynamic range of the CCD and the weak signal from our samples, the direct beam was overexposed for all speckle patterns contributing to this analysis. The tail of this bright peak spans the whole *q*-range of the detector, adding a diffuse background. This has not been a problem in earlier experiments on quantifoil using the same setup, as the ones shown in section 4.3.4 and the low-*q*-region where the peak is strongest is not used in the FEM analysis. At first thought, one would expect effects connected to this to fall off in a Gaussian manner with *q*. If however, the signal decreases faster than the tail of the direct beam, a positive *q*-dependence could result. The issue of overexposing the central beam could be mitigated in future experiments by using a significantly lower exposure time with a significantly higher spatial sampling.

Effects connected to the electron beam include beam current decrease and beam flicker. The effect of the beam current decrease was checked for by inspecting the mean intensities of all speckle patterns acquired over the 4 min total acquisition time in a representative dataset, its decrease was not significant. Beam flicker is problematic for FEM because it introduces an additional contribution to the variance, which should be proportional to the intensity [26]. Especially in interplay with the strong diffuse background from the direct beam tail artifacts could appear.

Other effects connected to the detector could play a role. Effects for CCDs include e.g. variations in gain per pixel, variations in quantum efficiency per pixel, and readout noise. However, they should be largely dealt with by the application of a dark reference and a gain reference to every diffraction pattern (DP) as is standardly implemented in our setup. However, the datasets were taken very shortly after major service works on the microscope. Those included a column split, baking, and detachment of the CCD. Following this and the realignment of the CCD new references were taken and applied in the software. A mistake concerning the choice of the right references or a reference not being applied can not be ruled out.

Lastly and notably, when scrutinizing the analysis and the data, a large number of negative pixel values were found. The higher q, the more negative values and starting at \approx half the q-range of the detector there were more negative than positive values found. Finding negative pixel values is surprising because one would expect to obtain only positive pixel values from a CCD. Eliminating those negative values by adding the minimal value found in any speckle pattern to all pixels of all speckle patterns in the dataset did however not lead to any significant difference in the resulting normalized variance curve. This suggests that the algorithm is robust against negative pixel values, which is not self-evident as square roots are taken during the analysis. However, still another source of negative values was found, the subtraction of background streaks. This step is performed via the py4DSTEM functions "get_bksbtr_DP" and "get_darkreference" following the standard procedure and it would be surprising if it changed the data in a detrimental way. However, incompatibility of this procedure with the specific data or specific other functions used in the analysis or further mistakes in the analysis cannot be fully ruled out. In conclusion, the negative pixel values are worrying because they could hint at possible problems in the analysis or the data itself.

Peak fitting on this experimental data would be impaired by the discussed artifact. One could treat the artifact as a linear background and subtract it as done in fig. 4.14 for the nm-thin sample. For the Å-thin sample, this was not done, because the direct beam peak extended to *q* for small probe sizes produces too much ambiguity in the choice of linear fit. However, also for the nm-thin sample there is no good physical explanation for the linearity of the artifact. Accordingly, there is no physical grounding for this particular "background removal". Additionally, while for intensity signals as in EELS fitting in order to isolate overlaying signals is common practice, it is less clear how to justify this for variance data. For those reasons, fig. 4.14 should be taken with a pinch of salt, and the interpretation of results was conducted using the original normalized variance curves.

One other artifact visible in the dataset of the Å-thin sample is the steep increase of $V_N(q, Q)$ at small q in case of the 3 Å probe size. One source for this artifact could be saturation from the direct beam. For a small probe size in interplay with a very thin sample, it can cause high intensity at slightly higher q. Another possible source for this artifact is connected to the fact that two datasets were combined for this particular analysis. If the centering was not perfect, the two not perfectly overlapping direct beam discs would result in their effect reaching slightly



Figure 4.14: Normalized variance curves for all probe sizes for the nm-thin a-C sample, with linear subtraction of unknown artifact.

higher q values. Also, reflections inside the microscope can lead to the overlay of a 2nd shifted image and cause similar effects.

