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Atomic resolution imaging of light elements in low-dimensional materials

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DOI:
[10.33612/diss.192304075](https://doi.org/10.33612/diss.192304075)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2021

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):
de Graaf, S. (2021). *Atomic resolution imaging of light elements in low-dimensional materials*. [Thesis fully internal (DIV), University of Groningen]. University of Groningen. <https://doi.org/10.33612/diss.192304075>

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Atomic resolution imaging of light elements in low-dimensional materials

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PhD thesis
University of Groningen
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The work described in this thesis was performed in the Nanostructured Materials and Interfaces research group of the Zernike Institute for Advanced Materials at the University of Groningen, the Netherlands. This research was supported by the Zernike Institute for Advanced Materials.

Cover design by Janny de Graaf
Printed by Gildeprint

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Atomic resolution imaging of light elements in low-dimensional materials

PhD thesis

to obtain the degree of PhD at the
University of Groningen
on the authority of the
Rector Magnificus Prof. C. Wijmenga
and in accordance with
the decision by the College of Deans.

This thesis will be defended in public on
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To my family

CONTENTS

1.	INTRODUCTION	1
1.1	Scaling down: materials at the limit	2
1.2	Zooming in to the atomic scale.....	4
1.3	Outline of this thesis	7
1.4	References	8
2.	SCANNING TRANSMISSION ELECTRON MICROSCOPY: OPTICS, RESOLUTION AND CONTRAST	13
2.1	Operating principles of a scanning transmission electron microscope	14
2.2	Probe forming optics and electromagnetic lens aberrations	15
2.3	Probe spherical aberration correctors	20
2.4	High-brightness electron sources and electron monochromators	25
2.5	Image formation theory within the phase object approximation	27
2.6	Z-contrast imaging: high-angle annular dark-field	31
2.7	Imaging of light and heavy elements: integrated differential phase contrast.....	33
2.8	References	40
3.	SPECIMEN PREPARATION METHODS	45
3.1	Scanning electron microscopy: Imaging and structure analysis	46
3.2	Specimen preparation of bulk materials using the focused ion beam technique	47
3.3	Specimen preparation of two-dimensional materials.....	49
3.4	References	52
4.	IMAGING ATOMIC MOTION OF LIGHT ELEMENTS IN 2D MATERIALS WITH 30 kV ELECTRON MICROSCOPY	57
4.1	Introduction	58
4.2	Results and discussion	60
4.3	Conclusions	68

4.4	Experimental methods	68
4.5	References	69
4.6	Appendix	72
5.	RADIATION DAMAGE AND DEFECT DYNAMICS IN 2D WS₂: A LOW-VOLTAGE SCANNING TRANSMISSION ELECTRON MICROSCOPY STUDY	87
5.1	Introduction	88
5.2	Results and discussion	89
5.3	Conclusions	102
5.4	Experimental methods	102
5.5	References	103
5.6	Appendix	106
6.	RESOLVING HYDROGEN ATOMS AT METAL-METAL HYDRIDE INTERFACES	113
6.1	Introduction	114
6.2	Results and discussion	116
6.3	Conclusions	124
6.4	Experimental methods	125
6.5	References	126
6.6	Appendix	129
7.	SUMMARY	153
8.	SAMENVATTING	157
9.	LIST OF PUBLICATIONS	163
10.	ACKNOWLEDGEMENTS	167

Chapter 1

Introduction

Abstract

Smartphones, batteries, solar cells, there are many applications that rely on materials that have been scaled down to the level of only several atoms. As the world at the atomic scale is becoming more and more entangled with our daily lives, it is progressively more important to understand how materials behave at such incredibly small sizes. The most advanced electron microscopes can resolve the atomic structure of nearly all materials but lack the sensitivity to image light elements next to heavy ones, leaving a large class of materials unexplored at the atomic scale. This thesis is dedicated to the atomic resolution imaging of light elements next to heavy ones, particularly in monolayers of the two-dimensional material tungsten disulfide and in thin platelets of titanium monohydride embedded in titanium. The latter case is a proof-of-principle study that it is possible to image unambiguously the lightest of all atoms, hydrogen, next to more heavy metal atoms in a technologically relevant materials system.

1.1 Scaling down: materials at the limit

Nature has always been a source of inspiration for mankind, with all its beauty and mysteries that extend far beyond what can be seen by the naked eye. Looking up at the starry sky, we may feel small and insignificant in the vast universe with all its stars, planets and galaxies. In contrast, we may feel intrigued by the rather magical microscopic world at the atomic scale, with the tiniest imaginable elemental building blocks of life, the universe and everything¹. To put things in perspective (despite that the size of an atom is loosely defined due to its quantum mechanical nature), an atom is approximately three hundred million times smaller than a golf ball, which in turn is about three hundred million times smaller than the planet Earth. Most of the materials in nature therefore consist of an enormous amount of atoms e.g. there are 20×10^{18} (20.000.000.000.000.000, compared to the current² (July, 2021) world population estimate of 7.875.000.000) silicon and oxygen atoms in one grain of sand. It is not surprising that the macroscopic properties of materials do not depend solely on the nature of individual atoms, but in particular also on their collective arrangement in the form of crystalline or amorphous structures on the micrometer, nanometer and atomic scale. It is exactly these structure-properties relations that the field of materials science studies, in an effort to learn how the beauty and mysteries of nature come about.

For the past decades, there has been a strong driving force to scale down materials towards the nanometer and atomic scale, either for miniaturization purposes or to exploit unique properties that emerge only at those length scales and are not available in their macroscopic counterparts. For instance, the recently introduced extreme ultraviolet photolithography³⁻⁵ has pushed forward the industrial top-down production of nanostructured microelectronic devices (with smallest lateral features of about 13 nm) on centimeter scale silicon wafers, packing more and more transistors on computer chips to keep up with Moore's law, and to improve processing speed and power efficiency of electronic devices like computers and smartphones. On the other hand, nanometer sized pockets of crystalline phases, called precipitates, can be grown automatically by nature in the microscopic grains of macroscopic metals or metal alloys during heat treatment or other processes, making these alloys suitable for the most heavily-loaded parts in for instance airplanes^{6,7}. In fact, it often is a rather complicated geometrical puzzle to embed a crystalline precipitate in a crystalline host metal, as all atoms 'should fit' without substantially disturbing the other phase. Yet, nature

automatically finds the solution to this puzzle by adjusting the shape and orientation of the precipitate to line up as many atoms as possible, which can result in highly asymmetric precipitates such as long needles or thin sheets that are just several (tens) atoms wide^{8–12}. The nature of the precipitates, including the size, shape, crystal orientation relationship with the host material, strain, mechanical properties and interface formation directly affect the macroscopic properties of the host metal (alloy), and are therefore a particularly valuable tool in materials science and engineering to improve material properties.

With bottom-up deposition techniques (sub) nanometer thin films of all kinds of materials (metallic, semiconducting, insulating, magnetic, ferroelectric etc.) can be grown on substrates in an atom-by-atom fashion. Synthetic atomically sharp interfaces and heterostructures of (sub) nanometer films can then be formed, generating novel physical properties for applications in the field of optics, (opto) electronics, sensing, phase change materials and ferroelectrics^{13–16}. Some materials can in fact form stable atomically thin sheets, which leads to the discretization of one or more physical quantities in the thickness dimension which remain continuous in the lateral dimensions, and therefore such materials can be considered two-dimensional (2D) materials^{17–20}. Graphene, discovered in 2004²¹, is the most well-known 2D material, consisting of a single atomic carbon layer. After its discovery, a large number of other 2D materials have been identified, each with different physical characteristics. In particular the discovery of semiconducting (e.g. transition metal dichalcogenides^{22–26}) and insulating (e.g. hexagonal boron nitride^{27–30}) 2D materials, complementing the metallic behavior of graphene, have been crucial for the fabrication of 2D materials-based heterostructure devices, analogous to the standard three-dimensional (3D) silicon-based devices^{31–35}. With only one or few atomic planes, imperfections in 2D materials have a profound effect on many macroscopic properties, and may be intrinsically present (by the laws of thermodynamics), or introduced deliberately by the synthesis procedure. For example, while defects and strain may be beneficial for gas sensing³⁴ and single photon emission^{36,37}, highly perfect crystal structures are desirable for (opto) electronics^{35,38} and electron transport^{19,39}.

Thus, as materials are scaled down towards the atomic level, either by nature or through synthetic means, the influence of single atoms becomes progressively more important for macroscopic properties. Therefore, the microscopic inspection of such materials with single

atom resolution and sensitivity is crucial to complement materials processing and synthesis, and is indispensable to keep advancing the fields of materials science, nanotechnology and engineering.

1.2 Zooming in to the atomic scale

The invention of the electron microscope, as the embodiment of the theory of quantum mechanics and the theory of relativity, is arguably the greatest accomplishment of modern physics. Central to the operation of electron microscopes is the abstract quantum mechanical concept of the wave-particle duality, meaning that the behavior of all matter, no matter if as large as a planet or as small as an electron, can be described sometimes as a wave, sometimes as a particle, and sometimes as either. The wavelength of electron matter waves, taking relativistic effects into account, can be calculated according to⁴⁰

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2m_0eV \left(1 + \frac{eV}{2m_0c^2}\right)}} \quad (1.1)$$

where h is Planck's constant, p the electron's momentum, m_0 the electron rest mass, e the (absolute) electron charge, V the accelerating voltage and c the speed of light. Consequently, the electron wavelength is in the 7-2 pm range when accelerated by a voltage in the 30-300 kV range, as typically used in electron microscopes.

As the fundamental resolution limit of any microscope using a lens or aperture is limited to about half the wavelength according to the Rayleigh criterion, electron microscopes may be expected, to a first approximation, to resolve details down to the (single) picometer scale. This resolution improvement by about five orders of magnitude compared to the 300 nm resolution limit of visible-light microscopes employing an (average) photon wavelength of 500 nm, is the prime reason why electron microscopes have been invented. In practice, however, even state-of-the-art electron microscopes do not reach picometer resolution (due to a combination of engineering limits and fundamental reasons as described in chapter 2), but at best about 50 pm with 300 keV electrons (2 pm wavelength) and about 100 pm with 30 keV electrons (7 pm wavelength). Nevertheless, this resolving power is well below typical

interatomic distances, which is why electron microscopes play a central role in materials science to investigate microstructures of matter with atomic resolution.

The first electron microscope, invented by Ernst Ruska in 1931, soon after the foundations of quantum mechanics and relativity were laid, was of the transmission type, more or less identical to visible-light microscopes, and did not change fundamentally in the following decades⁴¹. In a transmission electron microscope (TEM) a highly accelerated (typically by 200 kV) electron plane wave is transmitted through a very thin specimen, such that an image of the specimen is formed below which is recorded by a camera (Fig. 1.1)⁴⁰.

Figure 1.1. Simplified schematic of TEM and STEM, showing some of the important lenses and emphasizing the different electron ray paths by red arrows. An image of the specimen is formed in parallel with TEM by recording the image with a camera in the detector plane, whereas it is formed sequentially in STEM by recording the intensity of (a part of) the diffraction pattern in the detector plane for every scan position.

Besides an image, also a diffraction pattern is formed, the reciprocal-space representation of the specimen, which results from the scattering of the coherent electron wave by the lattice in case of crystalline materials, and can provide detailed information on crystal structures. Simply by changing the strength of one or more lenses below the specimen, either the image or the diffraction pattern can then be projected onto and recorded by the camera. Once the TEM matured and became a reliable instrument, real-space images and reciprocal-space electron diffraction patterns enabled materials research with higher resolution than ever

before, confirming theoretical ideas like the existence of dislocations in 1956⁴². Since then, TEM has played a key role for the understanding of fundamental materials science.

Atomic resolution images of nearly all (crystalline) materials can be routinely obtained with modern TEM instruments. Although the atomic resolution images are closely related to the interatomic spacings and symmetry of the material, the exact position of atoms or atom columns cannot be readily identified, because some appear as bright dots and some appear as dark dots, and these dots can even be displaced with respect to the atom columns centers. Moreover, the contrast tends to invert when the focus or specimen thickness change (slightly)⁴⁰. This interpretation difficulty is a fundamental result of the interference-based image formation process in TEM, for which there is no straightforward solution.

Nowadays, the majority of materials scientists have switched from TEM to scanning TEM (STEM), as it does have the ability to produce easily interpretable images and also offers other advantages. With STEM an image is acquired sequentially (unlike TEM, where it is acquired in parallel) by raster scanning an electron probe over the specimen and collecting a part of the diffraction pattern with one or more detectors, generating an image pixel-by-pixel (Fig. 1.1). Next to the image(s), also chemical information can be acquired simultaneously with atomic resolution, for instance by collecting emitted characteristic X-rays or by measuring the energy spectrum of the transmitted electron beam, providing a rich structural and chemical dataset of the material of interest at atomic resolution, not possible with TEM.

Easily interpretable STEM images, where atoms or atom columns always appear as bright dots in a dark background, are generated by collecting specifically high-angle scattered electrons with a so-called high-angle annular dark-field (HAADF) detector^{43,44}. The power of HAADF-STEM is not only the ease of interpretation that allows direct identification of the position of the atom(s), but also its Z -contrast nature: the intensity of each bright dot is proportional to the (average) atomic number (Z) to the power 1.6-2.0^{44,45}, such that also the (relative) identification of the element is possible. For all these reasons, HAADF-STEM is the most popular electron microscopy technique in materials science to resolve atomic details of many materials. However, it has one major shortcoming that is a direct consequence of the about Z^2 contrast nature: whenever light elements are present next to heavy elements, then only the heavy ones are resolved and the light ones remain invisible.

Light element imaging has been enabled by the empirically developed annular bright-field (ABF)-STEM technique, which employs an annular detector that collects electrons much closer to the optical axis, but maintains interference effects that complicate interpretation e.g. atoms may sometimes appear as white or black dots, and contrast reversals can also occur^{46–49}. In recent years, partly during this research project, imaging techniques relying on a solid physical understanding of the image formation process have emerged, like differential phase contrast^{50–53} and ptychography^{54–58}, which generate images that are about linear in Z , and therefore combine high sensitivity and easy interpretability.

Many fields in materials science and nanotechnology exploit materials consisting of both light and heavy elements for current but also for future applications. For instance, metal oxides, nitrides, carbides and hydride precipitates in the field of metallurgy, oxide thin films for next-generation electronic devices, 2D materials with a plethora of potential applications, and energy materials like lithium anodes and hydrogen storage materials for sustainable energy purposes. Present day, enhancing sensitivity while maintaining good interpretability of STEM images is therefore one of the big challenges in the field of electron microscopy that needs to be overcome to potentially solve challenging problems in materials science and nanotechnology.

1.3 Outline of this thesis

Synthetic and natural low-dimensional nanostructured materials containing light elements are imaged with atomic resolution using integrated differential phase contrast (iDPC)-STEM. This imaging technique was developed just before the start of the research project, and had promising, but experimentally unexplored imaging characteristics. Chapter 2 introduces the operating principles and resolution limits of a modern STEM instrument, and special attention is given to the image formation process of iDPC-STEM and HAADF-STEM, which were always employed simultaneously in experiments performed in this thesis. Chapter 3 describes the protocols for the preparation of high-quality specimens, which is the most critical step in electron microscopy to obtain high-quality images. Chapter 4 describes the dynamics of single sulfur atoms next to heavy tungsten atoms in the 2D WS_2 which is observed by recording movies using ultralow-voltage 30 kV-STEM. It is demonstrated that the single sulfur atoms are clearly resolved in the iDPC-STEM movies, while they are practically invisible in the HAADF-STEM movies. Chapter 5 elaborates on the electron

radiation damage mechanisms and defect dynamics that occur during (ultra) low-voltage STEM imaging of 2D WS₂ with atomic resolution. The quantitative analysis of damage evolution indicates that ionization is the dominant mechanism leading to a twice as high damage rate during 30 kV-STEM imaging compared to the 60 kV-STEM benchmark. Finally, in chapter 6, the ultimate sensitivity of iDPC-STEM is demonstrated by imaging hydrogen atoms in a particular low-dimensional plate-like titanium hydride precipitate in a host titanium metal.

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Chapter 2

Scanning transmission electron microscopy: optics, resolution and contrast

Abstract

The scanning transmission electron microscope has been invaluable for materials science research, particularly after strong instrumental advancements in the last couple of decades enabling the direct imaging of nearly all hard materials with atomic resolution. In this chapter the operating principles of a scanning transmission electron microscope are treated, in particular the crucial role of advanced electron-optics hardware like field-emission guns, spherical aberration correctors and electron monochromators to form ever smaller electron probes, improving the attainable image resolution. Finally, the image formation process of materials is discussed in the framework of the phase object approximation, focusing specifically on high-angle annular dark field and integrated differential phase contrast imaging, which are the two main imaging techniques used throughout this dissertation.

2.1 Operating principles of a scanning transmission electron microscope

In a scanning transmission electron microscope (STEM), a coherent beam of electrons is generated by an electron source and then accelerated to a specific energy in the range 30-300 keV to attain a wavelength of 7-2 pm according to the De Broglie equation for matter waves. The electrons are then focused into a small probe by demagnifying the electron source with a condenser system consisting of several electromagnetic lenses and an aperture. An image is formed by raster scanning the finely focused electron probe over a thin specimen, and then collecting the transmitted electrons for every scan position with an electron detector below the specimen in the diffraction plane (Fig. 2.1). The final image resolution and contrast are a complex interplay of the size and shape of the electron probe, thickness of the specimen, electron-matter interactions and detector geometry.

Figure 2.1. Schematic of the components inside an advanced STEM, containing the most important electromagnetic lenses, a beam limiting aperture, with the position of the aberration corrector and monochromator indicated. The electron trajectory is indicated by the red arrows.

2.2 Probe forming optics and electromagnetic lens aberrations

The attainable STEM image resolution of a high-quality specimen is predominantly related to the size and shape of the electron probe formed by the optical characteristics of the probe forming lenses. In the condenser lens system, three condenser lenses are used to demagnify the electron source size while providing freedom to change the probe convergence semi-angle by adjusting their relative strength. The final strong focusing action forming the electron probe on the specimen is performed by the (upper) objective lens (Fig. 2.1).

When the electron wave function has a uniform phase front and a circular beam limiting condenser aperture is present, then the expected probe shape formed on the specimen is an Airy disk, which is the best-focused probe possible, only fundamentally limited by the diffraction of electrons with a full width at half maximum (FWHM) given by;

$$d = 0.61 \frac{\lambda}{\alpha} \quad (2.1)$$

Here λ is the electron wavelength and α is the probe convergence semi-angle. Accordingly, in the ideal case, an arbitrarily small probe can be formed by decreasing the electron wavelength or increasing the size of the beam limiting condenser aperture. There are, however, several fundamental electron optical phenomena causing phase variations of the electron wave function, which limit the optimal diffraction of the electron waves leading to probe broadening. To a first approximation, from a geometrical optics perspective, the probe broadening terms can be considered to be independent¹, as follows:

$$\begin{aligned} d_{eff}^2 &= d_{diff}^2 + d_{source}^2 + d_s^2 + d_c^2 \\ &= \left(0.61 \frac{\lambda}{\alpha}\right)^2 + \left(\frac{2}{\pi} \sqrt{\frac{I_p}{\beta}} \frac{1}{\alpha}\right)^2 + (0.5 C_s \alpha^3)^2 + \left(C_c \frac{\Delta E}{E_0} \alpha\right)^2 \end{aligned} \quad (2.2)$$

where the effective probe diameter (d_{eff}) is the quadrature sum of the probe broadening terms: the diffraction limit (d_{diff}), the finite electron source size (d_{source}), the spherical aberration (d_s) and the chromatic aberration (d_c) of the objective lens. With λ the electron

wavelength, α the probe convergence semi-angle, I_p the electron probe current, β the brightness of the electron source, C_s the spherical aberration of the objective lens, C_c the chromatic aberration of the objective lens, ΔE the energy spread of the electron beam, and E_0 the electron beam energy.

Figure 2.2. (a) Expected probe size of a focused 300 keV electron beam as a function of the probe convergence semi-angle based on geometrical optics, including the indicated probe broadening terms using typical values for the high-brightness electron source ($3.9 \times 10^{13} \text{ A m}^{-2} \text{ sr}^{-1}$), probe current (50 pA), spherical aberration (2.7 mm), chromatic aberration (2.7 mm) and energy spread (0.8 eV). Dashed black arrows indicate the optimal convergence semi-angle and probe size. Ray diagram of a lens with (b) spherical aberration and (c) chromatic aberration, colored arrows represent electron beams with different energy.

All these probe broadening terms together with the final effective probe size are plotted in Fig. 2.2a, clearly showing that the probe size is limited by the combined effect of all probe broadening terms. For instance, employing high probe currents with an insufficiently bright electron source increases the probe size beyond the diffraction limit, although still an arbitrarily small probe can be formed by opening up the probe convergence semi-angle. However, the spherical and chromatic aberrations of the objective lens prevent the use of a larger probe convergence semi-angle, as that would rapidly lead to probe broadening due to their cubic and linear proportionality with the convergence semi-angle, respectively.

The positive spherical aberration of the objective lens causes a stronger focusing of off-axial electrons compared to those closer to the optical axis (Fig. 2.2b). And chromatic aberration causes electrons with different energy (as electron sources do not produce monochromatic electron beams) to be focused to different points (Fig. 2.2c). Among all electromagnetic

lenses in the microscope, the objective lens is the dominant source of spherical and chromatic aberrations, being the only one focusing highly off-axis electrons, as opposed to all other lenses where the electron beam remains close to the optical axis producing negligible spherical and chromatic aberrations. Hence, for a given set of microscope characteristics and lens aberrations, there is an optimal convergence semi-angle that balances all these terms and produces the smallest possible probe size as shown in Fig. 2.2a.

Although such a geometrical optical analysis is useful to demonstrate probe broadening phenomena, the estimated probe sizes are generally larger than what can be achieved experimentally, which is a direct consequence of ignoring interference effects that do occur due to the electron's wave character. Therefore, for a complete and more accurate prediction of attainable probe sizes, both coherent as well as incoherent effects have to be accounted for.

None of the geometrical aberrations like spherical aberration, astigmatism and coma, destroy the coherency of the electron beam, thus they require a full wave-optical analysis to describe the electron wavefunction. On the other hand, spatial incoherence arises from the finite source size, where mutually incoherent electrons emitted from different positions are focused to a different lateral position on the specimen. Temporal incoherence is caused by chromatic aberration, where mutually incoherent electrons with different wavelength are focused at a different longitudinal position at the specimen. The probe broadening due to these incoherent effects should then be computed based on the weighted average of electron probe's intensity (rather than the wavefunction) at all lateral and longitudinal focus points.

Here the coherent probe broadening effects are analyzed by a wave-optical treatment, which then readily allows incorporation of spatial and temporal incoherence. The beam limiting aperture and the probe broadening effects can be mathematically described as taking place in the back-focal plane of the objective lens², leading to the following reciprocal space representation of the electron wave function:

$$\psi(\vec{k}) = A(\vec{k}) \cdot e^{-i\chi(\vec{k})} \quad (2.3)$$

where $A(\vec{k})$ is a circular aperture function transmitting electrons ($A(\vec{k}) = 1$) when the magnitude of the transverse wavevector $\vec{k}$ is smaller than k_{max} and blocking ($A(\vec{k}) = 0$) them otherwise, and $\chi(\vec{k})$ is the aberration function (including spherical aberration effects) phase shifting the electron wave away from the ideal phase front.

From a Fourier optics perspective, the focusing action of the objective lens, forming an incident probe in the specimen plane, can be described as a Fourier transform operation of the electron wave function in back-focal plane²:

$$\psi_{in}(\vec{r}) = \mathcal{F}\{\psi(\vec{k})\}(\vec{r}) = \mathcal{F}\{A(\vec{k}) \cdot e^{-i\chi(\vec{k})}\}(\vec{r}) \quad (2.4)$$

This indeed reduces to an Airy disk function in case a uniform phase front is present, as then the aberration function is unity, and the final probe shape is the Fourier transform of a circular aperture:

$$\psi_{in}(\vec{r}) = \mathcal{F}\{A(\vec{k})\}(\vec{r}) = \frac{2J_1(2\pi k_{max}|\vec{r}|)}{2\pi k_{max}|\vec{r}|} \quad (2.5)$$

where J_1 is a first-order Bessel function, and k_{max} is the largest wavevector passing through the condenser aperture. In reality, however, the phase front is never uniform, particularly due to the positive spherical aberration of the objective lens, producing a positive phase shift term (δ) that is rapidly (to the fourth power) increasing for off-axis electron trajectories. Here the aberration function is written as a function of the probe convergence semi-angle for convenience, according to $\alpha = k\lambda$:

$$\chi(\alpha) = \frac{2\pi}{\lambda} \delta = \frac{2\pi}{\lambda} \left(\frac{1}{2} \Delta f \alpha^2 + \frac{1}{4} C_s \alpha^4 \right) \quad (2.6)$$

In Eq. 2.6 Δf is the defocus of the electron probe, describing the probe position along the optical axis with respect to the specimen surface plane. Since the defocus can take positive and negative values (moving the probe up and down), it can be exploited to generate negative phase shifts, balancing the positive phase shift induced by the positive spherical aberration.

To maintain close to optimal diffraction conditions and avoid destructive interference effects, the phase shift should be kept less than a quarter wavelength, or equivalently $\pi/2$ radians. Solving Eq. 2.6 with this criterion yields an optimal value for the defocus of

$$\Delta f_{optimal} = \sqrt{\lambda C_S} \quad (2.7)$$

which then extends the maximum convergence semi-angle to an as large as possible value:

$$\alpha_{max} = \left(\frac{4\lambda}{C_S} \right)^{\frac{1}{4}} \quad (2.8)$$

Then a beam-limiting condenser aperture should be employed, blocking all electrons beyond this optimal convergence semi-angle. Consequently, the probe is then largely diffraction limited due to the minimized phase shift, and its size can be estimated according to the width of the Airy disk:

$$d_{min} \approx 0.61 \frac{\lambda}{\alpha_{max}} = 0.43 \lambda^{3/4} C_S^{1/4} \quad (2.9)$$

Using the electron wavelength of 1.97 pm for a 300 keV electron beam, and a spherical aberration value of 2.7 mm, the maximum probe convergence semi-angle is about 7.4 mrad, yielding an estimated probe diameter (halfway the first minimum) of 163 pm, smaller than expected based on the geometrical optics analysis, where the maximum probe convergence semi-angle is about 4 mrad.

Focusing the electrons into a sub-Å and even sub-0.5 Å probe, requires the minimization of spherical aberration and the other probe broadening terms. This is only possible with advanced electron optical hardware like high-brightness electron sources with low energy spread, spherical aberration correctors, chromatic aberration correctors or electron monochromators.

2.3 Probe spherical aberration correctors

Just several years after the invention of the TEM by Ernst Ruska in 1931³, Scherzer proved in 1936 that positive C_s and C_c are a fundamental physical property of circular symmetric electromagnetic lenses applying static fields without space charges⁴. Scherzer later showed that C_s and C_c can be corrected by employing non-round electromagnetic multipole lenses that produce negative C_s and C_c , compensating for those of the objective lens⁵. For precise and accurate manipulation of the electron trajectory within such correctors, very stringent machining tolerances and highly stable electronics and power supplies are required. Limited by the precision, accuracy and availability of required technologies, it has taken several decades to advance aberration correctors from idea to the first successful demonstration and improved imaging resolution, very close to the end of the 20th century about twenty years ago at the time of writing⁶.