Comparison of the FEM results of the two samples of different thicknesses is limited to the first peak as this is the only one clearly discernible for the thin sample due to weak SNR. The most significant difference is that the peak height maximum for the Å-thin sample is at the smallest probe size of 3 Å, while it is at a probe size of 10 Å for the 50 Å thick sample. This suggests that the structural correlation length in the thick sample is significantly longer than in the thin sample. Additionally, for the thin sample the peak is broader. This could suggest more variation in the structural features corresponding to the peak. However, it could also be connected to the low SNR or be an artifact of a badly tuned probe, e.g., of residual astigmatism.

Comparison with experimental data on quantifoil

The experimental data acquired on our magnetron sputtered samples, especially the ticker one, are in the following compared to experimental data on the a-C layer found on "Quantifoil" TEM grids, in the following referred to as just "quantifoil". Although the nominal thickness of the a-C was 50 Å, this should be taken with a pinch of salt, because the thickness of the a-C in question was not experimentally verified, and at the time of writing the retailer of quantifoil offers only grids with a-C layers of thickness 10 to 12 Å [32]. Unfortunately, the retailer of quantifoil does not reveal any details concerning the production of the a-C layer [32]. The data on quantifoil was acquired by Murray Gibson using the same experimental setup at our Nion microscope and analyzed by him using Mathematica code similar to our python analysis code.



Figure 4.15: Experimental normalized variance curves on quantifoil of nominal thickness 50 Å. Data obtained by Murray Gibson with the same experimental setup, normalized variance calculation performed by Murray Gibson using Mathematica code similiar to our python analysis code.

The $V_N(q, Q)$ curves calculated on the experimental data of our magnetron-sputtered Å-thin a-C and the Å-thin quantifoil a-C show good correspondence of peak positions for the first two peaks. There is no 3rd peak in the quantifoil data in the range of the supposed 3rd peak from our magnetron sputtered a-C. However, there is a 3rd peak at ≈ 0.85 Å⁻¹ and the relative peak heights differ. While for the magnetron sputtered a-C the first peak at 0.2 to 0.25 Å is higher than the 2nd peak at ≈ 0.45 Å for probe sizes up to 15 Å, for quantifoil the 2nd peak is slightly higher for probe sizes up to 10 Å, and significantly higher for probe sizes of 20 Å and above. This suggests that although similar structural features corresponding to the first two peaks are present in our data and the quantifoil data, which one is dominant differs. Also, for the quantifoil data the maximum peak height is reached at the smallest probe size of 5 Å compared to at 10 Å for the thick PVD sample, while it agrees to the thin PVD sample that also shows a peak height maximum at the smallest probe size. Notably, for quantifoil the peak height decreases monotonically with probe size for the first peak, similar as for the thin PVD sample. For the 2nd peak in the quantifoil data there is a decreasing trend of peak height with probe size, but it is not monotonous. Instead, the 20 Å probe size peak is higher than the 10 Å probe size peak and the 65 Å probe size peak is higher than the 35 Å probe size peak. That both peaks reach their maximum height at the smallest probe size suggests a correlation length scale of \geq 5 Å.

Comparison with experimental data from literature on diamond-like a-C

Chen et al. [11] performed FEM on 30 nm-thick diamond-like a-C produced by pulsed-laser deposition and annealed at different temperatures. Their low-temperature annealed diamond-like films have a supposed percentage of sp^3 coordinated atoms of 80%. Their normalized variance curves have peaks at 0.49 Å⁻¹ and 0.85 Å⁻¹. For their samples annealed at 1000°C an additional peak at 0.29 Å⁻¹ appears, which they connect to the graphitic interlayer distance [11]. There is little to no correspondence between their normalized variance curves and those obtained on our samples, which suggests that our samples neither have diamond-like ordering with a high proportion of sp^3 bonds nor feature layers with a homogenous interlayer spacing like graphite. There is however good correspondence with the experimental data on quantifoil, specifically for the two peaks at 0.49 Å⁻¹ and 0.85 Å⁻¹. As those peaks correspond to diamond-like ordering, this suggests that quantifoil has more diamond-like ordering with a higher proportion of sp^3 -bonded atoms.

Comparison with experimental data from literature on sp^2 -and- sp^3 -coordinated a-C

Ryu et al. performed and correlated 4D-STEM and STEM-EELS on an a-C stack produced in a manner similar to our samples via DC sputtering. They however varied the Ar pressure during deposition and so achieved two layers (the lower layer with \approx 66 mbar, the upper layer was deposited with \approx 6.6 mbar) with distinct structures, and subsequently investigated a cross-section of the sample. 4D-STEM data was acquired with a nm-sized probe and analyzed in terms of the radial intensity yielding bond lengths and also in terms of the radial variance. While the overall radial average intensity shows only weak diffuse peaks, the overall radial variance shows two distinct peaks at ≈ 0.45 Å⁻¹ attributed to graphitic structures, and ≈ 0.85 Å⁻¹ attributed to diamond-like structure [39], which was stronger for the upper layer. Those peaks correspond well to the experimental data on our magnetron-sputtered samples and on quantifoil. Note however, that for our magnetron-sputtered samples it is hard to make reliable statements about the peak at ≈ 0.85 Å⁻¹ and corresponding possible diamond-like structure due to the low SNR. Ryu et al. additionally performed STEM-EELS to obtain information about local coordination. They found signatures of both sp^2 and sp^3 bonding, with more sp^3 bonding in the upper layer, corresponding well to the results of their 4D-STEM analysis [39].

Comparison with structural models from recent literature

Caro et al. [40] performed atomistic simulations of the deposition and growth of a-C by PVD. The interatomic interactions for those simulations are described by a machine learning (ML) based Gaussian approximation potential model [40]. They produced a range of different structural models by varying the deposition energy of the carbon ions [41]. The structure of the models changes with this impact energy. Low impact energy leads to sp^2 -rich structures, whereas high impact energy leads to a higher proportion of sp^3 -bonded atoms [40]. In some PVD systems, the deposition energy can be changed by varying the bias applied between the sputter target and sample substrate. This however is not possible in our setup where no bias can be applied.

The simulations of diffracted intensity and normalized intensity variance data on those models [41] were conducted by Murray Gibson via Mathematica code. The results of those simulations on models produced with deposition energies ranging from 1 eV to 100 eV are shown in fig. 4.17.

Because in our PVD deposition setup no bias voltage can be applied it is difficult to tell the deposition energy. One might assume that it is close to zero because the particles are not accelerated towards the sample. The atoms can still possess a wide range of excess kinetic energies from being sputtered and potentially lose energy by colliding with Ar or other gas molecules on their way to the sample. Making quantitative statements about the deposition energies for our PVD grown samples would require simulations and would result in an energy range. It is nevertheless interesting to compare the experimental data to all four models as they represent a range of structures with different sp^2 to sp^3 ratios, with the 1 eV model representing the highest and the 100 eV model representing the lowest sp^2 to sp^3 ratio.

The simulated radially averaged diffracted intensities show peaks at q = 0.25 to 0.33 Å⁻¹, 0.44 to 0.48 Å⁻¹, and 0.8 to 0.9 Å⁻¹ (compared to the experimental peaks at q = 0.2 to 0.25 Å⁻¹, ≈ 0.45 Å⁻¹, and 0.7 to 0.8 Å⁻¹) plus an additional peak at a lower q values of ≈ 0.15 Å⁻¹ for higher deposition energies. The 2nd peak is the strongest and notably shifted to higher q for the 5 eV model and the 3rd peak tends to higher q with higher deposition energies. This could be taken as suggesting similar SRO compared to our samples but with some compression of the atomic spacings corresponding to the 2nd and 3rd peaks.

The simulated $V_N(q, Q)$ on the models [41] shows weak peaks in the range accessed by our experimental data and strong peaks at $q \approx 0.1$ Å⁻¹ (not shown in fig. 4.17 where the q range is reduced



Figure 4.16: Simulated normalized variance data on a-C models [41] from [40]. Model parameters: thickness of a-C film \approx 50 to 70 Å, deposition energies 1 to 100 eV



Figure 4.17: Simulated normalized variance data on a-C models [41] of \approx 50 to 70 Å thickness from [40] with deposition energies a) 1 eV, b) 5 eV, c) 20 eV, d) 100 eV.