Nowadays, there are two main competitive approaches for the C_s aberration correction based on this idea: quadrupole-octupole assemblies that can in principle (although practically challenging) also be extended to C_c correction, and hexapoles assemblies with round transfer lenses that only correct C_s ⁶⁻⁹. The hexapole based correctors are integrated in most contemporary STEMs due to their relatively simpler design and higher robustness, requiring only two hexapoles compared to more than ten multipoles in quadrupole-octupole correctors¹⁰⁻¹².

The principal multipole elements do eliminate C_s , but, due to their symmetry, introduce a plethora of higher order geometrical aberrations, some of which can be eliminated by a symmetrical corrector design and applying anti-symmetric multipole excitations¹³. In hexapole based correctors, for instance, two electromagnetic hexapole elements are symmetrically placed around the midplane of the corrector, where one round transfer lens doublet couples them together (with a magnification of -1), one adapter lens couples the condenser system to the corrector, and one transfer lens doublet couples the corrector to the objective lens (Fig. 2.3). Several deflectors and multipole stigmators must be integrated as well (not shown in Fig. 2.3) to minimize remaining higher order aberrations and also parasitic aberrations that arise due to inhomogeneities and machining imperfections in the corrector¹².

Figure 2.3. Schematic design of a hexapole based aberration corrector, placed in between the final condenser lens and the objective lens of the microscope. Deflectors and multipole stigmators required to adjust the electron beam trajectory are also present, but not shown here. The electron beam trajectory is represented by the axial ray and field ray, shown by the solid and dotted line, respectively.

Overall, residual and induced aberrations introduce a phase shift δ to the electron wave, similar to Eq. 2.6, but now include aberrations with non-round symmetry requiring a complex representation, using the notation of Haider¹², considering aberrations up to S_5 :

$$\begin{aligned} \chi(\alpha) = \frac{2\pi}{\lambda} \delta = \frac{2\pi}{\lambda} \text{Re} \left\{ \frac{1}{2} C_1 \alpha \bar{\alpha} + \frac{1}{2} A_1 \bar{\alpha}^2 \right. \\ + \frac{1}{3} A_2 \bar{\alpha}^3 + B_2 \alpha^2 \bar{\alpha} \\ + \frac{1}{4} C_3 \alpha^2 \bar{\alpha}^2 + \frac{1}{4} A_3 \bar{\alpha}^4 + S_3 \alpha^3 \bar{\alpha} \\ + \frac{1}{5} A_4 \bar{\alpha}^5 + D_4 \alpha^4 \bar{\alpha} + B_4 \alpha^3 \bar{\alpha}^2 \\ \left. + \frac{1}{6} C_5 \alpha^3 \bar{\alpha}^3 + \frac{1}{6} A_5 \bar{\alpha}^6 + S_5 \alpha^4 \bar{\alpha}^2 \right\} \end{aligned} \quad (2.10)$$

Here α is the complex valued (for mathematical convenience only) coordinate in the back-focal plane of the objective lens with $\bar{\alpha}$ its complex-conjugate, C_1 defocus, A_1 two-fold astigmatism, A_2 three-fold astigmatism, B_2 second-order axial coma, C_3 third-order spherical aberration, A_3 four-fold astigmatism, S_3 third-order star aberration, A_4 five-fold astigmatism, D_4 fourth-order three-lobe aberration, B_4 fourth-order axial coma, C_5 fifth-order spherical aberration A_5 six-fold astigmatism and S_5 fifth-order star aberration.

The ultimate goal of geometrical aberration correction is to achieve a uniform phase front of the electron wave function in the back focal plane of the objective lens extending to as large as possible transverse wavevectors. This directly enables the use of a larger beam limiting

condenser aperture, producing a smaller diffraction limited electron probe that in the end enhances imaging resolution. For instance, when only considering spherical aberration that is corrected from 2.7 mm to 5 μm (readily possible nowadays), the maximum convergence semi-angle and diffraction limited probe size with a 300 keV electron beam, is 44 mrad and 27 pm, respectively. In practice other aberrations are limiting the maximum convergence semi-angle, but values up to 30 mrad (for a 300 keV beam) are routinely possible, which together with spatial and temporal incoherence, lead to probe sizes of the order of 60 pm, enabling atomic resolution imaging of most materials.

For the work in this dissertation a Thermo Fisher Scientific (formerly FEI) Themis Z is employed, which is equipped with a CETCOR image C_s corrector (developed and manufactured by the CEOS company) and S-CORR probe C_s corrector (a joint product of CEOS and Thermo Fisher Scientific). Present day (2021), the S-CORR is among the most advanced hexapole based probe C_s corrector and it is integrated in the latest commercially available Thermo Fisher Scientific microscopes. The S-CORR provides an order of magnitude improvement in optical stability compared to its predecessor, and contains an additional weak hexapole stigmator in the midplane of the corrector to correct the six-fold astigmatism (A_5), enabling unprecedented sub- $\text{\AA}$ atomic resolution imaging in the 30-300 kV high-voltage range^{14,15}.

In Fig. 2.4a a schematic of the interior of the S-CORR is presented, containing the weak hexapole element at the midplane of the two principal hexapoles, unlike the conventional hexapole based correctors as in Fig. 2.3. The hexapole elements introduce large three-fold astigmatism (A_2) which is overall nullified by applying asymmetric excitations, but produces a blurred disk at the position of the weak hexapole element, as shown in Fig. 2.4b. In Fig. 2.4c, the effect of D_4 , A_5 and C_5 on the beam shape is shown when the weak hexapole is inactive, keeping A_5 uncorrected which is limiting particularly for low electron beam energies. However, when excited, the weak hexapole produces additional D_4 aberration at the entrance of the second hexapole, which in turn generates negative A_5 aberration when the electron beam passes through the second hexapole, correcting the A_5 aberration¹⁶.

Figure 2.4. (a) Schematic of the heart of the S-CORR probe aberration corrector, where a first-order axial electron ray is represented by the solid line. In (b-d) the electron beam cross-section is shown before and after every hexapole element. (b) Low-order aberrations dominate the electron beam shape, demonstrating how the first hexapole introduces large A_2 aberration leading to a blurred disk at the midplane. In (c,d) low-order aberrations dominating on the 240 μm scale are ignored, and only the high-order aberrations D_4 , A_5 and C_5 are considered, with the beam cross-section shown on a 1 μm scale. (c) Large 3 mm A_5 aberration remains with the weak hexapole turned off. (d) With the weak hexapole turned on, the A_5 aberration is corrected. Note that the D_4 and C_5 aberrations can be corrected by proper coupling of the corrector with the objective lens. (Courtesy of Alexander Henstra, Thermo Fisher Scientific).

The possibility to correct higher order aberrations is indispensable to produce sub-Å electron probes while operating the microscope at low-voltages, as then the longer electron wavelength increases the diffraction limited probe size. For instance, the electron wavelength increases by a factor of 3.5, from 1.97 pm to 6.98 pm, when reducing the accelerating voltage from 300 kV to 30 kV. Then an equivalent increase in probe convergence semi-angle is

required to obtain the same probe size, which would be about 70 mrad for 30 kV-STEM when it is 20 mrad (a typical value) for 300 kV-STEM.

Figure 2.5. Probe correction results for 30 kV-STEM alignment. (a) The aberration function according to Eq. 2.10 using experimentally measured aberration coefficient, with the green and purple circle representing the $\pi/2$ and 12π limit, respectively. The limiting aberrations and radii of the circles are denoted in the corners with corresponding colors. (b) The diffraction limited probe shape assuming a flat phase front up to 50 mrad. (c) Evolution of 3rd and 4th order aberration coefficients during the corrector tuning procedure.

With the S-CORR, such probe convergence semi-angles are now nearly in range, enabling unprecedentedly small electron probes while operating at 30 kV. In Fig. 2.5, a 30 kV S-CORR alignment performed by the present author, is shown, generating a nearly flat phase front, within the $\pi/2$ limit, up to 50 mrad, producing a sub-Å electron probe (Fig. 2.5a,b). Although such an alignment is possible, it is pushing the limits of the microscope's capabilities, thus requiring longer stabilization of the high-voltage, lens currents, room temperature and gentle tuning of the corrector. Using such an approach, the corrector reaches

a rather stable state as shown in Fig. 2.5c, where nearly 50 subsequent measurements (including corrections of S_3 , hence the occasional steps) of 3rd and 4th order aberrations are plotted at an interval of 5 minutes, and remain within 1.0 μm and 4.0 μm , respectively.

2.4 High-brightness electron sources and electron monochromators

The strong demagnifying power of geometrical aberration corrected STEMs, focusing the electron source size to sub-Å sized electron probes, fundamentally causes proportional probe current reduction. This is evident considering that the brightness of the electron source (defined as the emitted current per unit area A per solid angle Ω) is a conserved quantity at all planes conjugate to the image of the electron source, that is all planes in the microscope column where a beam cross-over occurs. Hence, focusing the beam in smaller probes is complemented by proportionally larger solid angles, which is, in the end, blocked by the acceptance angles of the lenses and the condenser aperture, reducing probe current. The required brightness of the electron source for a desired probe size and current can thus be readily estimated according to:

$$\beta = \frac{I}{A\Omega} = \frac{I}{\left(\frac{\pi d^2}{4}\right) \cdot (\pi\alpha^2)} \quad (2.11)$$

where I is the probe current, d is the probe diameter, and α the probe convergence semi-angle. For instance, the required brightness is $\sim 10^{13} \text{ A m}^{-2} \text{ sr}^{-1}$ when focusing the electron beam to a 60 pm probe with a 20 mrad convergence semi-angle and requiring 50 pA probe current. This is only possible with high-brightness field emission gun (FEG) electron sources, and not with tungsten filaments or lanthanum hexaboride (LaB_6) thermionic sources having orders of magnitude lower brightness¹.

Such FEG sources employ a single crystal tungsten wire with a sharp tip (radius 50-100 nm) from which electrons are extracted by a bias voltage of several kilovolts, after which they are further accelerated to the desired high-voltage of 30-300 kV¹⁷. Besides the substantially higher brightness, the smaller effective source size compared to tungsten filaments or thermionic sources is another advantage, requiring less demagnification by the condenser lens system and also reducing probe broadening due to spatial incoherence.

A cold FEG operates under ‘cold’ room temperature conditions and emits electrons close to the Fermi level by quantum mechanical tunneling generating a small electron energy spread of 0.3 eV. This is enabled by the very strong electric field at its sharp tip that locally (from a small area with diameter of about 5 nm) lowers and spatially narrows the potential barrier of the work function.

Schottky FEGs on the other hand are not truly FEGs, but in fact field-assisted thermionic emitters, where thermally excited electrons pass over the work function potential barrier having an emission area with a diameter of about 25 nm. Electron emission is possible by on the one hand reducing the work function with a zirconia coating and a strong electric field, and on the other hand thermally exciting the electrons by heating the source to about 1800K, which in the end also increases the energy spread to 0.8 eV^{1,18}. For hybrid S/TEM systems, however, Schottky FEGs are favorable due to their overall higher beam current, better stability and relaxed vacuum requirements¹⁷.

The energy spread of the electron source together with the chromatic aberration of the probe forming objective lens limit the attainable probe size due to temporal incoherence, and is particularly dominant during low-voltage imaging, as then the relative energy spread with respect to the electron beam energy reaches proportionally larger values. Strategies to minimize the effect of temporal incoherence include C_C aberration correctors that minimize the C_C coefficient, electron sources with reduced energy spread like cold FEGs, and electron monochromators that reduce the energy spread of the electron beam at the cost of available probe current^{17,18}.

The probe and image aberration corrected 30-300 kV Themis Z S/TEM microscope used for the research described in this dissertation is equipped with a high-brightness Schottky X-FEG ($\beta \sim 10^{13} \text{ A m}^{-2} \text{ sr}^{-1}$, $\Delta E = 0.8 \text{ eV}$) and an electron monochromator, offering the possibility for high-resolution low-voltage imaging. Fig. 2.6 demonstrates, based on geometrical optics, how an electron monochromator can substantially reduce the probe broadening due to chromatic aberration for a 30 keV electron beam.

Figure 2.6. Estimated probe size, based on geometrical optics, of a spherical aberration corrected 30 keV electron beam, using typical values for the high-brightness Schottky FEG ($\beta=3.1 \times 10^{12} \text{ A m}^{-2} \text{ sr}^{-1}$) with energy spread of 0.8 eV, probe current (50 pA), spherical aberration (2 μm) and chromatic aberration (2.7 mm). (a) With the monochromator turned off. (b) With the monochromator excited, reducing the energy spread from 0.8 eV to 0.3 eV.

The monochromator in this microscope is of the single Wien filter type and located between the electron source and the accelerator, as it includes an electrostatic deflector only effective on slower electrons. When the monochromator is excited, a transverse force, perpendicular to the optical axis, acts on the electron beam due to the perpendicular electric and magnetic fields in the Wien filter, dispersing the electron trajectory by their velocity^{19,20}. As the Wien filter focuses the round electron beam (at the entrance) in the dispersive plane, but not in the (perpendicular) non-dispersive plane, a line focus is created, which, for alignment convenience is compensated by an additional electric quadrupole field, generating a point focus²¹. The final dispersed electron beam is focused on the monochromator aperture, located just before the first condenser lens, which selects a portion of the electron beam, effectively decreasing the energy spread of the electron beam at the cost of beam current.

2.5 Image formation theory within the phase object approximation

As the finely focused electron probe is scanned across the specimen, the electrons diffract when they pass through the electron transparent specimen, creating a complex far-field diffraction pattern which is (partially) collected by one or more electron detectors, generating an image²². Hence, to understand the resolution and contrast of STEM images acquired by a

certain detector, it is crucial to describe the electron-matter interaction creating the diffraction pattern.

Figure 2.7. Simplified schematic of the electron trajectory through the microscope and scattering from the specimen, forming a far-field diffraction pattern of which the intensity is integrated by one or more electron detectors.

For high-quality STEM images, a specimen of the material of interest should be prepared as thin as possible, that is preferably thinner than about 50 nm, as otherwise the image quality is compromised due to inelastic scattering effects¹⁷. However, even for such a thin specimen, plural or multiple electron scattering events occur, complicating an analytical mathematical description. The complexity of the electron-matter interaction is relaxed only for thin specimens where single scattering events occur, allowing the application of the phase object approximation^{2,17,22}. In that case, the specimen is considered to be a phase object, only modifying the phase of the electron wave function as it passes through the specimen, which can be described by the transmission function in complex notation:

$$T(\vec{r}) = e^{i\varphi(\vec{r})} = e^{i\sigma V(\vec{r})} \quad (2.12)$$

Here $\varphi(\vec{r})$ is the position dependent specimen induced phase shift, equivalent to the product of the local specimen potential $V(\vec{r})$ and the interaction parameter $\sigma = \frac{2\pi me\lambda}{h^2}$, with e , m , λ and h the electron charge, relativistic electron mass, electron wavelength, and Planck's constant, respectively. The electron wave function emitted from the bottom surface of the specimen is then calculated by multiplying the incident wave function (Eq. 2.4) with the transmission function;

$$\psi_{out}(\vec{r}, \vec{r}_p) = \psi_{in}(\vec{r}) \cdot T(\vec{r} + \vec{r}_p) = \psi_{in}(\vec{r}) \cdot e^{i\varphi(\vec{r} + \vec{r}_p)} \quad (2.13)$$

where the scanning process is included by moving the specimen by $\vec{r}_p$. The transmitted phase shifted wave function generates a far-field diffraction pattern in the detector plane (Fig. 2.7), which is related to the specimen plane by a Fourier transform²:

$$\psi_D(\vec{k}, \vec{r}_p) = \mathcal{F}\{\psi_{out}(\vec{r}, \vec{r}_p)\}(\vec{k}) = \mathcal{F}\{\psi_{in}(\vec{r}) \cdot e^{i\varphi(\vec{r} + \vec{r}_p)}\}(\vec{k}) \quad (2.14)$$

The diffraction pattern may contain overlapping disks (as in Fig. 2.7), depending on the particular lattice spacings in the specimen and the convergence semi-angle of the probe, leading to interference fringes in the overlap region, producing a complicated diffraction pattern. As the electron detectors do not detect amplitude but rather the intensity, the intensity (or probability density, in quantum mechanical terms) has to be considered:

$$I_D(\vec{k}, \vec{r}_p) = |\psi_D(\vec{k}, \vec{r}_p)|^2 \quad (2.15)$$

which, in the framework of the phase object approximation, is the mathematical description of the electron diffraction pattern, called the convergent beam electron diffraction (CBED) pattern or Ronchigram². Due to the convergent beam illumination, the CBED pattern consists of (overlapping) disks rather than spots, where, for obvious reasons, the bright central disk is called the bright-field disk. As a final step to describe the image formation process, the electron detectors can be readily incorporated by integrating the diffraction pattern intensity

over the detector function, $D(\vec{k}) = 1$ for all wavevectors collected by the detector and zero otherwise:

$$I^{STEM}(\vec{r}_p) = \iint_{-\infty}^{+\infty} D(\vec{k}) I_D(\vec{k}, \vec{r}_p) d^2\vec{k} = \iint_{-\infty}^{+\infty} D(\vec{k}) |\psi_D(\vec{k}, \vec{r}_p)|^2 d^2\vec{k} \quad (2.16)$$

This is the general mathematical description of the STEM image formation process of a phase object specimen. Interestingly, the resolution limit of STEM imaging can be directly derived from Eq. 2.16 by substituting the relevant wavefunctions, and is

$$d = \frac{1}{2k_{BF}} = \frac{\lambda}{2\alpha} \quad (2.17)$$

where k_{BF} is the radius of the bright-field disk in the CBED pattern, determined by the electron wavelength and the probe convergence semi-angle. This resolution limit also makes sense intuitively, as all contrast in STEM images arises from interference effects in the overlap region of diffracted disks (as long as the detector is large enough to capture them) which ceases once their separation is equal to or larger than their diameter²³. For instance, images acquired with a 300 keV electron beam and a probe convergence semi-angle of 20 mrad cannot exceed 49 pm resolution.

To analyze the contrast transfer functions (CTF) of STEM imaging in the framework of linear imaging theory, it is convenient to describe Eq. 2.16 in the Fourier domain, leading to the following general equation²:

$$\begin{aligned} \mathcal{F}\{I^{STEM}(\vec{r}_p)\}(\vec{k}_p) &= CTF_S \cdot \mathcal{F}\{\sin \varphi(\vec{r})\}(\vec{k}_p) \\ &+ CTF_C \cdot \mathcal{F}\{1 - \cos \varphi(\vec{r})\}(\vec{k}_p) \end{aligned} \quad (2.18)$$

Hence, STEM imaging of a phase object is non-linear in general, as it includes a combination of two CTFs and two objects, namely CTF_S and $\sin \varphi(\vec{r})$, where the CTF_S is fully sample independent, and CTF_C and $1 - \cos \varphi(\vec{r})$, where the CTF_C has a sample dependence.

2.6 Z-contrast imaging: high-angle annular dark-field

For the last three decades, high-angle annular dark-field (HAADF)-STEM has been by far the most popular imaging technique for materials science research, as it produces easily interpretable images with atomic number (Z)-contrast providing simultaneous structural and compositional information, even down to the atomic scale after the introduction of aberration correctors. The dark-field imaging mode originates from the central hole of the detector that is (much) larger than the bright-field disk (the detector in Fig. 2.7), generating a dark image of vacuum, and the detector outer rim extends to high angles, only collecting high-angle scattered electrons^{1,18,23–25}.

A rudimentary, yet insightful, explanation of the HAADF-STEM image contrast mechanism is based on the particle nature of the electron beam. The energetic electrons have sufficient energy to penetrate the electron cloud and closely approach the positively charged atom nucleus, resulting in Rutherford scattering to high-angles with a probability proportional to Z^2 , or about $Z^{1.7}$ when considering the screening effects from the core electrons. Then, with a sub-Å probe in an aberration corrected STEM, crystals that are aligned along their crystallographic zone-axis can be robustly imaged (very insensitive to specimen thickness and defocus) with atomic resolution where the intensity at the position of the atom columns is proportional to about $Z^{1.7}$.

From the wave nature perspective of the electron beam, HAADF-STEM can be considered incoherent imaging, arising from incoherent thermal diffuse scattering that is dominant over coherent diffraction effects at large scattering angles. Any coherent effects, like the interference pattern in the overlap region of diffraction disks, are washed out due to the relatively wide angular range of the HAADF detector^{26–28}.

In other words, the HAADF-STEM image can, to a first approximation, be assumed to be a linear imaging mode, as the cross-correlation of the electron probe with a sample dependent object^{2,22,23}:

$$I_{HAADF}(\vec{r}_p) \propto (|\psi_{in}(\vec{r})|^2 \star O(\vec{r}))(\vec{r}_p) = (I_{in}(\vec{r}) \star O(\vec{r}))(\vec{r}_p) \quad (2.19)$$

Note that the object is cross-correlated with the intensity of the electron probe rather than the amplitude, losing all phase information, leading to the incoherent imaging. A full analytical derivation of the ADF-STEM (the general case of dark-field imaging, collecting any electrons outside the bright-field disk, not just the high-angle scattered ones) image formation, in the framework of the phase object approximation can be derived from Eq. 2.18²⁹:

$$I_{ADF}(\vec{r}_p) \approx C \cdot (|\psi_{in}(\vec{r})|^2 \star (1 - \cos \varphi(\vec{r}))) (\vec{r}_p) \quad (2.20)$$

where C is a sample dependent scaling factor, rendering (HA)ADF-STEM in fact not entirely a linear imaging method. More importantly, the object that is being imaged is identified as $1 - \cos \varphi(\vec{r})$, which, in the limit of small phase shifts, can be approximated as $\frac{1}{2}\varphi^2(\vec{r})$, closely related to the about Z^2 image contrast nature of (HA)ADF-STEM. The effective CTF can then be determined by Fourier transforming Eq. 2.20:

$$\mathcal{F}\{I_{ADF}(\vec{r}_p)\}(\vec{k}_p) = C \cdot \overline{\mathcal{F}\{|\psi_{in}(\vec{r})|^2\}}(\vec{k}_p) \cdot \mathcal{F}\{1 - \cos \varphi(\vec{r})\}(\vec{k}_p) \quad (2.21)$$

from which the effective CTF is defined as $C \cdot \overline{\mathcal{F}\{|\psi_{in}(\vec{r})|^2\}}(\vec{k}_p)$, which is the Fourier transformed probe intensity multiplied by a sample dependent pre-factor, demonstrating that (HA)ADF-STEM is indeed an incoherent imaging technique, as no phase information is present in the CTF.

Despite being non-linear, (HA)ADF-STEM is often the preferred technique to image materials with atomic resolution using modern aberration correct microscopes, specifically due to its incoherent imaging nature generating directly interpretable images where atoms are always imaged as bright dots in a dark background. Also, due to the channeling of electron down atom columns, the phase object approximation can be extended to (at least holds qualitatively for) thicker specimen as well, implying that the Z-contrast nature of (HA)ADF-STEM images also applies for thicker specimen³⁰. The major downside of (HA)ADF-STEM is that it is generally not possible to image light and heavy atoms together (such as oxygen, nitrogen, carbon or hydrogen atoms next to metal atoms), a direct consequence of its $\sim Z^{1.7}$ contrast nature.

2.7 Imaging of light and heavy elements: integrated differential phase contrast

After aberration correctors were successfully introduced and have become the benchmark in materials science research with STEM, the focus of further instrumental development has shifted from improving resolution to enhancing sensitivity to enable the imaging of light elements next to heavy ones. Integrated differential phase contrast (iDPC)-STEM is one of the latest developed imaging techniques that has this capability³¹, and is based on the differential phase contrast (DPC)-STEM technique first introduced by Dekker and de Lang in the 1970s³². An important part of the material presented below in this section centered around iDPC is based on the seminal work on this topic presented by Lazić, Bosch and Lazar in Ref. 31.

Figure 2.8. (a) Schematic of the electron trajectory as it passes along an atom nucleus³³. (b) The intensity of the detector segments (A,B) and their difference (A-B), yielding an anti-symmetric profile centered at the atom position³³. (c) In reality, the atomic electrostatic potential does not rigidly shift the Ronchigram, but rather causes an intensity redistribution³⁴. (d) Using four detector quadrants (A,B,C,D), two orthogonal DPC images can be constructed³³.

With DPC-STEM, the signals from diametrically opposing detector segments are subtracted, yielding a signal closely resembling the gradient (or differential) of the phase of the specimen, which has been shown to be proportional to the in-plane magnetic or electrostatic fields³². Therefore, in the past decades, DPC-STEM was mainly used to image electric or magnetic fields structures at low-to-medium magnification^{35–37}. In the 2010s the topic was rejuvenated by DPC-STEM demonstrations in an aberration corrected microscopes, yielding the first atomic-scale electric fields images^{33,38–40}.

The contrast in DPC-STEM images originates from the deflection of fast electrons by the positively charged atom nuclei, as schematically illustrated in Fig. 2.8a, indeed producing a signal resembling the derivative of a function that peaks at the atom position (Fig. 2.8b). This deflection of the incident electron beam by the atom nucleus causes a complicated intensity redistribution of the diffraction pattern, rather than a rigid shift, which would require electric fields on a scale larger than the probe size (Fig. 2.8c)^{34,41}. The imaging mode can be readily extended to four detector segments to extract two orthogonal vector components of the electric or magnetic field, shown in Fig. 2.8d.

Despite the complicated interactions of the probe and specimen leading to the intensity redistribution of the diffraction pattern, there is a surprisingly simple and measurable physical quantity relating the CBED pattern characteristics to the electron-matter interaction: the center-of-mass (COM) of the CBED pattern scales linearly with the gradient of the phase shift introduced to the electron beam by the specimen, as described by the following equation^{31,42}:

$$\vec{I}^{COM}(\vec{r}_p) = \frac{1}{2\pi} \left(|\psi_{in}(\vec{r})|^2 \star \vec{\nabla} \varphi(\vec{r}) \right) (\vec{r}_p) \quad (2.22)$$

This equation reveals that COM-STEM, where the COM of the CBED pattern is measured at every scan position, is a linear imaging technique that images the gradient of the phase of the specimen ($\vec{\nabla} \varphi(\vec{r})$, which is a vector image) with a CTF defined by the incident probe intensity as $\frac{1}{2\pi} |\psi_{in}(\vec{r})|^2$.

For ultimate sensitivity, however, it is desirable to have a technique capable of imaging the phase shift caused by the specimen (as in Eq. 2.12), which is the most subtle electron-matter

interaction. Hence, integrating the COM-STEM vector image (Eq. 2.22) is an obvious mathematical operation to obtain an image that is linear with the phase rather than its gradient, yielding the integrated COM (iCOM)-STEM scalar image (see the article of Lazić, Bosch and Lazar for a complete derivation³¹):

$$\mathcal{F}\{I^{iCOM}(\vec{r}_P)\}(\vec{k}_P) = \frac{\vec{k}_P \cdot \mathcal{F}\{\vec{I}^{COM}(\vec{r}_P)\}(\vec{k}_P)}{2\pi k_P^2} \quad (2.23)$$

where the integration is performed in the Fourier domain. After substituting Eq. 2.22 in Eq. 2.23, and applying the inverse Fourier transform, the mathematical form of iCOM-STEM imaging is obtained:

$$I^{iCOM}(\vec{r}_P) = \frac{1}{2\pi} (|\psi_{in}(\vec{r})|^2 \star \varphi(\vec{r}))(\vec{r}_P) \quad (2.24)$$

Indeed showing that iCOM-STEM is a truly linear imaging technique of the phase of a thin specimen, which is about linear with the atomic number rather than its square as for (HA)ADF-STEM, directly enabling the imaging of light elements next to heavy ones^{31,41}. Additionally, the CTF is again defined as the intensity of the incident probe, which is a positive-definite function providing frequency transfer up to the fundamental resolution limit. Therefore, similar to (HA)ADF-STEM images, iCOM-STEM images are also easily interpretable where atoms appear as white dots in a dark background, but with the advantage of higher sensitivity.