to the experimentally accessed q range). Those peaks would correspond to correlated atomic spacings of \approx 10 Å, which could be explained by fullerene-like structures where inter-atomic distances span the range of 1.4 to 7 Å [12]. However, a proportion of fullerene-like structures making this feature so dominant would be surprising and is not seen by visual inspection of the 3D atomic structure models of Ref. [40]. The peak might rather be an artifact of some kind. The 1 eV model presents a broad peak at 0.2 to 0.4 $Å^{-1}$ and another broad peak at 0.45 to 0.7 $Å^{-1}$. The height of the former is maximal for the smallest probe size of 5 Å and decreases with increasing probe size, suggesting a structural correlation length of ≤ 5 Å. The height of the latter shows little dependence on probe size compared to the noise level. Both peaks are broader and lie at higher *q* values than the comparable peaks in all experimental datasets. The correlation length deduced from the first peak matches that of the Å-thin magnetron sputtered sample and that of the quantifoil sample. The 5 eV model presents a narrower peak at 0.25 to 0.38 ${\rm \AA}^{-1}$ and another broad peak at 0.45 to 0.7 Å⁻¹. The height of the former has a maximum for a probe size of 10 Å, suggesting a structural correlation length scale of 10 Å. The height of the latter is maximal for the largest probe size of 50 Å, suggesting a structural correlation length scale of \geq 50 Å. The correlation length scale deduced from the first peak matches that of the 50 Å thick magnetron sputtered sample, the correlation length deduced from the latter however does not match the experimental data. The 20 eV model presents yet narrower peaks at 0.2 to 0.3 $Å^{-1}$ and 0.5 to 0.6 $Å^{-1}$ and an additional peak at 0.4 Å⁻¹ for probe sizes \geq 17.5 Å. The height of the latter two peaks is maximal for the largest probe size of 50 Å suggesting a structural correlation length of \geq 50 Å. From the first peak, it is difficult to deduce a correlation length. On the whole, the 20 eV model shows little similarity to the experimental data. The 100 eV model presents comparably narrow peaks at 0.2 to 0.3 $Å^{-1}$ and at 0.5 to 0.55 $Å^{-1}$. The height of the former is maximal for the smallest probe size of 5 Å and decreases with increasing probe size, suggesting a structural correlation length of \leq 5 Å. The height of the latter is maximal for the largest probe size of 50 Å and decreases with decreasing probe size, suggesting a structural correlation length of \geq 50 Å. The 100 eV model shows more likeness to the experimental data than the 20 eV model, however, the similarities are rather limited. Notably, for all but the 20 eV model the peak at q = 0.2 to 0.5 Å⁻¹ is significantly higher than the one at 0.4 to 0.7 $Å^{-1}$. This roughly corresponds to the experimental data on the 50 Å thick magnetron sputtered sample, however, the comparable peaks for the experimental data appear at lower q. The apparent large correlation length scales of \geq 32.5 Å corresponding to the higher-q peaks for all but the 1 eV sample are contrary to the correlation lengths of all our experimental data. However, as they are also contrary to the small correlation length scales corresponding to the lower-q peaks they might rather be an artifact. At large, there is only mediocre

correspondence between any of the simulations on the models and the experimental data.

Sample purity

One remaining question is the purity of our magnetron-sputtered a-C samples. We assume that oxygen contamination which we found in our evaporated a-Si is much less of an issue for our a-C samples because of the carbon-oxygen-bond being weaker than the silicon-oxygen-bond [42] and the sputtering taking place at room temperature, hence providing less activation energy for reaction with residual oxygen in the chamber.

Another atomic species frequently found in a-C is hydrogen. Cho et al. [43] studied the sp^2 to sp^3 ratio of 100 nm thick magnetron sputtered a-C via nuclear magnetic resonance. Their samples were produced in a very similar manner to our samples, by DC magnetron sputtering at room temperature, using graphite as a target and Ar as sputter gas. The difference is that they added a variable amount of hydrogen gas to the argon. They don't specify how much hydrogen was added, but their resulting samples contain 13 to 35% H. The sp^2 to sp^3 ratio in those samples is found to be relatively independent of the H concentration in this range. Only above 23% H sp^3 bonded carbon atoms are found to be saturated by H. Comparing these results to our case, where no hydrogen was added on purpose, suggest that even though we cannot rule out some hydrogen content in our a-C samples, the concentrations should be so low as not to significantly influence sp^2 to sp^3 ratio.

4.3.5 Sources of uncertainty in FEM

Performing FEM in a STEM involves two experimental challenges: generating a suitable probe and accurately measuring the speckle patterns. The main difficulty in generating the probe is keeping it coherent because the sensitivity of FEM to MRO depends on coherent diffraction across the illuminated volume. Also, to be precise, the measured coherence length scales in the sample are determined by the probe coherence length rather than simply the probe size. Accordingly, if the coherence of the probe is insufficient it is very hard to draw any conclusions about the coherence length scales in the sample [26].

Additionally, aberrations affect the illuminated sample volume and lower probe coherence. During data acquisition care was taken to minimize aberrations by manual fine-tuning of focus and astigmatism after every change of probe size and of focus whenever moving to another sample area. However, with increasing probe size manual tuning becomes more difficult due to the decreased resolution.

The main hurdle concerning the detection of the speckle patterns is noise. One noise contribution is shot noise. It is especially relevant in case of thin low-atomic-number samples such as ours. Shot noise is Poissonian and has a \sqrt{I} dependence on the intensity *I*. In typical STEM imaging and diffraction shot noise is small compared to the number of counts, however, as in FEM small variations from the average intensity are analyzed, and its contribution becomes significant. Shot noise introduces a systematic error as well as a random uncertainty to V_N . The systematic error is an additive term proportional to the reciprocal of the average intensity $\frac{1}{\langle I \rangle}$, the random uncertainty is $\frac{2\sqrt{2}}{\sqrt{N \langle I \rangle}}$ where N is the number of spatial samples, i.e., probe positions. The shot noise contribution generally increases strongly with increasing *q* (it grows with q^4 , since the $I \propto \frac{1}{q^4}$). Especially problematic is that shot noise may have a *q*-dependence. The maxima in both the systematic and the random contribution occur at minima of I(q) and therefore reduce the visibility of peaks even more. Also, it is possible that spurious peaks appear. Both shot noise contributions can be minimized by increasing the signal intensity. The random uncertainty can additionally be minimized by increasing the signal intensity.

An increased signal intensity can be accomplished by increasing the exposure time. This however will increase the time needed for acquisition. Also, a longer exposure increases the electron dose, which has to be done with care for beam-sensitive samples. Increasing the spatial sampling is a better option for increasing the SNR. It however also increases the acquisition time and more importantly increases the size of the datasets which complicates their handling and increases the computing power necessary to analyze them. In our current setup, the acquisition of a single dataset with one probe size and 1024 probe positions takes 4 to 5 min and it will have a size of \approx 17 GB. Another contribution to experimental noise comes from the camera, in our case a CCD, affected amongst others by dark current and readout noise.

Additional contributions to experimental noise come from variations in the electron beam intensity, so-called "beam flicker", and from thickness variations in the sample. Those two contributions, regardless of their different origins lead to a similar type of noise, producing an additive systematic error proportional to some constant and a random uncertainty that is again proportional to $\frac{1}{\sqrt{N}}$, the reciprocal of the square root of the spatial sampling. Beam flicker is a significant contribution for c-FEGs [26].

Sample thickness variations are present in our samples as seen from fig. 4.11. The relative thick-

ness fluctuations are assumed to be less pronounced in the nm-thin sample compared to the Å-thin sample, considering the bigger number of deposited atoms together with the law of big numbers [44].

Chapter 5

Conclusions and outlook

5.1 Conclusions

We successfully produced a-C samples of nm and Å thickness by PVD (specifically, magnetron sputtering without bias voltage). ADF imaging of monolayer patches of the Å-thin sample shows random polygons, similar to the structures found by Refs. [8, 34, 35] for monolayer a-C produced by other deposition methods. Our ADF images suggest layered growth which would lead to predominantly sp^2 bonding.