Besides being linked through basic mathematical operations, these COM-based imaging techniques also have a solid physical basis through Gauss's law and Poisson's equation:

$$\nabla^2 \varphi(\vec{r}) = \sigma \nabla^2 V_z(\vec{r}) = -\sigma \vec{\nabla} \cdot \vec{E}_z(\vec{r}) = -\frac{\sigma}{\epsilon_0} \rho_z(\vec{r}) \quad (2.25)$$

which shows how the phase $\varphi(\vec{r})$, the projected electrostatic potential $V_z(\vec{r})$, projected electric field $\vec{E}_z(\vec{r})$, and projected charge density distribution $\rho_z(\vec{r})$ are physically complementary, such that by measuring one, all the others can be calculated. Now also the

final complementing COM-STEM based image can be identified as the differentiated COM (dCOM)-STEM image, obtained by computing the gradient of the COM-STEM image, yielding a scalar image that is proportional with the charge density distribution:

$$I^{dCOM}(\vec{r}_p) = \vec{\nabla} \cdot \vec{I}^{COM}(\vec{r}_p) = \frac{1}{2\pi} (|\psi_{in}(\vec{r})|^2 \star \nabla^2 \varphi(\vec{r}))(\vec{r}_p) \quad (2.26)$$

Substituting the physical relations of electrostatic potential, electric field and charge density distribution in the (i/d)COM-STEM equations followed by Fourier transforming, then directly demonstrate the complete linearity of (i/d)COM-STEM imaging with a simple and well-defined CTF and physically complementary electrostatic objects:

$$\mathcal{F}\{I^{iCOM}(\vec{r}_p)\}(\vec{k}_p) = \frac{1}{2\pi} \overline{\mathcal{F}\{|\psi_{in}(\vec{r})|^2\}}(\vec{k}_p) \cdot \mathcal{F}\{\sigma V_z(\vec{r})\}(\vec{k}_p) \quad (2.27)$$

$$\mathcal{F}\{\vec{I}^{COM}(\vec{r}_p)\}(\vec{k}_p) = \frac{1}{2\pi} \overline{\mathcal{F}\{|\psi_{in}(\vec{r})|^2\}}(\vec{k}_p) \cdot \mathcal{F}\{-\sigma \vec{E}_z(\vec{r})\}(\vec{k}_p) \quad (2.28)$$

$$\mathcal{F}\{I^{dCOM}(\vec{r}_p)\}(\vec{k}_p) = \frac{1}{2\pi} \overline{\mathcal{F}\{|\psi_{in}(\vec{r})|^2\}}(\vec{k}_p) \cdot \mathcal{F}\left\{-\frac{\sigma}{\epsilon_0} \rho_z(\vec{r})\right\}(\vec{k}_p) \quad (2.29)$$

In practice, there are several ways to measure the COM of the CBED pattern, for instance, with a pixelated detector the COM can be measured with absolute accuracy, although such detectors currently have long ($\sim$ millisecond per probe position) readout times (but faster cameras are being developed^{43,44}), produce substantial datasets (one image per scan position) requiring extensive postprocessing and also are not compatible with electron energy loss spectroscopy (EELS)^{45–48}. A faster ($\sim$ microsecond per probe position) and more straightforward approach is the use of a circular or annular detector, based on existing electron detection technology, consisting of multiple (at least three) equally sized segments to approximate the COM, which in fact has been shown to work rather well. In addition, a segmented annular detector has the advantage of being compatible with EELS due to the central hole in the detector^{31,34,49}.

Figure 2.9. Detector geometry, acquisition and calculation of DPC-STEM based (simulated) images of TiH along (001) axis, schematically shown in the top-left corner, with Ti and H atoms in blue and red, respectively. (a) Four detector quadrants capture predominantly the bright-field disk, and each produce one image. (b) Two orthogonal vector components of the COM of the CBED pattern are approximated by subtracting the images from diametrically opposing elements, yielding DPC_x and DPC_y . (c) The DPC-STEM vector image is formed by DPC_x and DPC_y and the vector field is represented using color and intensity for the direction and magnitude, respectively. The DPC-STEM vector image integrated to form the iDPC-STEM image, and differentiated to form the dDPC-STEM image.

With just four detector segments the two orthogonal components of the COM can be approximated by subtracting the signal of diametrically opposing segments (Fig. 2.9a,b):

$$\begin{aligned} I^{DPC_x}(\vec{r}_p) &\propto I^A(\vec{r}_p) - I^B(\vec{r}_p) \\ I^{DPC_y}(\vec{r}_p) &\propto I^C(\vec{r}_p) - I^D(\vec{r}_p) \end{aligned} \quad (2.30)$$

The terms in Eq. 2.30 then produce the DPC-STEM vector image, representing the projected electric field of a thin specimen:

$$\vec{I}^{DPC}(\vec{r}_p) = I^{DPC_x}(\vec{r}_p) \cdot \vec{e}_x + I^{DPC_y}(\vec{r}_p) \cdot \vec{e}_y \quad (2.31)$$

Then the integrated DPC (iDPC)-STEM image can be computed by substituting Eq. 2.31 in Eq. 2.23, followed by an inverse Fourier transform, and is proportional to the projected electrostatic potential of the specimen:

$$I^{iDPC}(\vec{r}_p) = \mathcal{F}^{-1} \left\{ \frac{\vec{k}_p \cdot \mathcal{F}\{\vec{I}^{DPC}(\vec{r}_p)\}(\vec{k}_p)}{2\pi k_p^2} \right\}(\vec{r}_p) \quad (2.32)$$

The final complementing dDPC-STEM image, representing the projected charge density distribution can be computed similarly, by substituting Eq. 2.31 in Eq. 2.26, yielding:

$$I^{dDPC}(\vec{r}_p) = \vec{\nabla} \cdot \vec{I}^{DPC}(\vec{r}_p) \quad (2.33)$$

Hence, based on the approximation of the COM using four detector segments, an DPC-STEM image is formed, from which the iDPC-STEM and dDPC-STEM images are computed through integration and differentiation, respectively. Alternatively, as per Eq. 2.25, the DPC-STEM and dDPC-STEM images can be computed from the iDPC-STEM image by computing the gradient and the Laplacian of the iDPC-STEM image, respectively:

$$\vec{I}^{DPC}(\vec{r}_p) = \nabla I^{iDPC}(\vec{r}_p) \quad (2.34)$$

$$I^{dDPC}(\vec{r}_p) = \nabla^2 I^{iDPC}(\vec{r}_p) \quad (2.35)$$

The simulated result in Fig. 2.9c demonstrates the high sensitivity of (i/d)DPC-STEM, even capable of imaging hydrogen atoms, which is also experimentally verified in this dissertation in chapter 6⁴⁹.

Based on Eqs 2.34 and 2.35, it is already clear that the DPC-STEM and dDPC-STEM images generally contain more noise than the iDCP-STEM images, as differentiation (of experimental data) generally introduces high frequency noise. Hence, it is expected that the noise increases for each differentiation step, being the most in dDPC-STEM followed by DPC-STEM, and the least in iDPC-STEM images.

In fact, iDPC-STEM has a high signal-to-noise ratio (SNR) for fundamental reasons, higher than for instance bright-field (BF)-STEM (which resembles bright-field TEM through the principles of reciprocity²³) or ADF-STEM, as shown in Fig. 2.10a. The high electron

collection efficiency of the detector is one contribution to the higher SNR: particularly (a large part of) the bright field disk of the CBED pattern is collected, which contains the majority of the electrons in the diffraction pattern (Fig. 2.10b). More important, however, is the integration step involved in the calculation of iDPC-STEM images, which reduces high frequency noise, effectively the result of the k_F^2 term in the denominator in Eq. 2.32, which dominantly scales down high frequencies.

Figure 2.10. (a) Signal-to-noise ratio comparison of BF-STEM, iDPC-STEM and ADF-STEM³¹. (b) Detector geometries are illustrated to scale, with radii of $0 - 0.5k_{BF}$ for BF-STEM, $0 - k_{BF}$ for iDPC-STEM and $k_{BF} - 5k_{BF}$ for ADF-STEM. (c) Integrating the conservative electric field along any path (l_1 and l_2) from a reference (ref.) to a point of interest (P) must yield the same electrostatic potential²⁹.

The noise reduction property also has a physical basis related to the integration property of a vector field: only the integration of a conservative vector field (which the electric field is) yields a scalar image (the electrostatic potential), all noise that is present in the DPC-STEM image is therefore an additional nonconservative component on top of the conservative electric vector field. Moreover, the result of integration of a conservative vector field is physically enforced to be invariant to the path taken e.g. the electrostatic potential at a certain coordinate must always be the same with respect to an arbitrary reference (Fig. 2.10c). As

the two-dimensional integration of the DPC-STEM electric vector field image can be interpreted as averaging over all possible paths, any noise that is present in the DPC-STEM vector image will be averaged out.

The DPC-STEM imaging technique thus provides a complete electrostatic analysis of a thin specimen, based on the approximate measurement of the COM using several detector segments, which is also relatively insensitive to a central hole, making DPC-STEM imaging compatible with electron energy loss spectroscopy (EELS)⁵⁰. For the direct imaging of light elements next to heavy ones, or the imaging of beam-sensitive materials requiring low-dose conditions, in particular the iDPC-STEM shows clear advantages over conventional STEM imaging techniques.

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Chapter 3

Specimen preparation methods

Abstract

It is well known to experimentalists in the field of electron microscopy and materials science that the quality of atomic resolution scanning transmission electron microscope images of materials is often limited by the specimen and not the microscope. Besides requiring as thin as possible specimens, there are many other possible parameters with a potential negative effect, like grain size, crystal orientation, residual stress, purity, preparation damage layers, oxide layers and surface contaminations. In this chapter the necessary tools and preparation protocols for high-quality specimens of bulk materials and two-dimensional materials are treated.

3.1 Scanning electron microscopy: Imaging and structure analysis

An indispensable microscope for materials science research is the scanning electron microscope (SEM), as it covers the magnification range between that of visible light microscopes and S/TEMs. The large chamber and long working distance from the objective lens to the specimen are among the most valuable characteristics of a SEM, allowing the inspection of centimeter scale bulk samples with a large magnification range, spanning the macro, meso and nanoscale.

Figure 3.1. Schematic of the electron-matter interaction volume when a primary electron beam (with a typical energy of 1-30 keV) hits a bulk specimen with the subsequent generation of electrons, x-rays and photons.

The image formation principles of a SEM are identical to that of a STEM i.e. a focused electron probe is raster scanned across the specimen and one or more signals are detected synchronically. However, the electron beam is accelerated to much lower energies, typically not higher than 30 kV, resulting in probe sizes and maximum resolution of the order of a few nm¹. Also the electron-matter interactions have a different nature, because the bulk specimens that are generally inspected with SEM fully absorb the electron beam's energy and subsequently generate Auger electrons, secondary electrons (SE), backscattered electrons (BSE), X-rays and photons from a rather large interaction volume (Fig. 3.1)^{2,3}. For imaging, a combination of SE and BSE signals is collected by various detectors, where their relative position with respect to the specimen and the attractive or repulsive bias voltage determines the ratio of detected SE and BSE². Images of bulk specimens dominantly formed by SE have the best resolution and provide topological information with a very intuitive depth-of-field and nearly three dimensional appearance, because low-energy (less than about 50 eV) SE can

only escape into the vacuum when they are generated close (few nm) to the surface keeping the effective interaction volume small⁴. On the other hand, BSE-dominant images have poorer resolution but provide compositional information, as they are the high-energy (kV range) Rutherford scattered primary electrons and emerge from much deeper in the specimen⁵.

Nowadays, also STEM functionality is incorporated in modern SEMs by using several detectors located below the specimen, enabling low-magnification STEM-in-SEM imaging of electron transparent specimens with a reduced thickness of less than about 100 nm, which also enhances resolution due to the reduced interaction volume². Typically, multiple STEM detectors are available: a central circular detector that collects (a part of) the bright-field disk for BF-STEM imaging, and one or more (segmented) annular dark-field detectors for (HA)ADF-STEM images. Such imaging modes are particularly useful to quickly inspect large areas of thin specimen and locate tiny regions that are interesting for atomic resolution STEM imaging.

Besides imaging, also signals related to the chemistry and crystal phases can be extracted by detecting the characteristic X-rays and electron diffraction patterns, respectively. For bulk specimen a so-called Kikuchi diffraction pattern is formed by the scattering of BSE from lattice planes, thus consisting of many bands with a symmetry directly related to the crystal structure, allowing identification of the relevant crystal phase and its orientation by using an electron detector camera that is located above the specimen's surface and corresponding software⁵. This technique is called electron backscatter diffraction (EBSD) and its signal is enhanced by tilting the specimen by 70° away from to the optical axis. Using this technique a plethora of information about the microstructure and crystallography can be extracted, including the grain size and shape distribution, grain boundaries, strain, texture and crystal structures⁶.

3.2 Specimen preparation of bulk materials using the focused ion beam technique

Dual-beam systems employing a focused ion beam (FIB) next to the electron beam are among the most valuable and versatile tools to prepare high-quality specimen of bulk materials for S/TEM characterization. Within such an instruments, an ion beam (generally gallium ions)

is generated, accelerated and focused into a nanometer sized spot to locally remove material, which is possible by sputtering due to the ion high atomic number and large momentum and energy transfer⁷.

Prior to such localized milling, a thin layer (100-500 nm) of carbon or platinum is deposited by (a combination of) electron and ion beam induced deposition of a precursor gas, which is injected through a syringe near the focal point of the electron and ion beam. Such layers protect the material at the region of interest from damage and amorphization by the ion beam, avoid local charging effects by enhancing electrical conductivity, and promote uniform milling by avoiding crystallographic or element dependent sputtering^{8,9}. By careful milling, a lamella of material with typical dimensions of 10x2x5 μm is then attached to a sharp tungsten needle that is controlled by an electronic micromanipulator, after which the lamella is extracted from the bulk and attached to a TEM grid and cut off the needle. Finally, the specimen is thinned down to electron transparency, which follows a rather general protocol i.e. a progressively more gentle ion beam should be used as the specimen becomes thinner to minimize the surface damage layer. This is achieved by reducing both the accelerating voltage from 30 kV to as low as 0.5 kV, to lower the penetration depth and corresponding damage layer thickness, and ion beam current, to lower the material removal rate.

The protocol for the preparation of a STEM specimen from bulk titanium containing titanium hydride precipitates is presented in Fig. 3.2 (more details are presented in chapter 6) and requires all the tools previously described. Initially pure titanium was ground and electrochemically polished to achieve sufficiently smooth surface for microstructure analysis using SEM and EBSD. A desired side effect is the introduction of hydrogen into the titanium from the acidic electrochemically polishing solution, leading to supersaturation and the nucleation and growth of titanium hydride precipitates¹⁰. The presumable single crystal of titanium is then imaged with BSE-SEM images (Fig. 3.2a), which revealed a microstructure with long and narrow bands, where the c-axis of the hexagonal close-packed titanium is nearly in-plane based on EBSD analysis (Fig. 3.2b). In fact, the crystal orientation of these long and narrow grains is very suitable for the preparation of a cross-sectional lamella using the FIB, step-by-step presented in Fig. 3.2c-h using SE images and HAADF-STEM images.

Figure 3.2. SEM images of the main steps in the preparation of high-quality S/TEM specimen from a polished bulk Ti specimen. (a) BSE-image of region of interest. (b) EBSD analysis of the white square marked in (a), with crystal orientation represented by color and unit cell orientation. (c) SE-image of the electron and ion beam deposited platinum film, at the position marked by the white rectangle in (a). (d) SE-image of the exposed lamella. (e) SE-image of the lamella platinum welded to the needle. (f) SE-image of the lamella welded to the TEM grid. (g) SE-image of the thinned lamella. (h) HAADF-STEM image of the thinned lamella showing electron transparency.

3.3 Specimen preparation of two-dimensional materials

Two-dimensional (2D) materials are stable atomically thin sheets of materials comprising only one or few atomic layers e.g. one in the case of graphene and three in the case of transition metal dichalcogenides (TMDs). The focus in this dissertation is on 2D TMDs for the widespread interest they have received since about the 2010s, particularly due to their semiconducting behavior complementing metallic 2D materials like graphene¹¹. Additionally, 2D TMDs host many other properties that are useful for applications including sensing, catalysis and (opto)electronics and are tunable by composition, crystal structure, interfaces and defects^{12–18}.

In general, 2D materials can be prepared with either bottom-up methods, such as the popular chemical vapor deposition (CVD), or with top-down methods like micro-mechanical exfoliation (with the Scotch tape method) and liquid phase exfoliation of bulk crystals which is possible due to the weak interlayer van-der-Waals forces¹⁹. Such 2D TMDs have reduced lateral dimensions in the 1-100 μm range when synthesized with CVD and in the 1-10 μm range when exfoliated. Moreover, also thicker parts are present, particularly for exfoliated TMDs, where monolayer parts are practically always attached to thicker flakes. Arguably the most popular substrate for the deposition of 2D TMDs is a silicon wafer with a 100-300 nm thick oxide layer, because on the one hand its compatibility with standard cleanroom techniques is convenient for device fabrication, whilst on the other hand interference based thickness inspection with single layer sensitivity is possible with visible light microscopes^{20–22}.

Hence, transferring 2D materials from the silicon substrate to a TEM grid requires a rather different S/TEM specimen preparation protocol than used for bulk materials, because they cannot readily be handled using conventional techniques. In fact, the criteria of a high-quality 2D material specimen are much more stringent compared to bulk materials, as any thin overlayer such as a few nanometers of hydrocarbon contamination readily obscures the 2D material, inhibiting high-quality atomic resolution S/TEM analysis. For that reason, various transfer methods have been developed in recent years with the aim of producing large area suspended 2D materials with minimal contamination, including the use of sacrificial polymer films^{23,24}, sacrificial metal films^{25–27}, viscoelastic stamps^{28–30}, polymer free based protocols using water^{31,32}, liquid-interfaces³³, surface energy^{34,35}, and also direct transfer approaches^{36–38}.

In this dissertation, the 2D materials specimens are prepared with an optimized direct transfer protocol as schematically shown in Fig. 3.3, which was found to produce sufficiently large clean areas free of hydrocarbon contamination. Briefly, a perforated carbon coated TEM grid is placed on top of the 2D material of interest whilst monitoring with a long working distance visible light microscope (Fig. 3.3a,b). Then a liquid interface is formed between the 2D material and the carbon support film by adding one drop of isopropanol (a low surface energy volatile solvent) that directly wets all surfaces (Fig. 3.3c,d). Once it has evaporated at room

temperature the carbon support film, the 2D material and the substrate are strongly adhered (Fig. 3.3e).

Figure 3.3. Step-by-step schematic of the preparation protocol used here for high-quality STEM specimen of 2D materials. (a) 2D materials are identified with a visible light microscope, (b) and a Quantifoil TEM grid is placed on top with the carbon film facing down. (c) One drop of isopropanol is put on top of the TEM grid, (d) which wets the substrate-TEM grid interface and evaporates at room temperature, (e) creating strong adhesion between the 2D material and the TEM grid. (f) The substrate carrying the TEM grid is submerged in a 1M KOH solution until the grid detaches (5-15 minutes), (g) then taken from the beaker with a self-closing tweezers, and left to dry at 70-80 °C to evaporate all residual liquid (5-10 minutes). (i) The TEM grid is placed on filter paper (carbon face up) and (j) floated on deionized water to dissolve crystalized KOH. (k) Finally, the floating TEM grid is scooped with filter paper and (l) dried at 70-80 °C, (m) creating a high-quality and clean 2D materials specimen.

Subsequently, the substrate carrying the TEM grid is carefully submerged into a solution (1M KOH) that slowly dissolves the SiO₂ layer, and detaches the TEM grid (5-15 minutes) with the 2D material (Fig. 3.3f). The grid should be taken very carefully from the KOH solution with a self-closing tweezers (for convenience) and dried gently in an atmospheric furnace 70-80 °C (Fig. 3.3g,h). Otherwise, when opening the tweezers, the surface tension of the residual liquid at the tip of the tweezers readily pulls the TEM grid and ruptures the fragile carbon

film. When completely dry, the grid is placed on filter paper and floated on deionized water with the carbon film facing up (Fig. 3.3j), several minutes later scooped with filter paper (Fig. 3.3k) and again gently dried in an atmospheric furnace 70-80 °C (Fig. 3.3l,m). The final cleaning step may be repeated to dissolve all KOH crystals.

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3. Specimen preparation methods

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Chapter 4

Imaging atomic motion of light elements in 2D materials with 30 kV electron microscopy

Abstract

Scanning transmission electron microscopy (STEM) is the most widespread adopted tool for atomic scale characterization of two-dimensional (2D) materials. However, damage free imaging of 2D materials with electrons has remained problematic even with powerful low-voltage 60 kV-microscopes. An additional challenge is the observation of light elements in combination with heavy elements, particularly when recording fast dynamical phenomena. Here, we demonstrate that 2D WS₂ suffers from electron radiation damage during 30 kV-STEM imaging, and we capture beam-induced defect dynamics in real-time by atomic electrostatic potential imaging using integrated differential phase contrast (iDPC)-STEM. The fast imaging of atomic electrostatic potentials with iDPC-STEM reveals the presence and motion of single sulfur atoms near defects and edges in WS₂ that are otherwise invisible with conventional annular dark-field STEM, and has a vast speed and data processing advantage over electron detector camera-based STEM techniques like electron ptychography.

This chapter is adapted from: S. de Graaf, M. Ahmadi, I. Lazić, E. G. T. Bosch, B. J. Kooi, Imaging atomic motion of light elements in 2D materials with 30 kV electron microscopy. Under review for publication in Nanoscale (2021).

4.1 Introduction

Two-dimensional materials are a hot topic of research for their large potential in future applications by virtue of their reduced dimensions and tunable properties. Also, novel properties can emerge that are not present in the bulk. Semiconducting transition metal dichalcogenides (TMDs) are among the most extensively investigated 2D materials, and have found their use in various fields such as spintronics¹, neuromorphics², optoelectronics³, sensing⁴ and catalysis⁵.

Scanning transmission electron microscopy is the most popular tool for the direct observation of crystalline structures, grain boundaries and defects of 2D materials that contribute to their macroscopic properties. Moreover, STEM is the only available tool capable of (sub) nanometer sculpting e.g. to create nanometer sized holes for DNA sequencing⁶, and for the manipulation of single atoms^{7,8}. Another major advantage of scanning an electron probe (with STEM) over parallel electron wave illumination (with TEM), is the ability to simultaneously employ multiple electron detectors for imaging as well as for spectroscopy purposes, such that atomically resolved images and chemical maps can be acquired simultaneously. Also, direct control of resolution and depth-of-focus is possible with STEM and not with TEM^{9–12}. Moreover, the interpretation of atomic resolution STEM images is generally also more straightforward, since atoms may appear white or black when deviated from perfect focus with TEM, although this can be largely resolved with extra aberration correction hardware¹³.

The development of low-voltage aberration corrected microscopes has been crucial for the (largely) damage free imaging of 2D materials. Nowadays, modern microscopes operating at 60 kV are widely and routinely used to image 2D materials with atomic resolution. Although radiation damage of pristine graphene is then fully prevented, defects in graphene and insulating and semiconducting 2D materials remain susceptible to radiation damage despite the milder imaging conditions. In an effort to further understand and potentially reduce radiation damage, state-of-the-art S/TEM systems have been developed in recent years, operating at low-voltages of 30 kV¹⁴, 20 kV¹⁵ and even 15 kV^{16,17}. Where particular the SALVE microscope has been leading the electron radiation damage research by atomic resolution low-voltage TEM imaging of various 2D materials^{13,15,18–20}. However, specifically these low-voltage STEM systems have only demonstrated real atomic resolution on graphene

and not on any other 2D materials, leaving the investigation of semiconducting 2D materials like TMDs and the electron-matter interactions with low-voltage STEM unexplored.

Enhancing imaging sensitivity is as important as pushing the imaging resolution at reduced voltages, i.e. resolution is useless without contrast. Emerging techniques such as integrated differential phase contrast (iDPC)-STEM^{21,22} and the recently demonstrated super-resolution electron ptychography^{23,24} are capable of reaching substantially higher sensitivity than the conventional annular dark-field (ADF)-STEM. With this latter technique, relatively light elements are invisible or have reduced contrast, possibly below the noise level, as it images the square of the electrostatic potential^{9,22}, providing nearly atomic number squared ($Z^{1.6-2.0}$) contrast²⁵. On the other hand, iDPC-STEM and electron ptychography are capable of atomic electrostatic potential imaging, which is about linear in $Z^{21,23,24,26}$. This substantially improves sensitivity as we have recently demonstrated by the direct imaging of hydrogen atoms in titanium hydride using iDPC-STEM²⁷.

Observing dynamical phenomena, like phase transitions or single atom motion, is generally more valuable for the fundamental understanding of materials than single snapshots of static materials. However, such experiments require a STEM imaging technique that is both sensitive and fast, which to date has not been demonstrated.

Here we observe beam-induced radiation damage and defect dynamics in semiconducting 2D WS₂ by recording atomic electrostatic potential movies with iDPC-STEM using a primary electron energy of 30 keV. Imaging with iDPC-STEM enables the use of lower electron doses or higher framerates relative to conventional STEM techniques, and produces electrostatic potential images in real-time during acquisition. WS₂ is a member of the family of TMDs, which have a characteristic layered structure that is easily separable into their monolayer constituents by virtue of the weak interlayer van der Waals forces. The intralayer forces have a mixed covalent-ionic nature and the monolayer consists of a plane of tungsten (W) atoms that is sandwiched between two planes of sulfur (S) atoms. In the WS₂ that we study here, the W atoms are trigonal prismatically coordinated (2H structure) with six S atoms, rendering the WS₂ monolayer a direct semiconductor. The S atoms overlap when viewed perpendicular to the plane as a result of the trigonal prismatic coordination. The projected atomic number of W and the two S atom stack (which we refer to as S₂) is $Z=74$ and $Z=32$, respectively. A single sulfur vacancy (V_S) has a projected atomic number of $Z=16$, and a single tungsten

vacancy (V_W) or a double sulfur vacancy (V_{2S}) yields a local vacuum. The relatively large contrast in projected atomic number is the rationale for using here an atomic electrostatic potential imaging technique.

4.2 Results and discussion

In Fig. 4.1 we compare simultaneously acquired atomic resolution iDPC-STEM and ADF-STEM images of a 2H WS_2 monolayer. The two selected regions (Fig. 4.1a-d and Fig. 4.1e-h) contain various elements and defects: W, S_2 , V_W , V_S and V_{2S} .

Figure 4.1. Atomically resolved experimental 30 kV-STEM images of a 2H WS_2 monolayer with single (V_S) and a double (V_{2S}) sulfur vacancies. Simultaneously acquired images of two regions with different defects are shown in (a-d) and (e-h). The images in (a-d) and (e-h) are, from top to bottom: electrostatic potential (iDPC-STEM), square of the electrostatic potential (ADF-STEM), electric vector field (DPC-STEM) and magnitude of electric field (magnitude of DPC-STEM). The lower image quality of (e-h) is caused by a combination of crystal misalignment and minor residual low-order aberrations, which is particularly visible by the reduced sulfur atom signal in the ADF-STEM image. Line profiles of W, S_2 , V_S and V_{2S} are extracted from the marked rectangles in the iDPC-STEM (a,e) and ADF-STEM (b,f) images and are plotted in (i,j). The WS_2 schematic in (a) indicates the position of W and S_2 with magenta and cyan dots, respectively, and applies to all images. The V_S and V_{2S} defects are indicated in (c,d) and (g,h). Field strength in (c,g) is represented according to the color wheel inset in (c).