The main structural analysis was performed via FEM on both samples. For the Å-thin sample, our current detector's SNR was not sufficient to resolve anything but the first peak. This peak however as well as the results for the nm-thin sample correspond to graphite-like structures with a low proportion of hexagonal rings, in accord with what was suggested by the ADF imaging. Conclusions about the influence of sample thickness on structure are limited, but what the data does suggest is a significantly shorter correlation length scale in the Å-thin sample compared to the nm-thin sample. We also compared the experimental data on our samples to data on nm-thin a-C found in commercial "Quantifoil" TEM grids [32] and to simulations on recent structural models of a-C formed with different deposition energies. While we found reasonable correspondence with quantifoil, the correspondence with any of the models was at best mediocre. This could hint at the models just not modeling magnetron sputtering well. Also, it should be noted that our PVD setup did not allow precise control over the deposition parameters, most notably the deposition energy.

What should also be noted is that during the analysis of our data, we encountered a so far not fully

explained artifact that could hint at problems in the data acquisition setup or the data analysis code. This artifact should not qualitatively change the conclusions about the structure of the materials. However, before our FEM setup is used for further projects it should be diligently scrutinized. A helpful approach to narrow down the sources of errors leading to the observed artifacts would be, for example, to artificially create datasets featuring various artifacts using image editing software. By running the analysis code on them, one can test the influence of these artifacts on the analysis.

5.2 Outlook

Concerning the determination of correlation length scales, there exists a second, more quantitative, method in addition to directly comparing the peak heights. Gibson et al. developed a method of extracting the correlation length scale, valid for the case of paracrystalline samples and the assumption that the pair-pair-correlation function has a Gaussian form [3]. The method can be applied to variable resolution FEM datasets, like the ones we acquired. Unfortunately, this method could not be successfully applied to our datasets, because the quality of our normalized variance curves did not allow for the method to yield meaningful results. This is likely connected to the artifacts discussed in section 4.3.4. Anyways, the reader interested in the method is referred to Ref. [3].

Concerning the type of datasets, variable resolution FEM is not the only possibility, but there also exists variable coherence FEM [23]. When both resolution and coherence are varied, so-called fluctuation maps can be obtained. Those maps contain the maximum amount of information obtainable by FEM at the point of writing this thesis. Gibson et al. showed [3] that fluctuation maps directly measure a so-called pair-persistence function. It is named like this because it corresponds to the pair-pair correlations in the sample and the length scales at which they decay.

FEM on itself does not directly yield the atomic structure [2]. In this project, we relied heavily on comparisons with experimental data and computer models from the literature for structural interpretation of the data. However, in the literature, also the possibility to obtain structural models directly from FEM data via reverse Monte Carlo methods has been explored [28] and seems like a promising path for FEM. If at some point in the future, possibly with a direct electron detector implemented in our setup, there can be FEM data of high quality obtained, it would be worthwhile to try to apply reverse Monte Carlo methods to it. Additionally, to determine the structures of amorphous materials, ideally, global and local information should be acquired as given global structure parameters do not correspond uniquely to structural models [9]. So FEM, which provides global statistical information would be well complemented by techniques that provide local information.

If one had a sample with large monolayer regions like in Refs. [8, 34, 35] one could perform atomic resolution imaging and ring statistics [8], optimally on a large scale using scan maps and automated atom and bonding recognition like in [45, 46]. Then additionally performing FEM on the same thin samples, which hopefully be possible in our setup with a prospective direct electron detector would yield a direct correspondence between atomic positions in 2D and the FEM data. This could be very helpful for verification and further development of FEM.

One more information one could wish for is knowing the 3D atomic structure of the sample on which FEM is performed. An approach for reconstructing the 3D atomic positions of small portions of material is atomic electron tomography. This method combined with atom-tracing algorithms has been used to image the 3D structure of grain boundaries and defects at atomic resolution [47] and also recently to determine the 3D structure of amorphous materials, mainly nanoparticles [48, 49], simulations have been performed on an a-Si nanoparticle [50]. Tomography on thin films is more challenging, because images acquired at different tilt angles contain different volumes of the thin film, but was accomplished for an amorphous Ta thin film via a a specialized iterative reconstruction algorithm [49].