All of these features are present in the atomic electrostatic potential images captured using iDPC-STEM, with clearly distinguishable contrast between S_2 , V_S and V_{2S} , matching quantitatively with image simulations (Appendix, Fig. S4.2). The ADF-STEM images also contain signals from both W and S_2 , however, without appreciable contrast between S_2 , V_S and V_{2S} . The intensity line profiles shown in Fig. 4.1i,j quantify the critical improvement in sensitivity of iDPC-STEM compared to ADF-STEM to detect all atoms and defects present.

The atomic electric field is displayed as a (colorized) vector field and vector magnitude image in Fig. 4.1c,d and Fig. 4.1g,h. These images are two different representations of the same differential phase contrast (DPC)-STEM vector image that is complementing the atomic electrostatic potential (iDPC-STEM) scalar image^{21,26,28}. In these images, nodes exist at positions where the projected electric field is zero. This occurs at high-symmetry points where the electric field cancels out i.e. at the atom positions, bridge sites and hollow sites. Anomalies such as V_S and V_{2S} are readily detected by their distinct shape in atomic electric field images as outlined in Fig. 4.1c,d,g,h. Moreover, the sulfur atoms and its vacancies remain detectable even when the WS_2 is tilted a few degrees with respect to the electron beam optical axis (Appendix, Fig. S4.3). Hence, both atomic electrostatic potentials and atomic electric fields, which are retrieved from the same detector data, have robust single atom sensitivity and are powerful methods to detect light elements.

We observe the formation of point defects, defect complexes and agglomerates, one-dimensional (1D) defects and holes under influence of the 30 keV electron beam (Movie S1-S3). To capture these dynamics with a large field of view and a practically useful framerate (e.g. 10-20 seconds per frame of a $10 \times 10 \text{ nm}^2$ area), a lower effective electron dose than in Fig. 4.1 has to be used. The five times lower electron dose (from $7.4 \times 10^4 \text{ e}/\text{\AA}^2$ to $1.5 \times 10^4 \text{ e}/\text{\AA}^2$, see Appendix section 4.6.2) typically causes loss of signal from the light elements such as S_2 and S in the ADF-STEM images, such that then only contrast from W remains (Appendix section 4.6.5, Figs. S4.5-S4.7). This is not the case for the atomic electrostatic potential image where all features remain detectable, as has been demonstrated with ultralow-dose imaging of zeolites^{22,29} and metal-organic frameworks³⁰, due to the intrinsic high sensitivity and noise suppression property of iDPC-STEM^{21,22}.

We first show the creation and dynamics of V_W , V_S and V_{2S} point defects by four subsequent frames in Fig. 4.2. The defects present are schematically indicated in the electric field

magnitude images Fig. 4.2e-h. The time interval between the frames is in this case 14.0 seconds, but these frames were cut from a larger overview and the actual time to record each field of view shown was 1.0 second.

Figure 4.2. Four frame sequence displaying point defect creation and motion induced by the 30 keV electron beam. The rows display simultaneously acquired images of the electrostatic potential (iDPC-STEM) (a-d), electric field magnitude (DPC-STEM) (e-h), and square of the electrostatic potential (ADF-STEM) (i-l). The defects present are schematically indicated in the electric field magnitude images.

In the first frame, V_s and V_{2s} are randomly distributed, which have agglomerated in the second frame. Hence, the point defects are mobilized under influence of the 30 keV electron beam. The defects are particularly visible in the electric field and atomic electrostatic potential images but are practically invisible in the ADF-STEM image. The third frame shows that a W atom, originally residing at the center of the sulfur vacancy agglomerate, has moved about 1 nm to a W-W bridge position. The ejected W atom was likely destabilized due to undercoordination at its original position in the sulfur defect agglomerate. Finally, in the fourth frame the W atom has moved back to its original site and sulfur defects have lined

up to create a 1D sulfur vacancy line (SVL)^{31,32}. Note that this process is largely invisible in the ADF-STEM image, except for the short moment (single frame) the tungsten vacancy is present.

We observed that formation of SVLs is the dominant mechanism to accommodate sulfur vacancies in WS₂ upon exposure to the 30 keV electron beam, similar to what has been observed for MoS₂ with an electron beam energy of 60 keV or when the specimen is heated to elevated temperatures³³. An example of this process is shown in Fig. 4.3, where the same area as in Fig. 4.2 is presented, but 15 frames later.

Figure 4.3. Four frame sequence showing how point defects agglomerate into line defects induced by the 30 keV electron beam. The columns display simultaneously acquired images of the electrostatic potential (iDPC-STEM) (a-d), electric field magnitude (DPC-STEM) (e-h), and square of the electrostatic potential (ADF-STEM) (i-l). The defects present are schematically indicated in the electric field magnitude images.

Holes are created as well in WS₂ after prolonged exposure (nearly 50 frames after Fig. 4.3) to the 30 keV electron beam. Prior to this, the WS₂ is in a highly defective state with a high density of point defects and SVLs. Further exposure first leads to loss of W atoms and is then

(within several frames) followed by rapidly growing holes. We observe single atom motion at the exposed hole edges, of which the dynamics at W-terminated zigzag edges are displayed in Fig. 4.4.

Figure 4.4. Sequence of frames revealing single atom motion at WS_2 edges induced by the 30 keV electron beam. The rows display simultaneously acquired images of the atomic electrostatic potential (iDPC-STEM) (a-c), atomic electric field magnitude (DPC-STEM) (d-f), and square of the electrostatic potential (ADF-STEM) (g-i). Colored arrows point at specific edge atoms present.

The two edges are both terminated by W atoms, but they have a different symmetry, because one of the edges is a true W-terminated zigzag edge (diagonal edge), whereas the other edge

(vertical edge) was originally an S-terminated edge, where the S atoms have been removed by the electron beam. Here we show how W and S atoms are appearing at the edges and bond to exposed undercoordinated W edge atoms. This is evident beyond any doubt in the atomic electrostatic potential images, and just noticeable in the electric field images as well, although more difficult to interpret if the latter would have to stand alone. In contrast, in the ADF-STEM image only the W atoms are robustly visible, and a lot of atomic structure details are thus missing.

Attaining atomic resolution with 30 keV electrons is fundamentally more challenging than using more conservative energies of 60 keV and 80 keV, because the resolution is proportionally limited by the electron wavelength, which, at 30 keV, is longer by about 43% and 67% compared to 60 and 80 keV, respectively. To achieve atomic resolution with the longer wavelength, advanced and highly-stable geometrical aberration correctors are required that enable the increase of the numerical aperture of the probe forming lens (see Appendix). In addition, a more monochromatic electron beam is necessary to minimize probe broadening due to chromatic aberrations. This can be achieved with a cold field-emission electron gun or an electron monochromator as we use here, which limits the available electron dose and thus demands the use of a dose efficient imaging technique such as iDPC-STEM.

The strong efforts in the last decade to achieve atomic resolution at accelerating voltages much lower than the traditional 200 and 300 kV were strongly motivated by prospects of reduced electron beam damage allowing materials to be studied in their intrinsic state for prolonged times. Indeed, the knock-on displacement damage is greatly reduced when lowering the accelerating voltage to 80 or 60 kV. In particular for carbon-based materials, like carbon nanotubes and graphene, this development towards lower accelerating voltages has been very successful. However, caution is required since damage by other mechanisms, in particular radiolysis, aggravate for less conductive materials such as semiconductors and insulators.

The active radiation damage mechanisms for semiconducting 2D materials have only been experimentally investigated using low-voltage TEM. Such experiments have recently uncovered a possible new two-step damage mechanism that is only activated at ultralow electron beam energies: long lived electronic excitations may enable knock-on damage when electrons arrive at a sufficiently high rate, which were previously considered to be

independent physical processes²⁰. However, since the energy delivery process by the electron beam is different for STEM compared to TEM, with local illumination, substantially higher dose rates, lower beam current, longer time between impinging electrons and sequential scanning, also different radiation damage mechanisms may be active, such that it is crucial to investigate the radiation damage of semiconducting 2D materials using also 30 kV-STEM.

The present results show that the 2D WS₂ analyzed here is not inert to the 30 keV electron beam. Sulfur vacancies are readily created, and they diffuse through the material as is evident from the formation of SVLs. The mechanisms that provide energy for such processes must be dominantly related to ionization effects and to a much lesser extent knock-on displacement. In particular, the ionization cross-section increases with decreasing electron beam energy and is more profound in semiconducting materials (which is the case here for the 2H WS₂)^{34,35}. On the other hand, 30 keV is well below the knock-on displacement threshold of S and W, since, respectively, only about 2.1 eV and 370 meV is transferred upon head-on collision of the primary 30 keV electron beam with the atom nuclei³⁶. A comparison with 60 keV for the same WS₂ material shows that the dynamics of damage formation is rather different for 30 and 60 kV, even worsening the situation at the lower accelerating voltage (Chapter 5). More in general, the electron beam damage mechanisms at play at these low beam energies are not fully understood, and remain an active area of research^{20,37}.

The ability to image atomic electrostatic potentials of 2D WS₂ with high framerate at 30 kV is an improvement over the previously reported 30 kV ADF-STEM image of graphene¹⁴. Mainly due to the fact that graphene is not susceptible to beam damage at these low voltages, such image quality can be improved by increasing the electron dose. The 2D WS₂ that we study here, however, is sensitive to ionization damage and directly restricts the electron dose. We have demonstrated that the image quality of ADF-STEM deteriorates under these conditions (compare Fig. 4.1 to Figs. 4.2-4.4), whereas atomic electrostatic potential imaging remains of high quality due to the inherent high sensitivity and noise suppression property of iDPC-STEM.

Consequently, capturing the atomic electrostatic potential image with high framerate is not only possible from an image quality perspective, but also from a technical perspective, because iDPC-STEM employs solid-state electron detectors that have equivalent readout speeds to, for example, ADF detectors. In the iDPC-STEM images, however, the contrast

between W and S₂ is limited, such that the combination of the ADF-STEM and iDPC-STEM image is still necessary to differentiate between them. There are two reasons that contribute to this effect. The dominant contribution is of fundamental nature: the finite resolution of the electron microscope bandwidth limits the potential from W atoms more strongly than the S atoms³⁸, reducing the contrast of I_W/I_{S_2} from about 1.8 to 1.25. The other smaller contribution is the finite accuracy of iDPC-STEM to image atomic electrostatic potentials, which increases the relative intensity of S compared to W, see Appendix section 4.6.5 and Fig. S4.4.

Atomic electrostatic potential imaging can be achieved with absolute accuracy with electron ptychography, or when truly integrated center-of-mass (iCOM)-STEM imaging is performed^{21,22}, which is only approximated (although rather well with even only four detector segments) by iDPC-STEM. The advantage of electron ptychography is that it can further improve contrast with its super-resolution capabilities. However, iDPC-STEM is considerably more suitable for dynamical phenomena studies than electron ptychography, due to its direct imaging and vast speed advantage, because the several solid-state electron detectors that iDPC-STEM employs are two to three orders of magnitude faster than electron detecting cameras used for electron ptychography and 4D STEM, although the speed of such camera detectors is expected to improve in the near future^{39,40}. For instance, four image frames of 512×512 pixels are acquired in about 1 minute with iDPC-STEM in this work (and up to 100 times higher frame rates are readily possible), but take at least 35 minutes with 4D STEM, which additionally produces large datasets (68 GB versus 17 MB for iDPC-STEM) and requires time consuming and complex reconstruction schemes for electron ptychography^{23,24,41}. We note, however, that even the fastest iDPC-STEM acquisition of a reasonable field-of-view is limited to a frame time of 0.1-1.0 second, by no means fast enough for many physical phenomena occurring on shorter timescales. Nevertheless, the fact that iDPC-STEM is not intrinsically limited by the readout speed of the detectors, but rather the electron dose, is promising for potential high-speed imaging capabilities when instrumental advancements enable much higher electron dose rate. Moreover, the accuracy of iDPC-STEM can be readily improved, approaching the absolute accuracy of iCOM-STEM, by employing more solid-state electron detectors than the four that we use here, without compromising speed.

Furthermore, simultaneous imaging and electron energy loss spectroscopy (EELS) cannot be performed with electron ptychography, because all electrons are blocked by the camera, although recently the idea of performing electron ptychography using a camera with a central hole has been reported⁴². iDPC-STEM is directly compatible with EELS, as its detector already has a central hole. This is of particular importance considering the advent of ultra-high energy resolution EELS⁴³, and fast and sensitive direct electron detectors for EELS⁴⁴ that are opening up new fields in electron microscopy e.g. the ability to directly measure vibrational spectra to investigate phonon modes in nanostructured materials at atomic resolution^{45–48}.

4.3 Conclusions

In summary, we have demonstrated that defect dynamics in 2D WS₂ can be imaged with enhanced sensitivity and high framerates using the low electron beam energy of 30 keV. This has been enabled by the atomic electrostatic potential imaging capability of iDPC-STEM and advancements in electron optics. At present, this is the only STEM imaging technique that combines high sensitivity and high framerates. The real-time iDPC-STEM movies reveal light sulfur atoms and their dynamics in WS₂ that are invisible with the traditional ADF-STEM. This approach can be directly applied to visualize light elements, like oxygen, carbon and nitrogen, in all 2D materials, and can be generalized to all other beam sensitive materials that require low electron dose and low beam energies. The possibility of combining this fast and sensitive imaging technique with powerful emerging electron spectroscopic capabilities has the potential to solve challenging problems in materials science.

4.4 Experimental methods

Monolayer parts of 2H WS₂ were exfoliated from a bulk single crystal (HQ Graphene) using the scotch tape method, and also grown directly on a silicon wafer using chemical vapor deposition (CVD). The 2D WS₂ flakes were identified using optical microscopy and transferred to a Quantifoil TEM grid using a polymer free method (for details see Chapter 3). A double aberration corrected 30-300 kV Thermo Fisher Scientific Themis Z S/TEM operating at 30 kV was used to image 2D WS₂ with atomic resolution. Geometrical and chromatic aberrations were minimized by careful alignment of the probe corrector, and by excitation of the monochromator, respectively. The probe convergence semi-angle was 33

mrad, the probe current 2.5-7.5 pA (depending on energy selecting aperture size), probe step size 15.92-22.52 pm, and the dwell time 40-50 μ s. The collection angles of the segmented DF4 detector (for iDPC-STEM imaging) and ADF detector were 9-36 mrad and 39-200 mrad, respectively. Detailed information on the sample preparation and the electron microscopy acquisition can be found in the Appendix, and the University of Groningen data repository⁴⁹.

4.5 References

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4. Imaging atomic motion of light elements in 2D materials with 30 kV electron microscopy

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4.6 Appendix

4.6.1 Sample preparation of 2D WS₂ for scanning transmission electron microscopy analysis

Monolayer flakes of WS₂ were either transferred to, or directly grown on, Si/SiO₂ (300 nm) substrates by, respectively, exfoliating bulk crystals (HQ Graphene) with the scotch tape method for Fig. 4.1a-d and Figs. 4.2 - 4.4, or using CVD for Fig. 4.1e-h. The monolayer flakes were identified using optical microscopy (Fig. S4.1a) and transferred to R 1.2/1.3 carbon Quantifoil TEM grids with a polymer free method (Fig. S4.1b-d).

Figure S4.1. Microscope images of the exfoliated WS₂ flake taken after different steps of the transfer method. (a) The exfoliated WS₂ flake on Si/SiO₂ (300 nm) substrate, with a monolayer part in the top right (dark contrast). (b) Perforated carbon support grid of the TEM grid is attached to the flake after the isopropanol has evaporated. Bottom left shows a part of the gold grid. (c) TEM grid with WS₂ flake is detached from the Si/SiO₂ substrate after etching in 1M KOH. (d) Overview ADF-STEM image of the WS₂ flake. Weak contrast of the monolayer part is visible at the upper right part of the flake.

First, the TEM grid is carefully put on top of the monolayer WS₂ with the carbon support film facing the flake. One droplet of isopropanol is placed on the TEM grid, which directly wets both the carbon film and the SiO₂ substrate to form a liquid interface between them. The

flexible TEM grid is pulled towards the flake and the substrate upon evaporation of the isopropanol, which results in strong adhesion of the TEM grid to the WS₂ flake and substrate (Fig. S4.1b). The entire stack (substrate/flake/TEM grid) is then immersed in a 1M KOH solution at room temperature to etch away the SiO₂, for as long as necessary to detach the TEM grid (usually 5-15 minutes). Then the TEM grid is carefully extracted from the solution with self-closing tweezers, which are then dried together (as otherwise the TEM grid sticks to the tweezer upon opening due to the liquid capillary) for 5-10 minutes in an atmospheric furnace at 70-80 °C. The dried TEM grid is floated on deionized water (with carbon support film facing up) for 15-30 minutes to rinse off precipitated KOH crystals. Note that the drying step prior to rinsing in water is crucial, as otherwise the carbon film is found to very easily detach from the gold grid when floating the grid on water. Finally, the grid is scooped with filter paper and dried for 5-10 minutes in an atmospheric furnace at 70-80 °C (Fig. S4.1c).

4.6.2 Scanning transmission electron microscopy experimental conditions and image processing

Here we have used a state-of-the-art 30-300 kV Thermo Fisher Themis Z scanning transmission electron microscope. The microscope is equipped with a high coherence, high brightness field-emission electron gun (X-FEG), electron monochromator, probe C_s corrector (S-CORR), image C_s corrector (CETCOR) and a segmented DF4 detector for iDPC-STEM imaging.

The microscope was stabilized over the weekend after changing the high-tension to 30 kV. Then the aberrations up to the 5th order were minimized with the probe corrector software to the measured values shown in Table 4.1. During the experiments, the first and second order aberrations were minimized using the OptiSTEM software, which employs a contrast optimization algorithm of atomic resolution ADF-STEM images. Finetuning of defocus (C1), first order astigmatism (A1) and coma (B2) was done manually.

These low aberration values produce a phase front with a phase difference less than $\pi/2$ up to 50 mrad, such that an optimal small electron probe can be obtained with a convergence semi-angle up to this value. In our case, however, the largest suitable limiting aperture was 33 mrad, restricting the fundamental achievable resolution to 1.06 Å, which we closely reached in experiment, because we do observe the WS₂ (20-20) planes (1.36 Å) and not the

next following (12-30) planes (1.03 Å). Resolution below 1 Å can be obtained with larger better matching limiting apertures such that the probe corrector is used to its full potential.

Table 4.1. A list of measured aberration values and confidence levels after tuning the probe C_s corrector at 30 keV.

Aberration	Value	95% confidence
WD	300 μ rad	N/A
C1	3 nm	1 nm
A1	2 nm	1 nm
A2	13 nm	43 nm
B2	28 nm	42 nm
C3	-540 nm	1 μ m
A3	210 nm	400 nm
S3	220 nm	330 nm
A4	3.4 μ m	2.7 μ m
D4	2.6 μ m	1.8 μ m
B4	4.2 μ m	3.4 μ m
C5	240 μ m	320 μ m
A5	240 μ m	47 μ m
S5	100 μ m	74 μ m

At these low electron beam energies, the probe broadening due to chromatic aberrations has substantial impact. For instance, atomic resolution could hardly be achieved without reducing the energy spread of the electron source. Hence, the energy spread was reduced by employing the monochromator, which was excited to a value of 0.35, after which the microscope was stabilized overnight. With the circular energy selecting apertures of 0.5 and 1.0 μ m that we employed, the maximum available probe current was about 3 pA and 8 pA, respectively. As the microscope is not equipped with a spectrometer we could not measure the energy spread, thus we estimate (based on the size of the dispersed beam and aperture size) the energy spread

as $\sim 0.2\text{-}0.3$ eV. The collection angles of the segmented DF4 detector and ADF detector were 9-36 mrad and 39-200 mrad, respectively.

For Fig. 4.1 an image of 512×512 pixels was acquired with 7.5 pA probe current, 40 $\mu\text{s}/\text{pixel}$ dwell time and a step size of 15.92 pm. For Figs. 4.2 - 4.4 a 200-frame movie of 512×512 pixels was acquired with 2.5 pA probe current, 50 $\mu\text{s}/\text{pixel}$ dwell time and a step size of 22.52 pm. Thus, the electron doses were about $7.4 \times 10^4 \text{ e}/\text{\AA}^2$ and $1.5 \times 10^4 \text{ e}/\text{\AA}^2$ for Fig. 4.1 and Figs. 4.2 - 4.4, respectively. Despite the larger energy spread, due to using a larger energy selecting aperture, the image quality of Fig. 4.1 is predominantly improved as a result of the more than 5 times as high electron dose.

Specimen drift is another critical component that should be minimized in order to be able to continuously capture the same field of view for prolonged acquisition times. The original images, from which Figs. 4.2 - 4.4 were extracted, have a field of view of about $11 \times 11 \text{ nm}^2$, and were acquired with a frame rate of 14.0 seconds per frame, yielding a total acquisition time of 2800 seconds, or about 45 minutes. In this case the specimen drifted 2.5 nm within the first 50 frames yielding a drift rate of 0.22 nm/min. Thereafter, in the remaining 150 frames, the specimen was virtually stable with a total drift distance of 1 nm (drift rate of 0.03 nm/min). This is possible by the active vibrational damping system of the microscope column, ultra-stable room temperature (maximal deviation of 0.2 $^\circ\text{C}/24$ hours), and the use of a piezo controlled stage.

The ADF- and iDPC-STEM images were bandpass filtered with Fiji^{50,51} using the ‘FFT Bandpass Filter’ with a low-pass filter of 3 pixels, and a high-pass filter of 10 pixels, a standard operation in 2D materials research. The DPC-STEM images were bandpass filtered in MATLAB with a Gaussian low-pass filter with standard deviation of 3.0 nm^{-1} , and a Gaussian high-pass filter with a standard deviation of 1.0 nm^{-1} . We explicitly note that low-pass filtering can be safely applied to any STEM imaging technique, as only noise and no information is present at frequencies beyond twice the convergence semi-angle (see below for detailed explanation). We observe that particularly the quality of ADF-STEM images improves by low-pass filtering, as a substantial amount of high-frequency noise is present that otherwise totally obscures the light elements in the raw images. On the other hand, high-pass filtering is beneficial for iDPC-STEM images, because iDPC-STEM has strong contrast transfer at low-frequency information, which is mainly surface adsorbates and carbon

contamination in this case. We refer the reader to our previous work for a comparison of filtering on ADF- and iDPC-STEM images²⁷. Furthermore, the DPC-STEM images were deliberately strongly low-pass filtered (removing not only high-frequency noise but also high-frequency information) to enhance visibility of defect features.

The separate frames of Figs. 4.2 - 4.4 are compiled to a movie and are attached as Movie S4.1, Movie S4.2 and Movie S4.3, respectively. There simultaneously acquired iDPC-STEM, DPC-STEM and ADF-STEM images are shown, with the effective elapsed time (for the whole field of view) indicated in the top left corner.

4.6.3 Comparison of experimental and simulated iDPC-STEM and ADF-STEM images of 2D WS₂

In Fig. S4.2 we compare the experimental images from Fig. 4.1 with multislice image simulations⁹. For the simulations we have used the experimental optical settings, assume an ideal aberration free probe, and account for thermal vibrations of the sample via a Gaussian distribution with a 5 pm standard deviation. We have introduced randomly distributed sulfur vacancies in the top and bottom sulfur layer, yielding several V_S and V_{2S} in the 2D WS₂.

The simulated (Fig. S4.2a) and experimental (Fig. S4.2c,d) iDPC-STEM images match strikingly well. Both show similar sensitivity for the sulfur atoms and their vacancies, which can be easily and robustly visually identified based on their relative intensities. In fact, there is also a good quantitative match as plotted in Fig. S4.2g. We note however, that the simulations reveal that four detector segments are not completely accurate in the electrostatic potential imaging, considering that the S₂ column has higher intensity than the heavier W atom. In the next section we discuss this observation in more detail.

On the other hand, the simulated ADF-STEM images (Fig. S4.2b) predict the sulfur atoms and also the vacancies to be visible and distinguishable by visual inspection. However, in experiment (Fig. S4.2e,f) we find the ADF-STEM images to be rather noisy (even after low-pass filtering) with limited robustness towards the light sulfur atoms such that the vacancies can hardly be identified. Also, the quantitative comparison in the intensity line profile plot (Fig. S4.2h) demonstrate that only the heavy W atoms are robustly imaged, but the S atoms have reduced intensity, not allowing one to distinguish the S atoms and vacancies visually.

Hence, this comparison emphasizes that iDPC-STEM is more sensitive and more dose-efficient compared to ADF-STEM. Clearly, this is expected based on the detector geometry: the ADF detector collects substantially less electrons than the DF4 detector. However, additionally, the high signal-to-noise ratio is an inherent property of iDPC-STEM due to the integration operation.

Figure S4.2. Comparison of simulated and experimental images (from Fig. 4.1) of point defects in 2D WS₂. Intensity line profiles containing sulfur vacancies and sulfur divacancies are extracted from the simulated iDPC-STEM (a) and ADF-STEM images (b) as indicated by the outlined areas, and plotted as black lines in (g) and (h), respectively. Identical defects are also extracted from the experimental iDPC-STEM (c,d) and ADF-STEM (e,f) images, and plotted in (g) and (h) with the same color coding as outlined in (c-f).

4.6.4 Robust atomic electrostatic potential imaging of light elements in 2D WS₂

The capability of robust imaging of misaligned materials is particularly valuable in the case of 2D TMDs with the 2H symmetry, because in that case the two chalcogen atoms in a monolayer overlap in projection when it is perfectly aligned along the (0001) crystal zone axis, boosting their atomic resolution signal. However, in practice the 2D TMDs can be easily misaligned with respect to the optical axis of the electron beam.

Figure S4.3. Images of a monolayer 2H WS₂ with V_s and V_{2s} were acquired from a region that was misaligned by a few degrees from the (0001) zone axis. It shows how iDPC-STEM (a) robustly images the sulfur vacancies with single sulfur atom sensitivity as opposed to ADF-STEM in (b). Line profiles from V_s and V_{2s} are shown in (c,d), from the rectangular regions marked in (a,b).

Slight bending/buckling of the suspended 2D material flake on the TEM grid can be expected, e.g. as a result of the strong capillary forces of the liquid used during TEM sample preparation that create residual stress upon drying. Hence, it is a challenging task to align the 2D material locally, since the alignment fluctuates on a lateral scale of just tens of nanometers. In Fig. S4.3 we show the simultaneously acquired iDPC-STEM and ADF-STEM image of a (few degrees) misaligned monolayer 2H WS₂. These results demonstrate that it is still possible to properly detect and distinguish single and double sulfur vacancies (V_s and V_{2s}) with iDPC-STEM, but not with ADF-STEM, which nearly lost all its sensitivity towards sulfur.

4.6.5 Simulated contrast and accuracy of atomic electrostatic potential imaging of 2D WS₂ with iDPC-STEM

The finite resolution of the electron microscope poses a fundamental limit on the contrast between W and S₂ in the case of a 2H WS₂ monolayer. Specifically, in the case of ADF-

STEM and iDPC-STEM, information is only transferred up to a wavevector (i.e., reciprocal length or frequency) that is twice the length of the largest wavevector present in the electron probe. In our case, with a convergence semi-angle of 33 mrad and electron wavelength of about 7 pm, the largest wavevector present in the electron probe is 4.7 nm^{-1} . Which corresponds to maximum information transfer at 9.4 nm^{-1} , or $1.06 \text{ \AA}$.