Ptychotomograpy, a technique where multiple ptychographic images at different tilts are used for reconstruction at lower electron doses seems a promising approach to minimize damage or structural change to the sample while imaging [51, 52]. To my knowledge, at the time of writing ptychotomography has not been attempted on amorphous thin films. However, it appears feasible at least for thicknesses of a few atomic layers and with a detector allowing for sufficient SNR, especially for beam-sensitive materials like amorphous carbon. Those requirements should be met by our prospective future setup equipped with a direct electron detector. Ptychotomography would be useful in combination with FEM firstly again for verification and development of FEM analysis. Secondly, one could on the experimental 3D structural models obtained via ptychotomography simulate FEM and compare the simulation results with experimental FEM data on the same sample. Thirdly, one could use FEM to verify the statistical significance of results obtained via defocused probe ptychotomography on small sample volumes by performing FEM both on the ptychography datasets and on a regular FEM dataset taken over orders of magnitude bigger sample areas.

For the latter method to be feasible, two hurdles need to be considered. Firstly, the variably-sized FEM probes are not produced by simply going out of focus and it is important to keep the FEM probe as focused as possible in order not to impair its coherence [26]. So to be precise, the defocused probe ptychography datasets would need to be acquired with a FEM probe and not with a merely defocused probe. The effects of such a probe on the ptychographic reconstructions remain to be tested. Secondly, FEM, which is typically performed on spatially undersampled datasets (i.e., the illuminated sample volumes for different probe positions do not overlap to ensure statistical independence) should be robust against oversampling, because the datasets used in defocused probe ptychography are oversampled. From reasoning based purely on the influence of statistical independence or dependence on variance, one would expect this to be the case. However, this simple assumption needs to be scrutinized.

We shortly tested the robustness of FEM against oversampling on an oversampled "ptychoFEM" dataset (on 50 Å-thick a-C layer with graphene) by comparing the normalized variance calculated on the full oversampled dataset with the normalized variance calculated on a non-oversampled subset. We found no significant difference in the normalized variances calculated from oversampled "ptychoFEM" datasets and their non-oversampled subsets, as shown in fig. 5.1. This suggests that FEM is at least to some degree robust against oversampling and could be performed on defocused probe ptychography datasets. Comparison with regular FEM datasets taken at the same or nearby sample areas shows that one of the peaks resolved there was not resolved by the "ptychoFEM" datasets. This could be connected to the smaller FOV and suggest that the corresponding structural feature was just not present in the "ptychoFEM" areas. It could also hint at the corresponding structural feature disappearing due to beam damage from the higher dose per area. However, it could also hint at a more fundamental problem with comparing FEM from datasets with different spatial sampling densities.

Notably, also the normalized variance is significantly higher for the "ptychoFEM" datasets compared to the regular FEM datasets. The strength of this effect is dependent on the ratio of the respective FOVs. In order to reach overlap with the same number or probe positions the FOVs were 8 nm for 20 Å probe size, and 32 nm for 20 Å probe size, while they were 128 nm for the regular FEM datasets. What causes this effect has to be further examined in the future. So far it should be noted that when the relative peak heights between different probe positions are to be examined, the FOV and spatial sampling should be kept the same for all probe positions.



Figure 5.1: Comparison of normalized variances calculated from oversampled "ptychoFEM" dataset, non-oversampled subset of this dataset, and regular FEM dataset a) recorded with probe size of 5 Å and FOVs of 8 nm, 8 nm, and 128 nm respectively, b) recorded with probe size of 20 Å and FOVs of 32 nm, 32 nm, and 128 nm respectively.

Another possibly complementary STEM technique is EELS. EELS does not only allow element identification but upon more detailed analysis can reveal structural information about bonding states, nearest-neighbor distributions, and coordination numbers as well as information about electronic structures, band gaps, or dielectric constants [12, 39, 53]. Firstly, a fundamentally different method of acquiring SRO structural information of a given sample is useful to cross-check and cross-correlate results, as was done in Ref. [39]. Secondly, with atomic resolution EELS this kind of information can be acquired very locally, to a degree hardly possible with FEM. Lastly, gaining information on electronic properties that are influenced by SRO and MRO that are measured by FEM would be highly interesting.

In conclusion, to thoroughly understand the structure of amorphous materials optimally structural information on different scales should be acquired. This could be achieved by combining multiple techniques. FEM is well-established for the study of statistical parameters of the structure of amorphous materials, but the technique is still developing in interesting directions. Other techniques like ptychography, tomography and EELS would be worthwhile to explore and test for the complementary structural and other information they can yield and how it can be correlated to the information yielded by FEM or even help to further develop FEM.

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