Figure S4.4. Simulated images of atomic electrostatic potentials of 2H WS₂ monolayer using the multislice approach. (a) The ‘true ground state’ atomic electrostatic potentials, which are the input for multislice simulations. (b) The atomic electrostatic potentials from (a) are bandwidth limited to the maximum transferrable wavevector to obtain the highest possible resolution image. (c) A simulated iCOM-STEM image (ideal version of iDPC-STEM when enough segments are used) based on the atomic electrostatic potentials in (a). (d) A simulated iDPC-STEM image using four detector segments based on the atomic electrostatic potentials in (a). Line profiles of the W and S₂ atomic electrostatic potentials are plotted in (e-h), corresponding to the marked rectangular area in (a-d).

In Fig. S4.4 we have simulated the atomic potential of a 2H WS₂ monolayer using the multislice approach with the Dr. Probe software⁵². We neglect atomic thermal vibrations and we assume an aberration free electron probe, to demonstrate the effects of finite resolution and reduced accuracy of atomic potential imaging with iDPC-STEM. In Fig. S4.4a the simulated atomic potentials of a 2H WS₂ monolayer are shown, which we use as the ‘true ground state’ for further comparison. The bandwidth limited atomic potentials of WS₂ are shown in Fig. S4.4b. The corresponding line profiles in Fig. S4.4e,f demonstrate how the contrast between W and S₂ reduces from a relative intensity of 1.8 to 1.25 by just imposing the fundamental information transfer limit.

In fact, the contrast between W and S₂ is slightly lower in the case of iCOM-STEM (Fig. S4.4c,g) and iDPC-STEM (Fig. S4.4d,h) than in the bandwidth limited case, because then less high frequency information transfer occurs than that assumed in Fig. S4.4b. The reason is that the contrast transfer functions (CTF) of iCOM-STEM and iDPC-STEM decreases linearly to zero at the maximum wave vector, whereas the (imposed) contrast transfer function for Fig. S4.4b keeps a value of one up to the maximum wave vector and then in a step becomes zero.

Note that iCOM-STEM can be considered the most ideal case of iDPC-STEM, that can be achieved when enough detector segments are used. It is important to stress here that the object of imaging (unlike in ADF-, (A)BF- or DPC-STEM) is truly the projected atomic electrostatic potential of the sample, rendering iCOM-STEM (without any approximations) a linear imaging technique. The CTF of iCOM-STEM is positive definite (no zero crossings) with full range frequency transfer near the optimal focus. With larger segment detectors, like commonly used in iDPC-STEM, the COM is determined with less precision (although even with only four detector segments rather well). Nevertheless, even in that case, iDPC-STEM is a dominantly linear imaging technique, with well-defined CTF (reflecting the symmetry of the detector used) including almost negligible correction terms²². The contribution of these terms become noticeable only far out of focus for thin samples or in general for rather thick samples¹⁰, where part of the sample is always out of focus.

The iDPC-STEM image (Fig. S4.4d,h) reveals that the intensity of the S₂ peak even exceeds that of W. This is a direct result of using only four detector segments to approximate the COM, but the accuracy can be readily improved by employing more detector segments. In experiment, however, we observe that the heavier W atom is usually equally bright or slightly brighter than the S₂ atoms.

In experiment both the specimen and the electron probe are not perfect i.e. atomic vibrations, chromatic aberration and finite source size always contribute to the image and cannot be excluded. To this end we have simulated atomic vibrations by the frozen phonon method, where each pixel is averaged over 50 randomly selected variants from a set of 200 pre-computed random atomic vibrations. Isotropic atomic Debye-Waller factors of 0.042 Å² and 0.398 Å² are used for W and S, respectively⁵³. Chromatic aberrations are accounted for by a defocus spread of 10 nm, assuming an energy spread of 0.25 eV and a chromatic aberration

of 2.5 mm. A finite electron source size of 60 pm (full-width at half maximum) is accounted for by applying a Gaussian convolution to the final images. Finally, also the finite electron dose directly affects the visibility of low signals, which we included by introducing Poisson noise to the images. Naturally, in the case of iDPC-STEM images the Poisson noise is first introduced to each of the detector segments and then the iDPC-STEM image is computed.

Figure S4.5. Image simulations of 2D WS₂ including atomic vibrations, chromatic aberration (C_c), finite source size (d_s) and finite electron dose. The top left panel indicates the position of W, S₂ and V_s by solid magenta circles, solid cyan circles and a dotted cyan circle, respectively, and applies to all other panels.

Fig. S4.5 presents the simulated ADF-STEM and iDPC-STEM images using such imaging conditions, where the electron dose spans three orders of magnitude and are a good representation of the experimental conditions. The general trend is that atomic vibrations have a minimal effect on the signal of sulfur atoms, but that chromatic aberration and finite

probe size lead to broadening of W, S₂ and S and also increase the background signal. A consequence of the latter is that low signals can be obscured and that resolution is lost particularly when combined with lower electron doses of $1 \times 10^3 \text{ e}/\text{\AA}^2$. This is well visible in the low-dose iDPC-STEM images, which remain of good quality only when chromatic aberration and finite source size are neglected, but loose resolution as soon as they are included.

For a semi-quantitative analysis we have extracted intensity profiles of W-S₂-W-S considering only infinite, $1 \times 10^5 \text{ e}/\text{\AA}^2$ and $1 \times 10^4 \text{ e}/\text{\AA}^2$ electron doses, as the latter two represent Fig. 4.1 and Fig. 4.2-4.4. These results are plotted in Fig. S4.6 for ADF-STEM and in Fig. S4.7 for iDPC-STEM. Single sulfur atoms are not visible in ADF-STEM images (accounting for atomic vibrations, chromatic aberration and finite source size) when the dose is $1 \times 10^5 \text{ e}/\text{\AA}^2$, and S₂ columns are hardly detected when the dose is further reduced to $1 \times 10^4 \text{ e}/\text{\AA}^2$. This is not the case for iDPC-STEM where all atoms present remain both detectable and distinguishable in all considered cases.

Figure S4.6. Intensity profiles extracted from simulated ADF-STEM images in Fig. S4.5, considering various probe broadening effects and also atomic vibrations of the specimen. (a-c) No vibrations and a perfect probe; (d-f) atomic vibrations and a perfect probe; (g-i) atomic vibrations and chromatic aberration; (j-l) atomic vibrations, chromatic aberration and a finite source size.

4. Imaging atomic motion of light elements in 2D materials with 30 kV electron microscopy

Figure S4.7. Intensity profiles extracted from simulated iDPC-STEM images in Fig. S4.5, considering various probe broadening effects and also atomic vibrations of the specimen. (a-c) No vibrations and a perfect probe; (d-f) atomic vibrations and a perfect probe; (g-i) atomic vibrations and chromatic aberration; (j-l) atomic vibrations, chromatic aberration and a finite source size.

Chapter 5

Radiation damage and defect dynamics in 2D WS₂: A low-voltage scanning transmission electron microscopy study

Abstract

Modern low-voltage scanning transmission electron microscopes (STEM) have been invaluable for the atomic scale characterization of two-dimensional (2D) materials. Nevertheless, the observation of intrinsic structures of semiconducting and insulating 2D materials with 60 kV-microscopes has remained problematic due to electron radiation damage. In recent years, ultralow-voltage microscopes have been developed with the prospects of minimizing radiation damage of such 2D materials, however, to date only ultralow-voltage TEM investigations of semiconducting and insulating 2D materials have been reported, but similar results using STEM, despite being more widely adopted, are still missing. Here we report a quantitative analysis of radiation damage and beam-induced defect dynamics in semiconducting 2D WS₂ during 30 kV and 60 kV-STEM imaging, particularly by recording atomic resolution electrostatic potential movies using integrated differential phase contrast to visualize both the light sulfur and heavy tungsten atoms. Our results demonstrate that electron radiation damage of 2D WS₂ aggravates by a factor of two when halving the electron beam energy from 60 keV to 30 keV, from which we conclude electronic excitation and ionization to be the dominant mechanism inducing defects and damage during low-voltage STEM imaging of semiconducting 2D materials.

This chapter is adapted from: S. de Graaf, B. J. Kooi, Radiation damage and defect dynamics in 2D WS₂: A low-voltage scanning transmission electron microscopy study. Under review for publication in 2D Materials (2021).

5.1 Introduction

Two-dimensional transition metal dichalcogenides (TMDs) host a variety of unique properties, unavailable in their bulk counterparts, that are attractive for fundamental condensed-matter research and applications including (opto) electronic, photonics^{1,2}, spintronics³ and sensing⁴. The tunable properties are the virtue of TMDs, enabled by its strong structure-property relationship via the diverse chemical compositions, various crystal phases and rich library of defects⁵.

Aberration-corrected (scanning) transmission electron microscopy has been most valuable for the characterization of 2D TMDs. Specifically STEM is the best available tool for atomic resolution imaging and chemical characterization, and also for the manipulation down to the level of single atoms^{6,7}. Damage free imaging of conductive 2D materials like graphene has been facilitated by modern low-voltage microscopes that operate below the knock-on damage threshold, which is typically 80 kV⁸. Then the primary electrons cannot transfer sufficient energy to displace or sputter single atoms upon a head-on elastic collision with the atom nuclei. At the same time, insulating and semiconducting 2D materials like many TMDs, suffer from electronic excitation and ionization damage by inelastic scattering of the primary energetic electron by the atom's electron cloud, which starts dominating when the electron beam energy decreases below the knock-on threshold. In addition, 2D materials can also be damaged by chemical etching with oxygen radicals that are formed by the electron beam from the residual gases in the microscope column and water on the specimen, which can be minimized by an (ultra) high-vacuum environment and clean specimens⁹. Due to the balance of knock-on displacement damage and ionization damage, it is expected that electron radiation damage can never be fully prevented for insulating or semiconducting 2D materials^{10–12}.

Nevertheless, with the ultimate goal to image intrinsic structures of 2D materials with STEM, it is extremely valuable to know which electron beam energy is most suitable for the imaging of semiconducting 2D materials while minimizing radiation damage. To date, however, it is not well understood which damage mechanisms are at play in 2D materials at (ultra) low-voltages, despite the development of state-of-the-art ultralow-voltage microscopes operating at 30 kV¹³, 20 kV^{14,15} and 15 kV¹⁶. Interestingly, all quantitative investigations of radiation

damage are TEM based, but similar results for the principally different STEM are missing, despite being widely adopted by the 2D materials science community.

Here we report quantitative radiation damage analysis and electron beam-induced creation and evolution of defects in the semiconducting 2D TMD WS_2 , by recording atomic resolution movies using 30 kV and 60 kV-STEM. To visualize the light sulfur and heavier tungsten atoms simultaneously, we employ electrostatic potential imaging with integrated differential phase contrast (iDPC)-STEM¹⁷, next to the common annular dark-field (ADF)-STEM, which is more sensitive to heavy elements. It has recently been demonstrated that 30 kV iDPC-STEM is capable of imaging single sulfur atoms and its dynamics in 2D WS_2 , which are often practically invisible in ADF-STEM images¹⁸. In general, iDPC-STEM is the most robust method to image light elements next to heavy ones in various materials systems, including the imaging of oxygen atoms in hafnia-based ferroelectric devices^{19,20}, single molecules in the channels of zeolites²¹, and hydrogen atoms in titanium hydride²². Importantly, iDPC-STEM is currently the only option for the direct and fast acquisition of atomic electrostatic potential movies, as it has a major speed advantage over the competing integrated center of mass (iCOM)-STEM²³ and electron ptychography²⁴, which are practically limited to single images due to its orders of magnitude slower pixelated detectors, large datasets and extensive postprocessing.

5.2 Results and discussion

In Fig. 5.1 we show atomic resolution images of simple defects in 2D WS_2 that are induced by the 30 keV and 60 keV electron beam. Images of a sulfur vacancy (V_S) and a sulfur divacancy (V_{2S}) are shown in Fig. 5.1a,b (30 kV) and Fig. 5.1e,f (60 kV). Note that the images are extracted from movies for studying the defect dynamics and are thus not optimized high-dose single shot images (see Movie S5.1 for 30 kV-STEM and S5.2 for 60 kV-STEM).

Despite the lower dose imaging conditions, the V_S and V_{2S} defects are still identifiable and also differentiable in iDPC-STEM images for both accelerating voltages, as opposed to the ADF-STEM images. In the latter case the low signal from sulfur atoms combined with the lack of contrast between one and two sulfur atoms, complicates the robust identification of V_S and V_{2S} . Other commonly reported defects that we also observe are mirror grain boundaries (Fig. 5.1g-i) and sulfur vacancy lines (Fig. 5.1j-l). The mirror twin grain

boundaries are observed in the 4|4P form (according to the notation of ref.²⁵) with four-fold rings sharing a common chalcogen column (Fig. 5.1h), and also in the 4|4E form which has a structure similar to a double sulfur vacancy line. The mirror twin boundaries and sulfur vacancy lines generally form a connected network after prolonged exposure, which leads to inversion domains when forming a closed loop²⁶. The sulfur vacancy lines generally do not exceed a width of two sulfur atoms but occasionally grow wider similar to ref.²⁷. Hence, the sulfur atoms are also more clearly resolved by iDPC-STEM images of such line defects. Thus, electrostatic potential imaging with iDPC-STEM enables a more complete atom-by-atom evaluation of defect structures than ADF-STEM, even in cases of low-dose imaging. Such detailed experimental information on the beam-induced evolution of atomic structure is valuable for advancing the understanding of electron-matter interactions which in the end can contribute to the development of damage free imaging of matter with electron microscopes.

Figure 5.1. Atomic resolution images of common beam-induced defects in 2D WS₂. 30 kV iDPC-STEM (left panels) and ADF-STEM (right panels) images, respectively, of a (a) sulfur vacancy, (b) sulfur divacancy, (g) mirror twin grain boundary, (j) sulfur vacancy line. And similarly, 60 kV iDPC-STEM (left panels) and ADF-STEM (right panels) images of a (e) sulfur vacancy, (f) sulfur divacancy, (i) mirror twin grain boundary, (l) sulfur vacancy line. The generic idealized schematic models of a sulfur vacancy, sulfur divacancy, mirror twin boundary and double sulfur vacancy line are shown in (c), (d), (h) and (k), respectively. In the models W, S₂ and S are blue, orange and pink, respectively. Scale bar in (l) applies to all panels.

In an effort to investigate which electron-matter interactions are active during the low-voltage STEM imaging, we quantify the complete creation and evolution of defects in the atomic resolution movies, by measuring frame-by-frame the density of point defects, line defects and holes. To this end the single sulfur atom sensitivity by electrostatic potential imaging using iDPC-STEM is crucial, because the relatively light sulfur atoms have reduced intensity in ADF-STEM images, making their robust detection more challenging, in fact, often impossible. Using a template matching approach we have extracted the sulfur vacancy density for every frame in the movie as shown in Fig. 5.2a,b.

Figure 5.2. Quantitative analysis of electron radiation damage in 2D WS_2 during low-voltage 30 kV and 60 kV STEM imaging. (a) Single frame containing point defects, line defects and a hole, selected from a 60 kV iDPC-STEM movie. (b) Sulfur vacancies (white squares) and divacancies (red squares) are detected with template matching. (c) Line defects are identified as areas of compressive stress (blue points) based on real-space strain analysis. (d) Holes are found by intensity thresholding, of which only those larger than point defects (red area) are selected and smaller ones are ignored (white area). Quantitative evolution of the three stages of radiation damage including fitting with 95% confidence band is plotted in (e) for 30 kV-STEM and (f) for 60 kV-STEM.

The next stage of beam-induced damage is the rapid nucleation and growth of sulfur vacancy lines. The contracted W-W distance perpendicular to the line defects relative to the pristine

W sublattice allows identification of such defects with a strain analysis method. We employ a real-space strain analysis approach, which we found to be more robust than a reciprocal space method like geometrical phase analysis (Fig. 5.2c). Briefly, first the atom coordinates of the W atoms are detected in the ADF-STEM images with a scale-space method, then the W-W nearest-neighbor distance relative to the mean W-W distance is calculated and are averaged for every atom (see Appendix section 5.6.1 for detailed information). For this purpose the ADF-STEM images have an advantage over iDPC-STEM images, because the W and S₂ sublattices are readily separated by intensity thresholding in ADF-STEM images. This is not the case in the iDPC-STEM images where the W and S₂ intensities are very similar.

Finally, holes appear after prolonged exposure to the electron beam, which we identify based on intensity thresholding of ADF-STEM images combined with the criterium of a minimal area slightly larger than point defects (Fig. 5.2d). In general the holes appear at highly defective regions, e.g. at the intersection of line defects, or agglomerates of point defects, and are therefore also correlated with the material's defect history^{27–29}.

The resulting quantitative analysis of all defect stages is plotted in Fig. 5.2e,f as a function of electron dose, which is defined in detail in Appendix section 5.6.1. We have fitted the evolution of sulfur vacancies and the growth of holes as a function of electron dose with an asymptotic exponential function, and the growth of line defects with a linear function. The physical interpretation of the exponential function is that the generation rate of sulfur vacancies and growth rate of holes is proportional to the accumulated electron dose and the remaining sulfur atoms and material, respectively. The trend of sulfur vacancy densities evolution is similar for both accelerating voltages: it increases according to the asymptotic exponential function and saturates close to 10%, after which it gradually decays.

The indirect measurement of the sulfur vacancy line density renders it rather noisy, and is not reliable once the crystal is substantially damaged and other areas with contracted W-W distances are formed. Nevertheless, sulfur vacancy line density measurement is reliable in the initial stage including nucleation and growth. They appear once the sulfur vacancy density exceeds 6-8%, and, to a first approximation, grow about linearly in length with the accumulated electron dose. Moreover, the nucleation of the sulfur vacancy lines appears to depend predominantly on the sulfur vacancy density and not on the electron beam energy, in

agreement with the consensus in literature that sulfur vacancy lines are sinks of sulfur vacancies^{28,29}.

An interesting observation is that the sulfur vacancy density (corrected for remaining area) decreases once small holes are formed. This suggests that there is a driving force for sulfur vacancies to migrate towards exposed edges during electron beam exposure. In other words, during the destruction of edges by the electron beam, sulfur atoms are not only sputtered into the vacuum, but some also migrate away and annihilate existing vacancies, rendering the holes as sulfur atom sources. This agrees with the typical formation of metallic tungsten clusters near holes that are deficient in sulfur atoms.

Comparing the overall progression of radiation damage as a function of total accumulated electron dose indicates that the radiation damage is aggravated when the electron beam energy is reduced from 60 keV to 30 keV (Fig. 5.2e,f). For quantification we computed the damage onsets and growth rates in terms of characteristic electron doses (reciprocal of the damage cross-section) based on the fitting parameters, which are summarized in Table 5.1 (see the Appendix section 5.6.1 for fitting methods).

	30 keV	60 keV	Factor
Sulfur vacancies characteristic dose ($10^6 \text{ e } \text{\AA}^{-2}$)	0.25 $\pm$ 0.0	0.49 $\pm$ 0.0	2.0 $\pm$ 0.5
Sulfur vacancy lines onset dose ($10^6 \text{ e } \text{\AA}^{-2}$)	0.17 $\pm$ 0.0	0.75 $\pm$ 0.0	4.5 $\pm$ 1.0
Sulfur vacancy lines characteristic dose ($10^6 \text{ e } \text{\AA}^{-2}$)	2.4 $\pm$ 0.2	3.5 $\pm$ 0.2	1.4 $\pm$ 0.1
Holes onset dose ($10^6 \text{ e } \text{\AA}^{-2}$)	1.03 $\pm$ 0.0	1.41 $\pm$ 0.0	1.37 $\pm$ 0.0
Holes characteristic dose ($10^6 \text{ e } \text{\AA}^{-2}$)	3.9 $\pm$ 2	7.3 $\pm$ 0.7	1.9 $\pm$ 0.8

Table 5.1. Fitted electron doses with corresponding standard deviation required for the initiation (onset dose) and growth (characteristic dose) of the three main stages in the radiation damage of 2D WS₂. Note that the sulfur vacancies density is defined as their total length per unit area in nanometer units.

Overall, the quantitative analysis demonstrates that the three main stages of radiation damage, point defects, line defects and holes, develop faster when the electron beam energy is 30 keV compared to 60 keV. The point defects and holes develop about twice as fast, and the line defects 1.4 times as fast with accumulated electron dose. The linearized cross-sections for sulfur vacancy formation during 30 kV and 60 kV STEM imaging are 3.96 $\pm$ 0.90 barn and

2.03±0.21 barn, respectively, which are both about a factor two lower than those reported for similar TEM measurements on 2D MoS₂¹⁵. The stochastic nature of the nucleation of these damage stages is reflected in the more random values for the onset (see also Appendix, Fig. S5.1a). The nearly factor of two increase of radiation damage cross-section is in good agreement with the inelastic scattering cross-section (scaling as 1/E) according to the Bethe theory^{30,31}, which describes that more momentum and energy is transferred from the primary electrons to the atomic electrons as the velocity (*v*) of the incoming electrons decrease, resulting in a cross-section proportional to 1/*v*², or equivalently 1/E, for ionization¹¹. Hence, these results suggest that ionization is the dominant damage mechanism during the low-voltage STEM imaging of 2D WS₂, rather than elastic scattering effects like knock-on displacement or sputtering.

Moreover, we observe that the radiation damage during 30 kV-STEM imaging does not depend significantly on the time between consecutive electrons when it is varied from 4 ns to 64 ns (Appendix, Fig. S5.1b). This suggests that there is not a significant dose rate effect in this range, implying the total accumulated electron dose to be the dominant parameter i.e. a high probe current with short dwell time, or low probe current with long dwell time, produces the same damage as long as the total electron dose is equivalent.

Next we focus on more exotic defects, that we observe during the recording of atomic resolution movies using 30 kV and also 60 kV-STEM using simultaneously iDPC-STEM and ADF-STEM for the unambiguous identification of all sulfur and tungsten atoms. To the best of our knowledge these defects have neither been imaged before at 30 kV, nor using simultaneously iDPC-STEM and ADF-STEM at 60 kV. The first defect that we describe has been coined a trefoil defect, due to its peculiar three-fold symmetric shape that is the result of an effective 60° bond-rotation of the central six metal-chalcogen bonds^{32,33}. Interestingly, this defect has not been observed before in WS₂ at room temperature, but rather in its selenide counterpart.

With the electron beam energy of 60 keV we have never observed complete trefoil defects, only four partial trefoil defects in 400 frames. These partial defects consist of two 8-membered rings instead of three, and are always found directly next to existing sulfur vacancy lines. In Fig. 5.3a-d we show with iDPC-STEM images how such a defect structure appears near a sulfur vacancy line defect, and disappears two frames later. The

simultaneously acquired ADF-STEM images are shown in Fig. 5.3i-l, and are particularly useful to identify the W sublattice. The full dataset then readily allows the identification of all atoms from which the schematic in Fig. 5.3e-h is constructed.

Figure 5.3. Electron beam-induced creation and healing of a partial trefoil defect next to a sulfur vacancy line during 60kV-STEM imaging. (a-d) iDPC-STEM images, (e-h) Schematic structure evolution of the defect, with blue W atoms, orange S₂ columns, and pink single sulfur atoms (equivalent to sulfur vacancies). (i-l) Simultaneously acquired ADF-STEM images.

In the first frame (Fig. 5.3a), several of the central tungsten atoms are substantially under-coordinated due to the two neighboring sulfur divacancies. These tungsten atoms are bonded to only 2-4 sulfur atoms instead of six, as schematically illustrated in Fig. 5.3e. In the next frame (Fig. 5.3b), two sulfur atoms fill the void in the center of the divacancy cluster, forming two 8-membered rings and the effective 60° bond rotation. The single sulfur atom that was residing next to the divacancy cluster in the previous frame, has most likely moved to this position, considering that it requires the smallest possible displacement and its former

position has now become vacant³². Hence, it is reasonable to infer that undercoordination of the tungsten atoms is the driving force for such effective bond rotations in partial trefoil defects. Next to the two 8-membered rings, at the position where the third ring would be present for a complete trefoil defect, five single sulfur atoms are visible in the iDPC-STEM image in Fig. 5.3b-c, which can be interpreted as a local transformation from trigonal prismatic coordination to partial octahedral (as in the metallic 1T structure) or tetrahedral coordination. A small lateral displacement of several S₂ columns is visible in the iDPC-STEM image as a blurred asymmetric peak on the right hand side next to the sulfur vacancy line (Fig. 5.3b). The overall trefoil structure remains stable for two frames (Fig. 5.3b-c), and then reverts back to the original lattice including a cluster of five sulfur vacancies (Fig. 5.3d,h).

Figure 5.4. Electron beam-induced creation and healing of a complete trefoil defect during 30kV-STEM imaging. (a-c) iDPC-STEM images. (d-f) Schematic structure evolution of the defect, with blue W atoms, orange S₂ columns, and pink single sulfur atoms (equivalent to sulfur vacancies). (g-i) Simultaneously acquired ADF-STEM images.

When the electron beam energy is 30 keV, the trefoil defects are about equally rare. In 200 frames we have observed one partial trefoil and also one complete trefoil, the latter is shown in Fig. 5.4. In this case the trefoil defect is fully three-fold symmetric and does not form next to line defects, as opposed to the partial trefoil defects during 60 kV-STEM imaging. Also here we observe two sulfur divacancies (Fig. 5.4a), next to several sulfur vacancies, and relative displacements of sulfur atoms which we infer from the blurring of a sulfur column. In the next frame (Fig. 5.4b), the trefoil defect is present and has consumed several sulfur vacancies. The defect disappears already in the next frame as shown in Fig. 5.4c.

The rare experimental observations of short lived trefoil defects during 30 kV and 60 kV-STEM imaging indicate that their formation is a rather stochastic process and thermodynamically unstable. This is in agreement with first-principle calculations, that predict the trefoil defect to be unstable in WS₂ due to a 0.22 eV energy increase required for the bond rotation, which additionally has a substantial activation energy of 5.35 eV. This is opposite to the case of WSe₂, where the trefoil defect is stabilized by 1.31 eV and furthermore also has a reduced energy barrier of 3.12 eV, explaining why they are readily formed at room temperature³³. The partial trefoil defect in WS₂ is also predicted to be unstable with a positive formation energy of 0.14 eV relative to a cluster of two sulfur divacancies³⁴. Furthermore, the prerequisite for the formation of a trefoil defect is the clustering of chalcogen divacancies, requiring sufficiently mobile sulfur vacancies. Indeed, this clustering is a kinetically controlled stochastic process³². For this reason, trefoil defects have only been observed in WS₂ at elevated temperatures of 500 °C where the sulfur vacancy mobility is high^{32,35}. First-principle calculations predict the activation energy for sulfur vacancy migration in WS₂ to be at least 2.8-2.9 eV (and up to 4.6 eV when the lattice cannot relax sufficiently fast³³) when no other vacancies are present nearby^{33,34}. However, this energy is expected (based on calculations for WSe₂³³) to decrease approximately linearly by as much as 80% (to 0.5-0.9 eV), when the number of sulfur vacancies in the direct vicinity increases to a maximum of six.

Sulfur vacancy lines may provide thermodynamic stabilization facilitating heterogeneous nucleation of partial trefoil defects, if this is the case the stabilization is expected to be minor considering that the partial trefoil defects are present for only several frames before they dissolve during 60 kV-STEM imaging. Alternatively, the sulfur vacancy lines may be a

source and sink of sulfur atoms due to the enhanced migration rate of atoms along these line defects enabled by lower binding energies²⁸, kinetically enhancing the nucleation rate of partial trefoil defects near sulfur vacancy lines.

The electron-matter interactions that provide energy for the formation of trefoil defects are a complex combination of elastic and inelastic scattering events^{10,15}. On the one hand, sulfur atom migration is possible (in particular when the sulfur vacancy density is high) by elastic scattering of the primary electrons from sulfur nuclei, even when the electron beam energy is 30 keV, because upon a head-on elastic collision of the primary electrons with the sulfur or tungsten nuclei, the maximum energy transfer is respectively, 4.35 eV and 0.76 eV (60 keV beam) and 2.11 eV and 0.37 eV (30 keV beam)³⁶. On the other hand, the maximum energy transfer by elastic scattering is well below the high energy barriers that are involved in the formation of trefoil defects, particularly in case of the 30 keV electron beam. Therefore, predominantly inelastic scattering of the primary electrons from the atom's electron cloud causing electronic excitations must be involved in the formation of (partial) trefoil defects, in agreement with our quantitative radiation damage analysis.

The second defect that we describe here has a similar nature as the trefoil defect: a tungsten adatom induced bond rotational defect, which we observe during 30 kV and 60 kV-STEM imaging generally near sulfur vacancy lines or near the edges of holes. To the best of our knowledge, this defect type has not yet been reported.

In Fig. 5.5 we display the creation and evolution of this defect during 60 kV-STEM imaging. The adatom and the induced defect appear within one frame with a distinct triangular shape, particularly visible in the iDPC-STEM image (Fig. 5.5b), and is very stable until the WS₂ is fully destructed by the electron beam. We identify the adatom to be a W atom residing on top of another W atom in the WS₂ lattice, based on the twice as high intensity of this column in the ADF-STEM image (compare Fig. 5.5i with Fig. 5.5j). The iDPC-STEM images in Fig. 5.5a and Fig. 5.5b clearly reveal that the central W-W column has attracted the next-nearest S atoms as their position has become vacant, at the same time, the nearest S atoms have either combined with the next-nearest S atoms or have been removed by the electron beam. This collective displacement mechanism leads to the effective 60° bond rotation with the central W-W column bonded to three S₂ columns, creating the triangular shape with straight W-S₂-W edges.

Figure 5.5. Creation and evolution of a W-atom induced bond rotational defect and a sub-nanometer pore during 60 kV-STEM imaging. (a-d) iDPC-STEM images. (e-h) Schematic structure evolution of the defect, with blue W atoms, orange S₂ columns, pink single sulfur atoms and a cyan W adatom. (i-l) Simultaneously acquired ADF-STEM images.

The formation of nanopores³⁵ next to the adatom defect is a typical secondary effect that occurs once one of the undercoordinated W atoms surrounding the adatom defect is removed by the electron beam, followed by the outward relaxation of the remaining undercoordinated S atoms that were previously bonded to the removed W atom (Fig. 5.5c)³⁵. Such a relaxed edge structure (top left of the pore in Fig. 5.5c) likely passivates the undercoordinated S atom by forming again three stable S-W bonds, as schematically indicated in Fig. 5.5g, similar to the case of the partial trefoil defect in Fig. 5.3c. However, this edge structure is not always formed, as a single S atom remains protruding in the lower left part of the pore (Fig. 5.5c,d). In fact, the most stable edge structure contains not three single S atoms but rather one S₂ column as shown in the Appendix Fig. S5.2, requiring the removal of several more S atoms.

A practically identical defect is formed during 30 kV-STEM imaging as shown in Fig. 5.6. Here the W adatom and W vacancy are created within one image frame, suggesting that the adatom originates from the vacant position. Also in this case undercoordinated S atoms relax radially outward to form a nanopore. However, now the complete defect structure is not stable as it heals already in the next image frame.

Overall, during the continuous 30 and 60 kV-STEM imaging of 2D WS₂ we have observed the creation of various defects that are invariant to the electron beam energy, including point defects, line defects, trefoil defects, adatom bond rotation defects, nanopores and holes. The distinct difference that we observe between the two accelerating voltages is the increased generation and healing rate of defects when the electron beam energy is halved from 60 keV to 30 keV. This phenomenon emphasizes that more energy is transferred to the monolayer crystal during 30 kV-STEM imaging compared to 60 kV-STEM imaging, which emphasizes our claim that electronic excitation and ionization are the dominant electron-matter mechanisms proving energy for defect dynamics and radiation damage during low-voltage STEM analysis.

Figure 5.6. Creation and evolution of a W-adatom induced bond rotational defect and a sub-nanometer pore during 30 kV (a-d) iDPC-STEM and (e-h) simultaneous ADF-STEM imaging.

Relevant parameters for the radiation damage by electronic excitations and ionization are their temporal relaxation rate, spatial delocalization rate and the average time between

consecutive electrons during the illumination¹⁵. In semiconducting 2D materials, typical relaxation times of core holes, valence holes and plasmons are in the range of femtoseconds, picoseconds and nanoseconds, respectively, and delocalize over the lattice within femtoseconds^{15,37}. Even though the electron dose rate (impinging electrons per unit time per unit area) is typically 3-4 orders of magnitude higher for STEM (due to the focused probe) than for TEM (with parallel illumination), the average time between consecutive electrons is in the range of nanoseconds for STEM (with pA probe current), and in the tens of picoseconds range for TEM (with nA beam current). Therefore, excitations in semiconducting 2D materials have sufficient time to relax to the electronic ground state before the next electron arrives during STEM imaging, but not during TEM imaging where valence excitations persist during illumination due to the substantially higher electron arrival rate, and may generate multiple excitations in the end leading to ionization damage. This is also interesting considering that Kretschmer et al. recently demonstrated with first-principle calculations and 20 kV-TEM imaging that (core and) valence electron excitations in 2D MoS₂ can lower the atom's binding energy locally, enabling knock-on sputtering even at ultralow-voltages. Hence, such a multi-electron electronic excitation induced sputtering damage mechanism may be active during TEM imaging, but not in case of STEM. We note, however, that there is no fundamental reason which forbids a single electron to interact with both the electron cloud and the atom nuclei when it impinges on the specimen, in which case there is no difference in radiation damage expected between STEM or TEM in the framework of this mechanism. Nevertheless, this discussion emphasizes how TEM and STEM are principally different and thus may host different radiation damage mechanisms, where STEM has the advantage and possibility to adjust electron delivery to study, minimize and control radiation damage.

Strategies to minimize radiation damage of semiconducting 2D materials like WS₂ with low-voltage STEM should either focus on the reduction of the ionization cross-section by cooling the specimen to cryogenic temperatures^{10,38}, or minimization of damage probability by low-dose imaging. The latter requires the use of a dose-efficient imaging technique that maintains atomic resolution and high signal-to-noise-ratio under low-dose (in materials science perspective) conditions. The best available options in this context are sensitive electrostatic potential imaging techniques that optimize the image signal by collecting the majority of transmitted electrons, like iDPC-STEM, iCOM-STEM or electron ptychography²⁴. Of these

techniques, currently only iDPC-STEM is compatible with fast imaging, and maintains visible signal of both sulfur and tungsten atoms during low-dose imaging down to $5.2 \times 10^3 \text{ e } \text{\AA}^{-2}$ and also $1.7 \times 10^3 \text{ e } \text{\AA}^{-2}$, although slightly obscured by carbon contamination (Appendix, Fig. S5.3), similar to the demonstration of electron ptychography²⁴. In fact, iDPC-STEM has been applied for the ultralow-dose (down to $40 \text{ e } \text{\AA}^{-2}$) atomic resolution imaging of beam sensitive zeolites^{39,40}.

5.3 Conclusions

In summary, we have quantified radiation damage and investigated beam-induced defect dynamics in semiconducting 2D WS₂ during 30 kV and 60 kV-STEM imaging. Atomic resolution movies are recorded with the fast and direct electrostatic potential imaging technique iDPC-STEM, providing a complete picture and dynamics of all atoms present, not robustly visible in the simultaneously acquired ADF-STEM movies. Based on our quantitative radiation damage analysis, together with the observation of high-energy defect structures, we conclude that electronic excitation and ionization as caused by inelastic scattering are the dominant mechanisms leading to defects and damage in semiconducting 2D WS₂ during such low kV-STEM imaging. Accordingly, we observe that defect generation is about a factor of two faster at 30 kV than at 60 kV. Moreover, we illuminate the possible advantages of STEM over TEM imaging for the minimization of ionization damage, based on their principally different image formation process and the spatial and temporal characteristics of electronic excitations allowing energy dissipation in between every impinging electron.

5.4 Experimental methods

2D WS₂ flakes were transferred from a silicon wafer to a Quantifoil TEM grid using a clean polymer free method as described previously¹⁸. A double aberration corrected 30-300 kV Thermo Fisher Scientific Themis Z S/TEM operating at 30 kV and 60 kV was used for the acquisition of atomic resolution movies of 2D WS₂, with minimal geometrical and chromatic aberrations employing the S-CORR probe corrector and electron monochromator, respectively. For the 30 kV-STEM imaging the probe convergence semi-angle was 33 mrad, the probe current 2.5-7.5 pA (depending on energy selecting aperture size), probe step size 15.9-22.5 pm, and the dwell time 40-50 μs . The collection angles of the segmented DF4

detector (for iDPC-STEM imaging) and ADF detector were 9-36 mrad and 39-200 mrad, respectively. For the 60 kV-STEM imaging the probe convergence semi-angle was 28 mrad, the probe current 15 pA, probe step size 23.52 pm, and the dwell time 10 μ s. The collection angles of the segmented DF4 detector (for iDPC-STEM imaging) and ADF detector were 7-29 mrad and 31-186 mrad, respectively. The movies are processed with Fiji^{41,42} using the ‘FFT Bandpass Filter’, with a low-pass filter of 3 pixels, and high-pass filter of 10 pixels, a standard operation in 2D materials research to optimize image quality.

5.5 References

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5.6 Appendix

5.6.1 Real-space detection and fitting of defect evolution in 2D WS₂

Sulfur (di)vacancies are detected in real-space with the Template Matching plugin in Fiji⁴¹. To this end, a small square template of a sulfur divacancy is extracted from the experimental image, containing only the sulfur divacancy and three surrounding tungsten atoms. Using the normalized cross-correlation method, sulfur vacancies together with sulfur divacancies are detected when the threshold for the normalized cross-correlation image is 0.98, and sulfur divacancies are detected alone when the threshold is set to 0.99, requiring nearly perfect correlation. The sulfur vacancy density is then computed by dividing the total of missing sulfur atoms by the total sulfur atoms present in the field-of-view, corrected for the remaining area due to holes.

Tungsten atom positions are identified in each frame of the ADF-STEM movie using a scale-space approach written in MATLAB, which is a robust peak-finding method in (noisy) images with various pixel sizes and resolution⁴³. Each image frame is first optionally Gaussian low-pass filtered when substantially noisy, and then convoluted with a series of Laplacian of Gaussian (LoG) kernels having a standard deviation (defined as scales) ranging from 2-10 pixels, generating a stack of 2D convoluted images stored in a 3D scale-space matrix. The 3D matrix is then averaged along the scale dimension yielding one final 2D image, that contains distinct peaks at the tungsten atom position. Strong peaks are only produced in the scale image when the peak width in the experimental image and the LoG kernel are comparable, and the peaks are weak otherwise, rendering this method scale invariant. Tungsten atoms are then identified by intensity thresholding each scale image in the movie. Atom coordinates that are close to the edge of the frame are removed, preventing boundary effects. This complete procedure is automatically applied to every frame in the ADF-STEM movie, yielding all tungsten atom coordinates in space and time. Finally, the atom coordinates are refined to the center-of-mass of the atom peak in the original (optionally Gaussian low-pass filtered) image.

The strain analysis is performed in real-space, based on the atom coordinates determined by the scale-space approach. First, the radial distribution function is computed for the first 1-5 image frames where the crystal is still pristine, from which the nearest-neighbor distance is

calculated and defined as the reference W-W distance. Then, for each atom, the relative distance to each nearest-neighbor is calculated and averaged yielding an average ‘strain’ value and displayed as dots with proportional intensity.

Sulfur vacancy lines have a reduced perpendicular W-W distance, visible as an apparent compressive strain in the real-space strain maps. The real-space strain maps are processed by intensity thresholding (selecting only areas of apparent compressive strain) followed by morphological operations in Fiji⁴¹, producing binary images of the sulfur vacancy lines. From these binary images the sulfur vacancy line length is extracted using the Ridge Detection plugin in Fiji, and divided by the total area yielding the sulfur vacancy line density.

The fractional sulfur vacancy density and the hole density are fitted with an asymptotic exponential function derived by solving the differential equation

$$\frac{dn}{dD} = \sigma \cdot (1 - n) \quad (5.1)$$

yielding the following function after integration, describing the evolution of fractional defect density as a function of electron dose:

$$n = \begin{cases} 0 & D < D_0 \\ 1 - e^{-\sigma(D-D_0)} & D \geq D_0 \end{cases} \quad (5.2)$$

with n the fractional density of defects, D the accumulated electron dose, D_0 the onset dose and σ the cross-section. Where the electron dose is defined as

$$D = \frac{N^2 \cdot \frac{I_p}{|e|}}{(N \cdot d_{pixel})^2} = \frac{\frac{I_p}{|e|}}{d_{pixel}^2} \quad (5.3)$$

with N the number of pixels on the edge of the square image, I_p the probe current, e the electron charge, and d_{pixel} the step-size of the probe. Fitting these equation to the experimental results then produces the graphs in Fig. 5.2 and Fig. S5.1, and the values in Table 5.1.

Figure S5.1. Plot of the characteristic accumulated electron doses for the (a) nucleation and (b) growth of holes in 2D WS₂ for various specimens and electron beam energies during STEM imaging. Values are extracted from the fitting to asymptotic exponential function, and the error bars represent three standard deviations (99.7% confidence) of the fitting error and are not drawn when smaller than the symbol.

Figure S5.2. Dynamics and relaxation of sulfur atoms near edges of nanopores imaged with 60 kV iDPC-STEM (a-i). The edge structure can revert back and forth between metastable edge structures shown in (j,k), until the stable edge structure as in (l) is formed.

Figure S5.3. Effect of electron dose on the (a-d) iDPC-STEM and (e-h) ADF-STEM image quality of 2D WS₂. Images are acquired by fast scanning, and then multiple frames (1,3,10 and 20) are aligned and averaged to obtain images with artificial electron dose as indicated above the panels.

Chapter 6

Resolving hydrogen atoms at metal-metal hydride interfaces

Abstract

Hydrogen as a fuel can be stored safely with high volumetric density in metals. It can, however, also be detrimental to metals causing embrittlement. Understanding fundamental behavior of hydrogen at atomic scale is key to improve the properties of metal-metal hydride systems. However, currently, there is no robust technique capable of visualizing hydrogen atoms. Here, we demonstrate that hydrogen atoms can be imaged unprecedentedly with integrated differential phase contrast, a recently developed technique performed in a scanning transmission electron microscope. Images of the titanium-titanium monohydride interface reveal remarkable stability of the hydride phase, originating from the interplay between compressive stress and interfacial coherence. We also uncovered, thirty years after three models were proposed, which one describes the position of the hydrogen atoms with respect to the interface. Our work enables novel research on hydrides and is extendable to all materials containing light and heavy elements, including oxides, nitrides, carbides and borides.

This chapter is adapted from: S. de Graaf, J. Momand, C. Mitterbauer, S. Lazar, B. J. Kooi, Resolving hydrogen atoms at metal-metal hydride interfaces. Science Advances. 6 (2020).

6.1 Introduction

Hydrogen is the most abundant but also the most lightweight element in the universe. Therefore, its direct imaging with atomic-scale spatial resolution has, to date, remained elusive, despite the important role hydrogen plays in various fields such as hydrogen storage^{1,2} and hydrogen embrittlement³⁻⁵. Nowadays, the atomic structure of most crystals can be resolved by imaging techniques based on transmission electron microscopy (TEM) and scanning TEM (STEM), which have reached resolutions well below 100 pm, after the introduction of powerful field-emission electron sources and aberration correctors⁶⁻⁸. However, the challenge of imaging hydrogen has remained, not only because of its low weight but also particularly due to the weight difference between hydrogen and the host atoms in the crystal. Consequently, hydrogen has not been imaged before at an interface with vastly different concentrations of hydrogen on both sides of the interface, despite this being most interesting from a materials science perspective.

In an aberration-corrected STEM, the electrons are accelerated and focused into a subangstrom-sized probe that scans across the surface of a thin specimen (Fig. 6.1A). The incident electrons interact with the specimen's local electrostatic fields as they propagate through the material and produce a scattered exit beam of electrons that form a diffraction pattern in the detector plane. The detectors collect the electrons from a part of the diffraction pattern, of which the integrated intensity is related to the material's electrostatic field at the probe position.

The popular high-angle annular dark-field (HAADF) STEM technique collects the electrons scattered to high angles using an annular detector. This technique is not affected by the wave character of the electrons that gives interferences, complicating the interpretation of images. Consequently, HAADF-STEM images are readily interpretable, as atomic columns in a crystal are always imaged as bright dots in a dark surrounding with a dot brightness scaling with the average atomic number Z in the atomic column (typically $Z^{1.6-2.0}$)^{9,10}. Using this technique, even single carbon atoms can be detected in graphene¹¹⁻¹³, and boron and nitrogen can be distinguished in 2D-BN¹⁴. However, materials often consist of elements with a large difference in atomic number, such as heavy metal atoms next to light atoms like oxygen, nitrogen, carbon, or hydrogen, where the scattering strength of the light elements compared

with the heavy element is too low to be detected. Therefore, it is not possible to image light and heavy elements simultaneously with HAADF-STEM.

In annular bright-field (ABF) STEM, the collection angles are reduced drastically to get sufficient signal from light elements. Nowadays, light elements such as oxygen, nitrogen, and lithium can be imaged routinely with ABF-STEM^{15–17}. In the past decade, this also led to the breakthrough of imaging hydrogen in bulk crystals of YH₂¹⁸, VH₂¹⁹, and NbH₂²⁰. However, this is only possible under special circumstances, because the specimens must be very thin, i.e., less than 10 nm; otherwise, the signal from the hydrogen atoms cannot be detected. Unfortunately, not all materials can be thinned down to this level, due to limitations such as preparation-induced damage layers, surface oxides, or sample stability. In addition, the ABF-STEM technique automatically reintroduces the wave interference effects in the imaging, which can cause atom columns to appear white or black and generate image artefacts, making unambiguous detection of the light element challenging. Consequently, ABF-STEM cannot robustly image hydrogen atoms in realistic material systems, i.e., those that are thick and distorted, and has, therefore, been limited to model materials.

Here, we image hydrogen atoms at a metal-metal hydride interface with the recently developed integrated differential phase contrast (iDPC) technique. With this technique, coherently scattered electrons that fall inside the bright-field disk are collected with an annular detector that is segmented into four quadrants (Fig. 6.1A)²¹. Using DPC imaging^{22–24}, three complementary images are formed that represent the material's local projected electrostatic properties when the specimen is thin. Then, the projected electric field is imaged with DPC, the projected charge density with differentiated DPC (dDPC), and the projected potential with iDPC (see also the Appendix)²¹. The iDPC technique is particularly useful to generate sensitivity toward light elements^{25,26}. However, the direct relation between iDPC and the material's electrostatic properties only holds in cases where the specimen is ultrathin. Usually, the specimens are thicker, and the physical interpretation of the DPC images becomes less straightforward. Nevertheless, advantages of iDPC over ABF are (i) the capability to directly image the projected potential for thin specimens, (ii) a simpler contrast transfer function, i.e., less problems with the wave interference character and contrast reversals in the images, and (iii) an intrinsically better signal-to-noise ratio (SNR), which in

the end also provides the option to use lower doses, e.g., on vulnerable samples such as the beam-sensitive zeolite²⁷.

6.2 Results and discussion

To produce stable metal-metal hydride interfaces, we have chosen the Ti-TiH system, which is similar to the Zr-ZrH system that plays an important role as nuclear fuel cladding material in nuclear reactors²⁸. In contrast to earlier studies that image hydrogen in a dihydride like YH₂, here we study the monohydride γ -TiH. This hydride readily forms at low temperature and low hydrogen concentrations due to the high hydrogen mobility and low room temperature hydrogen solubility limit in hexagonal close-packed α -Ti^{29,30}. The structure of this phase has been identified by diffraction techniques already more than three decades ago^{29–31}. The γ -TiH crystal has a face-centered tetragonal (FCT) lattice that contains four titanium and four hydrogen atoms per unit cell (Fig. 6.1B). Half of the tetrahedral interstitial sites are occupied by hydrogen atoms that organize in two columns that are parallel to the *c* axis and are located on the face diagonal when viewed along the *c* axis (Fig. 6.1C). Ab initio calculations performed on the isomorphic γ -ZrH indicate that, despite a lower entropy contribution, this ordering of hydrogen in columns is more stable than the diamond-like occupation, where the hydrogen atoms occupy alternating tetrahedral sites³². A similar result, although described less explicitly, was obtained for γ -TiH³³.

Imaging the monohydride offers major benefits over a dihydride because in single images, we can image columns with identical surrounding of the host Ti atom columns where one type of column contains the hydrogen atoms and the other type, in principle, is empty. Wave interference effects of the scanning electron beam play a role during imaging; therefore, it cannot be ruled out that there is a certain atomic like signal in a column between Ti atom columns when no hydrogen atoms are present. In the monohydride, the difference between the signals coming from the hydrogen-filled columns and the empty columns can be directly compared, allowing for unambiguous interpretation that is not possible in the case of the dihydride. Imaging artefacts are often a challenge: In TEM and STEM, such artefacts generally have a symmetry related to the one of the underlying host lattices. In this respect, the monohydride offers a further advantage because the symmetry of the hydrogen sublattice is distinctly different from the one of the host titanium sublattice, and therefore, the weak

signals we measure for the hydrogen cannot be a faint displaced or distorted replica of the host.

Figure 6.1. Schematic of a STEM system and the γ -TiH crystal and its three possible interfaces with α -Ti. (A) iDPC images are captured with the quadrant detector (inner) and can be used simultaneously with the HAADF detector (outer). (B) Crystal structure model of the face-centered tetragonal (FCT) γ -TiH unit cell containing four hydrogen atoms that occupy tetrahedral sites. (C) Two columns in between the titanium columns are occupied by hydrogen atoms and two columns are empty. (D) Three potential models can describe the interface between γ -TiH and α -Ti.

Although γ -TiH has an approximately 15% larger unit cell volume compared with the α -Ti matrix, an apparently strain-free coherent interface is formed between them³⁴. Therefore, to accommodate the volume misfit, the lattice misfit perpendicular to the interface is about 16%, generating large compressive stress on the precipitate³¹. Consequently, the growth rate parallel to the interface is orders of magnitude higher than the perpendicular one, resulting in plate-shaped precipitates^{31,34}. The absolute position of the hydrogen atoms with respect to the interface has to date not yet been identified, because diffraction techniques do not transfer translational information and real-space atomic resolution images only provided information on the position of the titanium columns³⁴. Hence, there are three possible models, schematically depicted in Fig. 6.1D, which could not be distinguished using earlier techniques³⁴.

To image the interface edge-on, we align the α -Ti matrix along the [0001] direction, and then the FCT γ -TiH is imaged along [001]. However, the large volume expansion by the

incorporation of the γ -TiH precipitate in the Ti matrix leads to a severely strained system, where the misfit is accommodated plastically via dislocation motion in the Ti matrix^{31,35}. Consequently, an often-encountered challenge, particularly when thinning the sample to electron transparency, is that crystal bending across the interface misaligns the crystal locally and impedes proper atomically resolved images over the entire region of interest (Fig. S6.4). Because of these random imperfections in the crystal, it is essential to capture high-resolution images of large areas as fast as possible to locally obtain the highest possible quality of atomically resolved images while minimizing drift. In this context, the detectors that we use here have an advantage over pixelated detectors that were used in recent demonstrations of ptychographic reconstruction^{36–38}. The pixelated detector captures a complete diffraction pattern at every scan position, yielding a large four-dimensional dataset. With this abundant dataset, the local phase change can be retrieved for ultrathin specimens using an iterative phase retrieval algorithm. However, currently, a serious drawback of a pixelated detector is the two-orders-of-magnitude-longer pixel dwell time³⁶ compared with the HAADF, ABF, and quadrant DPC detectors. Hence, despite not being a model system for imaging due to strain, bending, and large sample thickness (see the Appendix section 6.6.1), we were able to find well-aligned areas at the interface by capturing large areas with small pixel size and quick readout times of several seconds. With this approach, we routinely imaged the edge-on interface with minimal residual misalignment with about 60-pm resolution (Fig. 6.2).

The image recorded with the HAADF detector can be interpreted directly by virtue of Z-contrast: It shows two distinguishable lattices separated by an atomically sharp interface that matches convincingly with the simulated image (Fig. 6.2A). Viewed along these crystal axes, the α -Ti (01 $\bar{1}$ 0) planes are parallel to the γ -TiH (1 $\bar{1}$ 0) planes at the interface, in agreement with the TEM studies that were performed over three decades ago^{31,34}. Although the Z-contrast image visualizes the titanium atoms well, it fails to transfer signal from the hydrogen atoms, which are expected in equivalent stoichiometry in the γ -TiH.

Next, we used ABF to image the α -Ti/ γ -TiH interface (Fig. 6.2B), although the specimen thickness of about 30 nm is substantially thicker than 10 nm, which is required to properly image hydrogen atoms with ABF. The titanium atoms are well resolved in the γ -TiH but poorly in the α -Ti. The high sensitivity of ABF imaging toward crystal orientation (see Fig. S6.11) combined with the inherent local bending of the specimen leads to the lower quality

of the ABF image compared with the HAADF image¹⁶. Nonetheless, in the γ -TiH, a weak contrast is visible between alternating atomic planes parallel and perpendicular to the interface, which indicates the presence of signal from the hydrogen columns. Close inspection suggests that either model I or III best describes the interface (Fig. 6.1D). However, being limited by the SNR and quality of the image, we cannot reliably determine the exact position of hydrogen columns.

Figure 6.2. Comparison of images of the interface between γ -TiH and α -Ti using different techniques. (A) HAADF. (B) Contrast-inverted ABF. (C) iDPC. (D) Contrast-inverted dDPC. (E) DPC magnitude. (F) DPC vector field using color wheel representation. Insets: Simulated images of a 30-nm-thick specimen of interface model I shown in Fig. 6.1D. Field of view is 3.5×3.5 nm.

As a final step, the DPC-based images of the interface were constructed using the segmented detector and are depicted in Fig. 6.2 (C to F). In the iDPC image, the Ti atoms are resolved accurately in the γ -TiH and the α -Ti matrix (Fig. 6.2C). Besides the bright Ti atoms, there is also a clear signal within the γ -TiH crystal that forms a checkerboard-like pattern with the symmetry that is expected for the hydrogen sublattice. With the convincing match between the experimental and simulated images and the extensive additional checks that we have performed (see the Appendix sections 6.6.2-6.6.8, e.g., providing different types of electron

energy loss spectroscopy information and results of extensive image simulations), we show that the hydrogen columns are imaged with iDPC and that the interface is best described by model I (Fig. 6.1D).

In the dDPC image (Fig. 6.2D), the Ti atoms are properly resolved throughout the entire image, in contrast to the ABF image where they were only well resolved in the γ -TiH. Also, the hydrogen atom columns are imaged, but, as in the ABF image, the faint signal is preventing accurate hydrogen column detection in the image. The DPC images in Fig. 6.2 (E and F) show the scalar field magnitude and the vector field, where the field direction is indicated by the color and the magnitude by the intensity. Figure 6.2E displays a rather complex field in the Ti matrix and a more easily interpretable field in the γ -TiH, which agrees well with the simulation. The field magnitude at the Ti atom columns in the γ -TiH is not radially symmetric, but is ellipse shaped and oriented in two orthogonal directions. This is a direct effect of the checkerboard-like ordered hydrogen columns and also allows us to confirm model I as the best description of the interface.

We have performed an SNR analysis of the hydrogen signal as a measure to quantify the hydrogen imaging capabilities of the different imaging techniques (Fig. 6.3). Note that we have applied an identical filtering procedure to all experimental images to ensure a fair comparison (see Fig. S6.6). Experimental intensity profiles are extracted by averaging the alternating (220) atomic planes (perpendicular to the interface) containing hydrogen columns (Ti-H-Ti) and the intermediate planes containing empty columns (Ti-empty-Ti). These are compared with the simulated intensity profiles of a 32.2-nm-thick specimen (see Fig. 6.3), but note that the iDPC images compare reasonably well with simulations holding for a large thickness range of 20 to 50 nm (Fig. S6.13). We define the SNR as the ratio of the relative intensity of the hydrogen signal and the SD of the averaged intensity profiles.

The HAADF intensity profiles only contain peaks from Ti and no signal from hydrogen; hence, as expected, the SNR is below unity (Fig. 6.3A). In the ABF image, the hydrogen atom columns are imaged with an SNR of 2–3 (Fig. 6.3B). However, also an image artefact is revealed: The intensity of the adjacent Ti atom columns is modulated with the symmetry of the checkerboard-like ordered hydrogen atoms. The SNR is also 2–3 in the dDPC image, where the hydrogen atoms produce the sharpest peak (Fig. 6.3C). However, at the same time, peaks are present in the empty columns, which complicate image interpretation. Last, the

intensity profiles from the iDPC image show that hydrogen atoms are imaged with the highest SNR of 4–5, and no image artefacts are present (Fig. 6.3D). The SNR of the iDPC image compared with that of the ABF image is improved, because on the one hand, the segmented detector collects more electrons, while on the other hand, the random noise is suppressed by its intrinsic noise suppression property^{21,27}. Furthermore, the inherently present specimen bending reduces signal from the hydrogen columns for ABF and substantially less for iDPC (see Figs. S6.7 and S6.11).

Figure 6.3. Comparison of the experimental and simulated intensity profiles of the γ -TiH at the metal-metal hydride interface and the experimental SNR of the hydrogen column signal. (A) HAADF. (B) ABF. (C) dDPC. (D) iDPC. The pink and yellow bands represent the experimental intensity profiles of the Ti-empty-Ti-empty-Ti and Ti-H-Ti-H-Ti columns, respectively. The width of the bands is twice the SD, centered around the average value. Solid dark lines are the simulated profiles for a 32.2-nm-thick γ -TiH crystal. The SNR of the hydrogen signal is extracted from the experimental profiles and plotted below. a.u., arbitrary units.

We did not observe any structural rearrangements of hydrogen atoms at the interface during the imaging, i.e., we were limited by carbon contamination and not by electron beam-induced damage. This is a remarkable observation, considering that (i) energetic electrons are impinging on the specimen during imaging, which can either transfer energy to the material or displace hydrogen or titanium atoms upon knock-on collisions³⁹, (ii) hydrogen atoms are highly mobile in titanium at room temperature, (iii) there is a step function in hydrogen concentration of about 50 atomic percent across the interface, and (iv) the γ -TiH is a metastable phase. Therefore, our observation is at first sight contrary to what is expected based on these considerations. However, energy transferred by inelastic collisions of the 300-keV primary electrons with the atoms can be quickly dissipated because of the metallic behavior of titanium hydrides⁴⁰. Knock-on collision of a primary electron with a hydrogen or

titanium atom can lead to a maximum energy transfer of 844 and 17.8 eV, respectively. This amount of energy is sufficiently high to displace hydrogen atoms but not titanium atoms, if we assume a typical binding energy of 25 eV⁴¹. Nevertheless, overall, the probability to displace a hydrogen atom may still be low, because the scattering cross section of the hydrogen atom is small and it decreases with increasing primary electron energy³⁹. Therefore, it is advantageous to image the titanium hydride with higher electron energies (like 300 keV) to minimize electron beam-induced damage. Furthermore, for a complete understanding, it is also critical to consider the effects of embedding the γ -TiH precipitate in the host metal. Ab initio simulations³³ have demonstrated that the γ -TiH precipitate cannot be stabilized by compressive stress imposed by the matrix alone. Only when the combined effect of compressive stress imposed by the matrix, and the coherency strains of the interface are taken into account, the γ -TiH precipitate is stabilized. These arguments rationalize our observation that the Ti/ γ -TiH interface remains stable during imaging and that electron beam-induced damage is not visible. We additionally observed that after preparation, the γ -TiH remains only crystalline in reasonably thick (e.g., 30 nm or thicker) parts of the specimen. We speculate that the thinner parts of the specimen are easier amorphized during preparation, as it may not have the mechanical rigidity to provide sufficient coherency strains and compressive stresses that stabilize the γ -TiH. Hence, the dynamic interplay between compressive stress and the formation of a coherent interface is directly responsible for the high stability of the Ti/ γ -TiH interface.

Figure 6.4. Comparison of high-quality images of γ -TiH far away from the interface. (A) HAADF. (B) Contrast-inverted ABF. (C) iDPC. Field of view is 3.13×3.13 nm.

Higher-quality images of the γ -TiH are captured further away from the interface where the crystal strain has relieved and local bending is much less a problem (Fig. 6.4). A result is that

the hydrogen columns appear more localized compared with the images that are recorded at the interface. Now, the checkerboard-like filling of the hydrogen columns in the γ -TiH lattice is visible in the ABF (Fig. 6.4B) and iDPC (Fig. 6.4C) images, which is lacking in the HAADF-STEM image (Fig. 6.4A). Here, we constructed the ABF image by summing the four images from the quadrant detector, because with the normal ABF geometry a signal from the hydrogen atoms could not be detected. A similar detector geometry was also used to image hydrogen in VH_2 ¹⁹. Our simulations show that in this case, a higher hydrogen column intensity can be achieved at the costs of localization (Fig. S6.8). Now, the hydrogen columns are also readily observable next to the titanium ones in the ABF image. Nevertheless, the hydrogen atoms are much better visualized in the iDPC image.

Figure 6.5. Comparison of the experimental and simulated intensity profiles of the γ -TiH under optimal imaging conditions and the SNR of the hydrogen column signal. (A) HAADF. (B) ABF. (C) iDPC. Here, the ABF is formed by summing the quadrants of the iDPC detector, such that the ABF and iDPC images use the exact identical raw data. The pink and yellow bands represent the experimental intensity profiles of the Ti-empty-Ti-empty-Ti and Ti-H-Ti-H-Ti columns, respectively. The width of the bands is twice the SD, centered around the average value. Solid dark lines are the simulated profiles for a 52-nm-thick γ -TiH crystal. The SNR of the hydrogen signal is extracted from the experimental profiles and plotted below.

Compared to Fig. 6.3, the experimental intensity profiles extracted from the images in Fig. 6.4 now match significantly better with the simulated ones as the crystal is better oriented (see Fig. 6.5). Particularly the profiles extracted from the HAADF and iDPC images agree nearly perfectly with the simulations. However, the intensity profile from the ABF image does not match well and contains high levels of noise. In fact, the noise in the iDPC image is three times lower than in the ABF image, which is a remarkable result, considering that the

ABF and iDPC images are constructed from the exact identical original signal. This demonstrates the intrinsic noise suppressing property of using in a clever way the four quadrants of the iDPC imaging technique.

Our experimental images and extensive image simulations of the γ -TiH unit cell (see the Appendix sections 6.6.2-6.6.8) allow us to conclude that iDPC has several major advantages over ABF imaging: (i) iDPC images the hydrogen columns with higher contrast and better localization. (ii) The atom column intensity oscillates substantially less as a function of specimen thickness. (iii) Contrast also does not reverse as long as the probe is focused into the specimen, unlike ABF imaging where the empty column and hydrogen-filled column reverse contrast for specimens thinner than about 10 nm. This furthermore shows that the iDPC technique produces easily interpretable images also when the specimen is thick. However, then, the iDPC image cannot be quantitatively interpreted as the material's projected potential. This is also evident, since we observe in the experiment and in the simulation that the atom intensities oscillate as a function of thickness and also that the relative contrast of the hydrogen atoms is higher than expected based on the atomic weights of hydrogen and titanium. Nevertheless, these simulation results demonstrate that, on fairly all aspects, iDPC images allow more straightforward interpretation and better imaging of the light element column next to an empty column. In ABF, the signals coming from the hydrogen column and the empty column are very similar and can reverse in contrast, which shows that ABF is prone to erroneous detection of light elements.

6.3 Conclusions

In summary, we have imaged hydrogen atoms in titanium monohydride at its interface with titanium using the recently developed iDPC-STEM technique. The images of the interface uncovered, 30 years after three models were proposed, the model that describes the positions of the hydrogen atoms with respect to the interface. We observed unexpected high stability of the titanium monohydride even during energetic electron irradiation conditions, originating from the combined effect of interfacial coherency strains and the compressive stress imposed by the matrix. Significantly, the capabilities of imaging hydrogen in the nonideal titanium-titanium monohydride system, with severe and limiting imperfections, demonstrate the ability and the prospects of iDPC-STEM as a robust imaging tool in materials research. This work paves the way to further advance our understanding of hydrogen in

solids, like retrieving local site occupancy, atomic vibrations, and mobility from iDPC images. Moreover, it can be extended to all material systems containing light elements next to heavy ones, like oxides, nitrides, carbides, and borides.

6.4 Experimental methods

6.4.1 Specimen preparation

A single crystal titanium sample was mechanically polished followed by twin-jet electrochemical polishing at room temperature with a TenuPol-3 from Struers to load the sample with hydrogen such that γ -TiH precipitates were formed. A TEM lamella was extracted from the sample using a Helios G4 CX dual beam system with a Ga focused ion beam. The lamella was thinned to electron transparency with the focused ion beam using progressively lower accelerating voltages. As a final step, a Gatan PIPS II polishing system was used to polish the lamella with 0.3-kV Ar ions.

6.4.2 Scanning transmission electron microscopy

For the imaging, we used a probe and image corrected Thermo Fisher Scientific Themis Z S/TEM system operating at 300 kV. The specimen was plasma cleaned for 3 min before insertion in the S/TEM column. For the imaging, a convergence semi-angle of 21 mrad was used, and the current was set to 50 pA for Fig. 6.2 and 14 pA for Fig. 6.4. Experimental images were identically filtered by applying a high-pass Gaussian filter and an average background subtraction filter.

6.4.3 Multislice simulations

The crystallographic models of the γ -TiH unit cell and the γ -TiH/ α -Ti interface were constructed with VESTA. The γ -TiH unit cell was adjusted (<2% change in lattice parameters) to obtain a coherent interface with α -Ti. These models were loaded in the Dr. Probe software for STEM image simulations. Microscope parameters were set equal to experimentally calibrated values, and aberrations were neglected except for defocus. The detector collection angles were also set to the experimentally calibrated values. The resulting images were convolved with a two-dimensional Gaussian function of 70-pm full-width at half maximum to account for finite probe size.

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6.6 Appendix

6.6.1 Specimen preparation and characteristics

Disks with a diameter of 3.05 mm diameter and a thickness of about 350 μm thick were spark eroded from a titanium single crystal having a purity of 99.99% (as purchased from Goodfellow). The disks were mechanically polished on both sides to a final thickness of about 50-60 μm using sequentially 1000, 2000 and 4000 grit SiC grinding paper. The mechanically polished disks were twin-jet electrochemically polished at room temperature using a TenuPol-3 from Struers. For the electrolyte a mixture of 600 ml methanol, 360 ml 2-butoxyethanol and 64 ml of perchloric acid (72%) was used. The applied bias voltage was 10 V, with maximum flowrate (10) of the electrolyte and maximum photosensitivity (10) of the photodiode. This resulted in a constant polishing current of 100 mA for 20 seconds until the polishing device detected perforation and stopped the polishing.

During this process of electrochemical polishing plate-shaped precipitates are produced within the titanium which (in a later stage) can be identified as $\gamma\text{-TiH}$. This process of hydride formation during electrochemical polishing is well-known^{31,34,42,43}. During this process the surface oxide on the titanium is continuously etched away into the liquid allowing hydrogen dissolution in the solid titanium. Since the solubility limit of hydrogen in Ti is low, the hydrogen easily precipitates in the form of thin $\gamma\text{-TiH}$ platelets. We spent considerable time in characterizing and optimizing the electrochemical polishing process in order to obtain a desired structure with relatively long planar interfaces of the $\gamma\text{-TiH}$ platelets in the Ti matrix without too much stresses and bending of the thin foil.

We analyzed the crystal orientation of the disk using electron backscatter diffraction (EBSD) in an FEI Nova NanoSEM 650 equipped with an Ametek EDAX-TSL EBSD system. A result from this analysis is shown in Fig. S6.1; it can be concluded that the sample consists mostly out of a millimeter sized grain with the c-axis tilted about 35° from the plane normal. However, there are also micrometer thick bands, extending throughout the millimeter sized crystal, that have the c-axis approximately in plane.

Figure S6.1. Electron backscatter diffraction map of the Ti sample. (A) Orientation imaging microscopy image reveals two dominant grain orientations. The corresponding inverse pole figure (B) shows that the c-axis of the larger (purple) grain is tilted about 35° with respect to the plane normal and the thin (turquoise) band has its c-axis 85° from the plane normal, or 5° from being in plane.

To obtain specimen with the desired c-axis normal to the sample plane we extracted lamellae from these thinner bands using a Helios G4 CX dual beam system with a Ga focused ion beam (FIB). A lamella was attached to a Cu TEM grid and thinned to electron transparency using progressively lower accelerating voltage from 30 kV down to 1 kV. During this stage the plate-shaped precipitates can be observed readily and they even show some further growth. The FIB thinned lamella was finally polished for 60 seconds on each side using a Gatan PIPS II Argon ion polishing system operating in stationary mode at 0.3 kV with gun angles of $\pm 10^\circ$. Prior to S/TEM imaging, we plasma cleaned the TEM grid with the FIB lamella for three minutes with a Fischione Model 1070 plasma cleaner, using a gas mixture of 25% O_2 and 75% Ar.

An overview image of the γ -TiH precipitates is shown in Fig. S6.2A. Despite the careful thinning procedure, we observed with S/TEM that the γ -TiH precipitates are amorphous close to the edge of the lamella where the foil is the thinnest (see Fig. S6.2B). As a consequence we were forced to image the interface relatively far away from the edge. For example, the images of the interface that we present in Fig. 6.2 are captured from an area indicated by the white rectangle in Fig. S6.2A. This area is approximately 100 nm away from the edge, and we estimate the local thickness to be in the range of 30-40 nm based on careful comparison with image simulations.

Figure S6.2. Amorphous γ -TiH in thin parts of the specimen. (A) Overview ABF-STEM image shows the γ -TiH precipitates in the α -Ti matrix. The images of the interface (Fig. 6.2) were captured in the area indicated by the white rectangle. (B) The HAADF-STEM image of the interface of the central thickest precipitate that was captured close to the thin edge of the lamella. It shows that the γ -TiH precipitate (on the left) is amorphous unlike the α -Ti host (on the right) which remains crystalline.

In bright-field TEM analysis we observe bending contours that extend far into the specimen (i.e. covering all areas that are still relatively thin). The crystal bending is a feature of the specimen that is inherent to the incorporation of the γ -TiH precipitates, with about 15% larger unit cell volume compared to the host Ti. With the Kikuchi patterns that we used to align the crystal we observed that the smallest length scale of the crystal bending is of the order of several nanometers. The crystal was also bent across the lamella with a periodicity of the order of hundreds of nanometers; however this is irrelevant considering the used field-of-view during imaging. After aligning the crystal as good as the specimen allowed at low magnification (with a field-of-view several hundreds of nanometers), we used the Kikuchi pattern to find areas close to the interface that were correctly aligned. With this approach we were able to capture the interface with atomic resolution; however a new issue that we encountered many times is that only one of the two phases, either the α -Ti or the γ -TiH, was properly resolved.

Figure S6.3. Crystal bending along the interface. (A) HAADF-STEM image shows that the Ti matrix gradually misaligns from top to bottom (which is about 25 nm). (B) In the iDPC-STEM image only the top 5 nm is well-aligned. Note, however, that the hydrogen columns are properly resolved in the γ -TiH precipitate along the entire interface.

An example that shows the crystal misalignment along the interface is depicted in Fig. S6.3. Here the interface was imaged with atomic resolution using HAADF-STEM (Fig. S6.3A) and iDPC-STEM (Fig. S6.3B) simultaneously. In the HAADF-STEM image both crystals are resolved with high quality at the top of the image, but the quality starts to degrade from around the center towards the bottom of the image.

We note that the interface is not atomically sharp; however this is not necessary to demonstrate the point here. At the lower part of the image the closest Ti columns in the host matrix are not separately resolved, but form streaks perpendicular to the interface. This is an effect of local stresses in the system (especially perpendicular to the interface where there is a 16% lattice mismatch between the precipitate and the matrix) that induce crystal bending such that the close Ti columns form streaks in projection. The misalignment of the Ti matrix is more apparent in the iDPC-STEM image, where only in the top 5 nm the α -Ti and γ -TiH are of rather good quality. In the remaining part of the image the Ti matrix forms streaks similarly to the HAADF-STEM image.

Furthermore, in the top part of the HAADF-STEM image there is an intensity difference of adjacent Ti atom columns in the HCP Ti. Since it is unlikely that these atomic columns differ, this observation strongly suggests the presence of a relatively large third-order astigmatism aberration. This aberration causes three-fold symmetric probe tails that can generate these effects when the azimuth of the three-fold symmetric probe tails matches that of the six-fold symmetric hexagonal lattice⁴⁴.

Considering all these characteristic imperfections of the specimen, we had to find areas where the local stresses were minimal such that both phases at the interface could be resolved with atomic resolution. In practice this means that we (1) aligned the crystal locally at relatively low magnification as good as possible (2) captured several images with high resolution (e.g. 1024×1024 pixels up to 4096×4096 pixels) and step sizes of 5 up to 25 pm with a pixel dwell time of 5-10 μ s (3) selected well aligned parts of the image based on the combined quality of the simultaneously acquired HAADF and iDPC or ABF image.

6.6.2 Identification of the γ -TiH phase with electron energy loss spectroscopy

We acquired spatially resolved electron energy loss spectra (EELS) of areas containing the Ti matrix and the γ -TiH precipitates with a Thermo Fisher Scientific™ Themis Z S/TEM

system operating at 300 kV equipped with a Gatan Enfium 977 system. Spectra were extracted from equally sized areas in the Ti matrix and γ -TiH precipitate (Fig. S6.4). From the low electron energy loss part we obtain the locations of the plasmon peaks in Ti and in γ -TiH at 17.6 eV and 19.4 eV, respectively, which matches well with previous studies (typically 17.6 eV and 19.6 eV)^{43,45} and thus can be used as a verification that γ -TiH precipitates are formed.

Figure S6.4. Plasmon mapping of Ti and γ -TiH. (A) Intensity map (with an energy window from 19.80 eV to 19.85 eV) shows the area from which we extracted the electron energy loss spectra. The γ -TiH precipitates appear with higher intensity compared to the darker Ti matrix due to the filtering. (B) The equally sized yellow and pink areas in (A) are integrated to yield the spectra for respectively α -Ti and γ -TiH. The peaks close to 20 eV correspond to the plasmon peaks, and are a fingerprint for the two phases.

From the high electron energy loss part of the spectrum we investigated if contaminants/dopants are present because titanium has a high affinity for carbon, nitrogen and oxygen (Fig. S6.5). The spectrum only contains an ionization edge starting at 456 eV which belongs to Ti $L_{2,3}$ edge (462 eV and 456 eV, respectively), and no signs of carbon, nitrogen and/or oxygen are present in the spectrum, because the C K edge (284 eV), N K edge (401 eV) and O K edge (532 eV) are missing. Hence, based on the EELS analysis we conclude that titanium hydride precipitates are present without any noticeable contaminants/dopants.

Figure S6.5. Inspection of contamination with core loss EELS. (A) Overview image of the area from which we acquired an electron energy loss spectrum. The actually scanned area of the spatially resolved spectrum was the same height as the pink highlighted area, but slightly wider to extend into the Ti matrix. (B) Integrated high-loss spectrum from the pink area in the γ -TiH precipitate as depicted in (A) is plotted. The absorption edges of C, N, O and Ti are located in this energy range but not detected as only the sharp edge from Ti is visible

6.6.3 Scanning transmission electron microscopy

For the atomic resolution imaging we used a probe and image corrected Themis Z S/TEM operating at 300 kV. Images were recorded with convergence semi-angle of 21 mrad and a probe current of 50 pA for Fig 6.2 and 14 pA for Fig. 6.4), a step size between 5 and 20 pm, image resolution of 1024×1024 pixels up to 4096×4096 pixels and a pixel dwell time of 1 up to 10 μ s.

6.6.4 Filtering procedure of the experimental images

All experimental images have been filtered identically with a high-pass Gaussian filter and an average background subtraction filter (ABSF)⁴⁶ (freely available at http://www.dmscripting.com/hrtem_filter.html). The high-pass Gaussian filter (with a standard deviation of 1.1 nm⁻¹, equivalent to 2.1 mrad) only attenuates information at low spatial frequencies and retains high frequency information e.g. this filter removes visualized carbon contamination and thickness variations, but keeps the atomic structure untouched. The average background subtraction filter removes background information (like noise and diffuse amorphous rings) from the entire Fourier spectrum of the image. The effect of the filters on the HAADF, ABF and iDPC images is shown in Fig. S6.6.

Figure S6.6. Effect of the applied spatial filter on images of γ -TiH. (A) HAADF (B) ABF (C) iDPC images. The average signal-to-noise ratio of the hydrogen signal is shown in the top left corner of each image.

The high-pass Gaussian filter is particularly helpful for the techniques that transfer low spatial frequency information i.e. HAADF and iDPC. However, this filter has most effect on the iDPC image, since carbon contamination is best visualized in the iDPC image as it is more sensitive to light elements than HAADF. It has a minor effect on the ABF image, as it does not image low spatial frequency information. The ABSF enhances the contrast of all images, but has most effect on the HAADF and ABF images. The high-contrast raw HAADF image is already interpretable, and this is further enhanced by noise removal due to the ABSF. The ABSF is, however, crucial for the ABF images, because these images are noisy, which obscures the crystalline structure to a large extent. The iDPC image is improved as well, however the carbon contamination remains.

For a fair comparison between the images it is therefore required to combine the two filters. In that case the HAADF and ABF are mainly enhanced by the ABSF, and the iDPC image by the high-pass Gaussian filter. This also gives the best average signal-to-noise ratio (SNR) of the hydrogen signal in the ABF and iDPC images (see insets in Fig. S6.6).

6.6.5 Reciprocal space analysis of the hydrogen signal in γ -TiH

We compare the Fourier Transforms (FT) of the images in Fig. 6.2A-D to investigate the strength of the signal from the hydrogen atoms. In Fig. S6.7 we show the fast FT (FFT) of the full source images, where the symmetry of the α -Ti and γ -TiH lattices are also indicated. The checkerboard-like ordering of the hydrogen columns in γ -TiH is present as superlattice reflections in the FFTs of the images. The relative intensity of the γ -TiH{110} superlattice reflections with respect to a reflection from the Ti lattice (here we use the γ -TiH{200} peaks as reference) indicates how well the long-range ordering of hydrogen columns is defined in the image. The four intensity profiles that connect the γ -TiH{200} peaks are averaged and shown in Fig. S6.7E. From these peaks the relative {110}/{200} intensity is calculated and inset in the FFTs.

In the case of the HAADF image there is no {110} peak present, but only a minor amount of streaking intensity that originates from the nearby α -Ti{10 $\bar{1}$ 0} peaks. In the dDPC image the relative intensity is close to half the value of the ABF and iDPC images. The ABF and iDPC images contain the highest relative strength of the super-reflections and are remarkably similar, indicating that the long-range {110} ordering is equally present in both images.

Despite this similarity of the ABF and iDPC images in reciprocal space, the iDPC image has a significantly better short-range transfer of intensity of the hydrogen columns in real space (compare Figs. 6.2B and C).

Figure S6.7. Reciprocal space analysis of the hydrogen signal. (A) HAADF, (B) ABF, (C) iDPC, (D) dDPC image. Dashed and solid lines connect the encircled low-index reflections from the HCP α -Ti and FCT γ -TiH lattices, respectively. Scale bar size is 5.0 nm⁻¹. (E) Averaged intensity profiles of the four lines connecting the γ -TiH{200} reflections encircled in red, from which the relative intensity γ -TiH{110}/ γ -TiH{200} is calculated and inset in the bottom-right of (A-D.)

The apparent discrepancy between the reciprocal space analysis and real-space analysis is caused by an imaging artefact in the ABF image. This is pointed out with Fig. 6.3B. There the average intensity profiles reveal that the Ti intensities are also modulated with a {110} periodicity. Hence, the combined effect of the hydrogen ordering in the γ -TiH crystal and the image artefact of the Ti atom column intensities, lead to the increased intensity of the {110} reflection in the FFT of the ABF image. Hence, the actual {110} intensity from the hydrogen atoms in the ABF image is lower than the iDPC image.

6.6.6 Multislice scanning transmission electron microscopy simulations

The three-dimensional models of γ -TiH and its interface with α -Ti are constructed with VESTA⁴⁷. The lattice parameters of freestanding γ -TiH are set to $a=4.20$ Å and $c=4.60$ Å and those of α -Ti to $a=2.9508$ Å and $c=4.6855$ Å³¹. For the models of the interface the γ -TiH unit cell is slightly adjusted by -0.6% for the a lattice parameter ($a=4.1730$ Å) and +1.9% for the c lattice parameter ($c=4.6855$ Å) to obtain a perfect coherent interface with the α -Ti where the interface plane is formed by $(10\bar{1}0)_\alpha // (1\bar{1}0)_\gamma$ and where in-plane the $[001]_\alpha // [001]_\gamma$ (and $[\bar{2}110]_\alpha // [110]_\gamma$) directions are parallel.

These models are loaded in software for multislice simulations called Dr. Probe⁴⁸. The models are always one unit cell thick and are cut in four equally thick slices. With this approach each slice contains one atomic plane in the case of γ -TiH (alternating Ti and H planes), whereas the α -Ti phase contains two empty slices and two Ti planes (alternating Ti and empty planes) as no atoms are present at $z=1/4$ and $z=3/4$. Atomic vibrations are accounted for with the frozen-lattice method, where the used Debye-Waller factors at 300 K are 0.52 Å² for Ti and 5.0 Å² for H. The factor for Ti is taken from the table in the work of Peng et al.⁴⁹, while we linearly extrapolated the Debye-Waller factor for H from the same table using the listed group I elements. It is assumed that the microscope has no aberrations except for defocus, and the operating conditions are set equal to the experimental settings of 300 kV and a convergence semi-angle of 21 mrad. In experiment, the corrector software reduces the high order aberrations to values close to zero, the first order aberrations (A1 and C1) to values below 0.5 nm and second order aberrations (A2 and B2) to values in the range of 5 nm. The probe step size is set to 10 pm or lower, depending on the size of the simulated image. The detectors and their collection angles are given in Table S6.1, which are equivalent to the calibrated experimental values. The final simulated ABF and HAADF images are then convolved with a two dimensional Gaussian function of 70 pm FWHM to account for the finite probe size. In addition to the normal ABF image, we also add the images from the four quadrant detectors to obtain an ABF-like image that we call DPC sum. The difference is that the inner collection angle is a bit smaller, and the outer collection angle extends into the dark field part of the diffraction pattern.

Detector name	Azimuthal range (°)	Inner collection angle (mrad)	Outer collection angle (mrad)
DPC_A	-45 – 45	10	40
DPC_B	45 – 135	10	40
DPC_C	135 – 225	10	40
DPC_D	225 – 315	10	40
ABF	0 – 360	11	18
HAADF	0 – 360	43	200

Table S6.1. List of the electron detectors and their corresponding collection angles that are used in experiment and simulation.

The images from the DPC_(A-D) detectors, however, are first processed to obtain the iDPC image, according to the method described in the work of Lazic et al.²¹. This processing procedure is as follows: first the opposite segments are subtracted (i.e. DPC_A – DPC_C and DPC_B – DPC_D, in the detector coordinates system) to obtain the orthogonal (x,y) differential phase contrast (DPC) images DPC_x and DPC_y by rotating the vector components to match the scanning (image) coordinates system²⁷. Periodic boundary conditions are constructed for the (non-periodic) interface by mirroring the DPC_x and DPC_y images, which is necessary to prevent aliasing effects for the simulations that cover a small field-of-view⁵⁰. Next, the DPC_x and DPC_y images are integrated in the Fourier domain to obtain the Fourier transformed iDPC image:

$$\mathcal{F}\{iDPC(x,y)\}(k_x,k_y) = \frac{k_x \cdot \mathcal{F}\{DPC_x(x,y)\}(k_x,k_y) + k_y \cdot \mathcal{F}\{DPC_y(x,y)\}(k_x,k_y)}{2\pi i(k_x^2 + k_y^2)} \quad (6.1)$$

Where k_x and k_y are the orthogonal k-vector components in the Fourier domain. The intensity in the Fourier transformed iDPC image at $k_x = k_y = 0$ is set to 0 to account for the singularity, before inverse Fourier transforming to obtain the real space iDPC image. Note that this is merely a constant that shifts the intensity of the image. Next, the iDPC image is convolved with the two dimensional Gaussian function of 70 pm FWHM to account for the finite probe size.

The iDPC image that is corrected for the finite probe size is used to obtain the DPC vector image and dDPC scalar image. The DPC image is obtained from the gradient of the iDPC image, which returns the two in-plane (x,y) vector components of the DPC image. This provides a physically regularized DPC image, where the non-conservative part of the noise is removed^{21,27}. Differentiating once more, by applying the divergence operator to the DPC vector image, yields the dDPC scalar image.

6.6.7 Multislice simulations of the γ -TiH unit cell with and without hydrogen atoms

In this section we show that the observed peaks in the experimental images, as depicted in Fig. 6.4, are indeed a result of the hydrogen atoms, instead of being an image artifact that stems from interference effects. For this purpose, we have simulated the γ -TiH unit cell with hydrogen atoms and without hydrogen atoms. In Fig. S6.8 we present the simulated ABF, DPC sum and iDPC images for the empty (Fig. S6.8A) and filled (Fig. S6.8B) γ -TiH unit cell. In this figure the intensity profile along the face diagonal (Fig. S6.8A), or a combined result of the two face diagonals (Fig. S6.8B) is mapped as a function of thickness. In this way the intensity profile contains three Ti atomic columns and two empty columns in Fig. S6.8A, and three Ti atomic columns, one empty column and one hydrogen atomic column in Fig. S6.8B. The lower half of the figure shows the simulated images for a selection of specimen thickness' in steps of 9.2 nm (or 20 unit cells).

In case of the ABF and DPC sum images, four broad peaks are present between the Ti columns in Fig. S6.8A for crystals thinner than about 12 nm and 6 nm, respectively. The iDPC image also shows this feature but for crystals with a thickness around 15-25 nm. This demonstrates that when no hydrogen atoms are present, the erroneous conclusions can be drawn that a dihydride crystal has been imaged, where the four tetrahedral columns are filled with hydrogen atoms.

Figure S6.8. Image simulations of the γ -TiH unit cell with and without hydrogen atoms. Simulated ABF ($\Delta f=0$ nm), DPC sum ($\Delta f=0$ nm) and iDPC ($\Delta f=-4$ nm) images of the γ -TiH unit cell images are compared. At the top part the intensity profiles (along the indicated white dashed line indicated below) as a function of thickness are shown. The bottom part shows the γ -TiH unit cell (A) without hydrogen atoms, and (B) with hydrogen atoms for various thicknesses. In (B) the relative hydrogen intensity is inset. The contrasts of the ABF and DPC sum images are inverted to ease the visual comparison.

The simulated images of the normal γ -TiH unit cell (Fig. S6.8B) show that the hydrogen columns can be imaged by the three methods since relatively bright peaks at the expected position are observed in all cases. The highest relative intensity of the hydrogen columns is achieved with iDPC, followed by DPC sum and least with ABF. In the case of ABF the crystal should be thinner than about 35 nm, otherwise the intensity from the hydrogen column is drastically reduced. The DPC sum image is able to transfer the signal from the hydrogen column with a rather stable contrast even for relatively thick specimen. However, the intensity at the location of the hydrogen column does not resemble a well-defined peak. This is clearly better in case of iDPC, where the contrast of the hydrogen column is the highest, and also a well-defined peak shape occurs.

Results shown in Fig. S6.8B hold for single defocus values. We repeated this for different defocus values and quantitatively analyzed and plotted all results in Fig. S6.9, Fig. S6.10 and Fig. S6.11, for ABF, DPC sum and iDPC imaging, respectively. In Fig. S6.9A,B the relative intensity of the hydrogen column and titanium column w.r.t. the empty column is plotted. This indeed shows that for ABF imaging the contrast reversal of the hydrogen and empty column at zero defocus (which is the operating value in experiment) for crystals thinner than about 10 nm. For more negative defocus, the contrast reversal increases in magnitude and extends to slightly thicker crystals, and also the contrast between the titanium column and empty column is reversed. For more positive defocus the contrast between the titanium column and empty column is again reversed. Hence, for ABF imaging it is crucial to stay close ($\Delta f = \pm 4$ nm or smaller) to zero defocus.

The same result is shown in Fig. S6.10, but now for the DPC sum image. This result is similar to the case of ABF, but with slightly less oscillatory behavior. The contrast reverses between the hydrogen and empty column only for negative defocus values for crystals thinner than about 10-20 nm. However, the contrast reverses between the titanium column and the empty column for both positive and negative defocus values. In Fig. S6.10C it is also apparent that the relative intensity of the hydrogen column w.r.t. the Ti column is remarkably independent from the crystal thickness, as has been shown in Fig. S6.8B. However, also for DPC sum imaging it is crucial to stay close ($\Delta f = \pm 4$ nm or smaller) to zero defocus.

Finally, the analysis of the iDPC imaging is shown in Fig. S6.11. Contrast reversals between the titanium and empty column occur for all positive defocus values, and occur between the

hydrogen and empty column for positive defocus values larger than 4 nm. However, for negative defocus values there are no contrast reversals, except for crystals thinner than about 4 nm for the most negative defocus value of -8 nm that we simulated. Physically this means that in the case of iDPC it is important to focus the probe into the specimen i.e. below the top surface. The value of the defocus is only limited by the specimen thickness, as it is the depth at which the projected electrostatic potential is probed by the converged beam waist allowing atomically resolved 3D iDPC imaging⁵¹. In addition, it shows enhanced contrast between the hydrogen and titanium columns as plotted in Fig. S6.11C.

The above image simulations clearly demonstrate that iDPC imaging provides better results than ABF and DPC sum imaging with best localization and highest contrast of the hydrogen column, largest thickness and defocus ranges without disturbing contrast reversals and oscillatory behavior.

Figure S6.9. Simulated relative intensity of the hydrogen and titanium atoms in the ABF image. The relative intensities of the (A) hydrogen and (B) titanium column w.r.t. the empty column are plotted as a function of crystal thickness for various defocus settings. The ratio of the former two defines the relative intensity of the hydrogen column in (C). We classified the results in three defocus windows: negative (-8 nm to -4 nm), close to zero (-2 nm to $+2$ nm), positive ($+4$ nm to $+8$ nm). The vertical scale limits are (A) -0.4 to 0.4 (B) -1.0 to 1.0 (C) -0.5 to 0.5 and allow direct comparison of Figs. S6.9, S6.10 and S6.11.

Figure S6.10. Simulated relative intensity of the hydrogen and titanium atoms in the DPC sum (ABF-like) image. The relative intensities of the (A) hydrogen and (B) titanium column w.r.t. the empty column are plotted as a function of crystal thickness for various defocus settings. The ratio of the former two defines the relative intensity of the hydrogen column in (C). We classified the results in three defocus windows: negative (-8 nm to -4 nm), close to zero (-2 nm to +2 nm), positive (+4 nm to +8 nm). The vertical scale limits are (A) -0.4 to 0.4 (B) -1.0 to 1.0 (C) -0.5 to 0.5 and allow direct comparison of Figs. S6.9, S6.10 and S6.11.

Figure S6.11. Simulated relative intensity of the hydrogen and titanium atoms in the iDPC image. The relative intensities of the (A) hydrogen and (B) titanium column w.r.t. the empty column are plotted as a function of crystal thickness for various defocus settings. The ratio of the former two defines the relative intensity of the hydrogen column in (C). We classified the results in three defocus windows: negative (-8 nm to -4 nm), close to zero (-2 nm to +2 nm), positive (+4 nm to +8 nm). The vertical scale limits are (A) -0.4 to 0.4 (B) -1.0 to 1.0 (C) -0.5 to 0.5 and allow direct comparison of Figs. S6.9, S6.10 and S6.11.

6.6.8 Multislice simulations of the tilted γ -TiH unit cell with and without hydrogen atoms

In the experiments the local alignment of the specimen was constrained by the small length scale crystal bending. From the experimental images usually only a small part was well aligned, which we assessed based on the combined quality of the HAADF and iDPC or ABF images. The combined effect of crystal tilt and the wave character behavior of particularly the iDPC and ABF imaging could potentially induce imaging artefacts that lead to erroneous detection of atomic columns. Therefore, we investigate if crystal tilt can introduce peaks in the image that could be wrongly attributed to hydrogen atomic columns.

To this purpose we have performed multislice image simulations of a titled γ -TiH unit cell, with and without the hydrogen atoms. We applied a crystal tilt of 0.5° (8.7 mrad) in x and y direction (i.e. the unit cell is tilted along a face diagonal), as these were approximately the maximum misalignments we encountered in experiments, especially near the interface. The reason why we chose to tilt the crystal along the face diagonal is that crystal tilt in the x or y direction would certainly not generate the asymmetry of intensity peaks that we observe i.e. this will not produce the ordered $\{110\}$ type of intensity peaks.

We present the results of these image simulations in Fig. S6.12 in the same way as we presented Fig. S6.8. However, now we show the intensity profile of the entire face diagonal only in the tilt direction in Fig. S6.12B, instead of the combined profile of both diagonals like we presented in Fig. S6.8B. We cannot use the intensity profile of the other (anti-)diagonal due to streaking of the titanium atomic columns. The intensity maps at the top panel can be used to compare the empty (Fig. S6.12A) and hydrogen (Fig. S6.12B) columns.

For the three imaging techniques the titanium atomic columns in Fig. S6.12A have asymmetric shapes as a consequence of the crystal tilt. The titanium atomic columns also appear to be displaced with respect to their actual position. This effect is mostly visible for ABF and DPC sum, and only minimally for iDPC where the atomic columns remain most localized. Furthermore, the apparent position of the atomic columns is very sensitive to thickness and can show relatively large jumps for minor increases in crystal thickness. This is most visible for DPC sum and ABF for about 15 nm thick crystal, and again at around 40 nm.

Figure S6.12. Image simulations of the tilted γ -TiH unit cell with and without hydrogen atoms. Simulated ABF ($\Delta f=0$ nm), DPC sum ($\Delta f=0$ nm) and iDPC ($\Delta f=-4$ nm) images of the tilted γ -TiH unit cell images are compared. On the top the intensity profiles (along the indicated dashed line below) as a function of thickness are shown. The bottom shows the γ -TiH unit cell (A) without hydrogen atoms and (B) with hydrogen atoms. The contrast of the ABF and DPC sum images are inverted to ease the visual comparison.

More relevant is that the empty unit cell (see Fig. S6.12A) contains apparent atomic columns between the titanium columns only for the DPC sum image, and not for ABF and iDPC images. When the crystal is not tilted, there are apparent atomic columns for all three imaging techniques. Hence, when the crystal is tilted, interference effects are reduced for ABF and iDPC, but not for DPC sum. When hydrogen atoms are present (see Fig. S6.12B) then only DPC sum and iDPC show visible contrast between the hydrogen and empty column, and ABF does not. The resulting checkerboard-like pattern remains most clearly visible when the crystal is thinner than about 30 nm for DPC sum imaging, as the contrast reduces for thicker crystals. Whereas the contrast remains best for iDPC imaging even for thick crystals.

Overall, these results demonstrate that iDPC imaging is least sensitive towards crystal tilt on several aspects. iDPC imaging shows the least atomic column displacement, and remains capable of imaging hydrogen atomic columns even for thick crystals despite the rather extreme crystal tilt. In contrast, ABF and DPC sum imaging show substantial displacement and also sudden jumps in apparent atomic column position. Furthermore, ABF imaging is not able to transfer any significant signal from the hydrogen columns and DPC sum imaging can do this only for crystals thinner than about 30 nm.

Figure S6.13. Comparison between experimental and simulated intensity profiles of the iDPC image of γ TiH at the interface with Ti. Normalized intensity profiles from the simulated (solid colored lines) iDPC image ($\Delta f = -4$ nm) are compared with the line profiles from the experimental (gray bands) image of Fig. 6.2C. The simulated specimen thicknesses are (A) 23.0 nm (B) 32.2 nm (C) 36.8 nm (D) 41.4 nm (E) 46.0 nm and (F) 50.6 nm. Vertical scale ranges from -0.1 to 1.2.

Summary

Designing and controlling the structure of materials at the micrometer, nanometer and atomic scale are key to engineer macroscopic material properties that meet specifications and performance levels for technological applications. To keep advancing technology, it is therefore critical to continuously reach a deeper understanding of the physics involved in the structure-properties relation of materials. Although macroscopic properties of materials can be measured by various rather trivial methods, the only way to precisely see the internal structure and its chemistry with atomic resolution is by aberration-corrected scanning transmission electron microscopy (STEM). Despite that the resolution of such contemporary microscopes is sufficient to image the atomic structure of practically all materials, it has remained a major challenge to robustly image light elements when they are present next to heavy ones. As a consequence, the exact atomic structure, including interfaces and defects, of many technologically relevant materials consisting of light and heavy elements has remained elusive and therefore limited technological advancements.

This dissertation focuses on the imaging of light elements next to heavy ones in natural and synthetic low-dimensional materials. Such materials generally have useful properties that emerge only once one or more dimensions approach the atomic scale, which can be exploited for many technological applications e.g. to strengthen metals or for next-generation microelectronics. To this end, the recently invented sensitive integrated differential phase contrast (iDPC)-STEM is employed, which images approximately the atomic electrostatic potential of a thin material by using a few detector segments in a clever way (Chapter 2). The images can then be directly interpreted, as single atoms or atom columns clearly show up as bright dots in a dark surrounding, of which the intensity scales approximately linearly with the (average) atomic number. This is a substantial improvement compared to existing techniques, which either form easily interpretable images but lack sensitivity (with high-angle annular dark-field (HAADF)-STEM), or are sensitive but produce ambiguous images (with annular bright-field (ABF)-STEM). In other words, the iDPC-STEM technique combines the traditional techniques, and only keeps their advantageous characteristics. However, as it was invented just before the start of this research project, these promising

prospects of iDPC-STEM are mainly based on theoretical grounds but have not been thoroughly tested in experiment by imaging real materials.

The two-dimensional (2D) semiconductor tungsten disulfide (WS_2) is investigated by recording atomic resolution movies in Chapters 4 and 5. This material consists of only three atomic layers, with a sheet of heavy tungsten atoms sandwiched between light sulfur ones, and belongs to the transition metal dichalcogenides, which is a versatile materials system where unique properties can emerge from atomic scale defect structures that are attractive for novel applications. Thus, observing how defects evolve in an atom-by-atom fashion, including both the heavy tungsten and the light sulfur atoms, is valuable information to link defect structures to macroscopic properties.

Electron-beam induced dynamics in 2D WS_2 are observed in real-time with ultralow-voltage 30 kV-STEM, and described in Chapter 4. Stable atomic resolution with a 30 keV electron beam is a major instrumental improvement compared to the 60 kV-STEM benchmark, and therefore marks the current frontier in STEM performance (Chapter 2). Electrostatic potential movies are recorded with iDPC-STEM, and reveal single sulfur atoms and their dynamics in the form of mobile sulfur vacancies that cluster into line defects, and sulfur atom motion along the edges of holes, all of which are practically invisible in the simultaneously acquired ADF-STEM movies. In fact, approximating the electrostatic potential with iDPC-STEM is currently the only suitable technique to study such atomic scale dynamics with high sensitivity, as emerging camera-based electrostatic potential imaging techniques, despite achieving absolute accuracy or super-resolution, are more suitable for single snapshots due to slower acquisition speeds, enormous datasets and extensive postprocessing.

This fast and sensitive atomic resolution imaging with 30 kV-STEM enabled for the first time the quantification of radiation damage during STEM imaging below electron beam energies of 60 keV (Chapter 5). Such experiments are vital to establish a fundamental understanding of the radiation damage mechanisms that occur at low electron beam energies, which may contribute to the ultimate goal of damage-free imaging of matter with electron microscopy. The radiation damage mechanisms in the semiconducting 2D WS_2 is investigated by quantifying the evolution of point defects, line defects and holes, and also by observing the dynamics of exotic defects during 30 kV and 60 kV-STEM imaging. The combined analysis reveals that the radiation damage rate is twice as high, and that complex defects are shorter-

lived, when the electron beam energy is halved from 60 keV to 30 keV. This indicates that inelastic scattering (upon a primary electron-electron collision) causing electronic excitation and ionization is the dominant mechanism leading to large scale defects and damage, whereas elastic scattering (upon a primary electron-nucleus collision) plays a secondary role by increasing sulfur atom migration rate.

Chapter 6 marks a breakthrough in the ultimate sensitivity by imaging hydrogen, the lightest of all atoms, in a titanium monohydride precipitate that is embedded in titanium. This hydride phase readily precipitates out at room temperature in titanium after absorbing miniscule amounts of hydrogen (for instance by exposure to acids), and can affect the structural integrity of titanium due to hydrogen embrittlement. It is shaped as a very thin sheet of only several (tens) atoms thick with lateral dimensions of few micrometers i.e. a natural low-dimensional material. By imaging the hydrogen and titanium atom columns at the atomically sharp titanium hydride/titanium interface with iDPC-STEM, the crystallographic puzzle of the interface structure is resolved, not possible with the traditional approaches like HAADF-STEM and ABF-STEM where the hydrogen atoms are not properly visible.

The imaging of light elements and their dynamics in various technologically relevant materials demonstrate that the entire periodic table is now territory of the electron microscope. This enables research of previously unexplored materials systems that contain light elements, which may lead to crucial insights in the physics of materials that contribute to technological advancement. For instance, this includes metal phases containing oxygen, nitrogen or carbon that play a central role throughout the field of metallurgy, complex oxide thin films for next-generation microelectronics, and lithium-based batteries or hydrogen storage materials for energy storage applications. Finally, despite not investigated in this dissertation, the combination of iDPC-STEM with (currently revolutionizing) electron energy loss spectroscopy is expected to play an important role in materials science research in the near future, by unraveling the rich physics and chemistry of materials at the atomic scale.

Samenvatting

Het ontwerpen en controleren van materiaalstructuren op de micrometer, nanometer en atomaire schaal, zijn essentieel om macroscopische materiaaleigenschappen te ontwikkelen die voldoen aan specificaties en prestatieniveaus van technologische toepassingen. Om de technologie verder te ontwikkelen is het daarom van groot belang om voortdurend een grondiger inzicht te verkrijgen in de fysica die nodig is om structuur-eigenschap relaties van materialen te begrijpen. Hoewel er verscheidene nogal triviale manieren zijn om macroscopische materiaaleigenschappen te meten, kan de interne atomaire structuur en de chemie ervan alleen met een aberratie gecorrigeerde scanning (=raster) transmissie elektronenmicroscop (STEM) precies afgebeeld worden. Ondanks dat de resolutie van dergelijke hedendaagse microscopen voldoende is om de atomaire structuur van vrijwel alle materialen in beeld te brengen, is het een grote uitdaging gebleven om atomen van lichte elementen af te beelden naast die van zware elementen. Als gevolg hiervan is de precieze atomaire structuur, inclusief grensvlakken en defecten, van veel technologische relevante materialen die bestaan uit lichte en zware elementen onduidelijk gebleven, wat beperkingen heeft opgeleverd voor de technologische vooruitgang.

Dit proefschrift richt zich op het afbeelden van atomen van lichte naast zware elementen in natuurlijk voorkomende en synthetische laagdimensionale materialen. Dergelijke materialen hebben over het algemeen bruikbare eigenschappen die pas ontstaan wanneer één of meer dimensies de atomaire schaal nadert, en welke kunnen worden benut voor technologische toepassingen, bijvoorbeeld om metalen te versterken of voor nieuwe generatie micro-elektronica. Om dit te realiseren is de recent uitgevonden en gevoelige *integrated differential phase contrast* (iDPC)-STEM-methode gebruikt, waarmee bij benadering het atomaire elektrostatische potentiaal van een dun materiaal wordt afgebeeld door een aantal detectorsegmenten op een slimme manier te gebruiken (Hoofdstuk 2). De resulterende afbeeldingen kunnen gemakkelijk worden geïnterpreteerd, aangezien losse atomen of atoomkolommen duidelijk zichtbaar zijn als heldere stippen in een donkere omgeving met een intensiteit die ongeveer lineair schaaft met het (gemiddelde) atoomnummer. Dit is een substantiële verbetering ten opzichte van bestaande beeldvormingstechnieken, die ofwel gemakkelijk interpreteerbare afbeeldingen vormen maar onvoldoende gevoelig zijn (met

high-angle annular dark-field (HAADF)-STEM), ofwel gevoelig zijn maar dubbelzinnige afbeeldingen produceren (met *annular bright-field* (ABF)-STEM). Met andere woorden, de iDPC-STEM-techniek combineert de traditionele technieken maar behoudt enkel hun voordelige eigenschappen. Aangezien iDPC-STEM is uitgevonden net voor het begin van dit onderzoeksproject, zijn de veelbelovende vooruitzichten voornamelijk gebaseerd op theorie, maar ontbreekt grondig experimenteel bewijs door middel van het in beeld brengen van echte materialen.

De tweedimensionale (2D) halfgeleider wolfram disulfide (WS_2) is onderzocht door films met atomaire resolutie op te nemen zoals beschreven is in Hoofdstuk 4 en Hoofdstuk 5 van dit proefschrift. Dit materiaal bestaat uit slechts drie atomaire lagen, met een laag zware wolframatomen ingeklemd tussen lagen met lichte zwavelatomen, en behoort tot de overgangsmetaal dichalcogenides, een veelzijdig materiaalsysteem waar unieke eigenschappen kunnen voortkomen uit atomaire defectstructuren die aantrekkelijk zijn voor nieuwe toepassingen. Daarom is het bestuderen van defecten, met name hoe zij zich atoom-voor-atoom ontwikkelen, inclusief de zware wolfram- en de licht zwavelatomen, waardevolle informatie om defectstructuren te koppelen aan macroscopische materiaaleigenschappen.

Elektronenbundel-geïnduceerde dynamica in 2D WS_2 is geobserveerd met ultra-lage spanning 30 kV-STEM, en beschreven in Hoofdstuk 4. Het realiseren van stabiele atomaire resolutie met een 30 keV elektronenbundel is een belangrijke instrumentale verbetering vergeleken met de 60 kV-STEM standaard, en markeert de huidige grens wat betreft STEM-prestaties (Hoofdstuk 2). Films van het elektrostatische potentiaal zijn opgenomen met iDPC-STEM, en onthullen zwavelatomen en hun dynamiek in de vorm van zwavelvacatures die groeperen in lijn-defecten, en zwavelatoombewegingen langs de randen van gaten, welke allemaal vrijwel onzichtbaar zijn in de gelijktijdig opgenomen ADF-STEM-film. Feitelijk is het benaderen van het elektrostatische potentiaal met iDPC-STEM momenteel de enige geschikte beeldvormingstechniek om dergelijke dynamiek op atomaire schaal met hoge gevoeligheid te bestuderen, aangezien opkomende camera-gebaseerde beeldvormingstechnieken van het elektrostatisch potentiaal, ondanks de absolute nauwkeurigheid of superresolutie mogelijkheid, meer geschikt zijn voor enkelvoudige

afbeeldingen vanwege de langzamere opnamesnelheid, enorme hoeveelheid data en uitgebreide nabewerking.

De snelle en gevoelige atomaire resolutie beeldvorming met 30 kV-STEM maakte voor het eerst de kwantificering van stralingsschade mogelijk tijdens STEM-beeldvorming gebruikmakend van lagere elektronenbundelenergieën dan 60 keV (Hoofdstuk 5). Dergelijke experimenten zijn van vitaal belang om fundamenteel begrip te krijgen van de stralingsschademechanismen die optreden bij lage elektronenbundelenergieën, wat kan bijdragen aan het ultieme doel om materie schadevrij af te beelden met elektronenmicroscopie. De stralingsschademechanismen in de halfgeleidende 2D WS₂ zijn onderzocht door de ontwikkeling van puntdefecten, lijnfecten en gaten te kwantificeren, en ook door de dynamiek van exotische defecten te observeren tijdens 30 kV en 60 kV-STEM-beeldvorming. De gecombineerde analyse laat zien dat de stralingsschade twee keer zo hoog is, en dat complexe defecten een kortere levensduur hebben, wanneer de elektronenbundelenergie wordt gehalveerd van 60 keV naar 30 keV. Dit geeft aan dat inelastische verstrooiing (bij een primaire elektron-elektronbotsing) die elektronische excitatie en ionisatie veroorzaakt, het dominante mechanisme is dat leidt tot defecten en grootschalige schade, terwijl elastische verstrooiing (bij een primaire elektron-kernbotsing) een secundaire rol speelt door het verhogen van zwavelatoom migratiesnelheid.

Hoofdstuk 6 markeert een doorbraak in de ultieme afbeeldingsgevoeligheid door waterstof, het allerlichtste atoom, in beeld te brengen in een titaanmonohydride precipitaat dat is ingesloten in titaan. Deze hydridefase precipiteert gemakkelijk bij kamertemperatuur in titaan na het absorberen van minuscule hoeveelheden waterstof (bijvoorbeeld door blootstelling aan zuren), en kan de structurele integriteit van titaan aantasten als gevolg van waterstofverbrossing. Het heeft de vorm van een zeer dunne plaat van slechts enkele (tientallen) atomen dik, met zijdelingse afmetingen van enkele micrometers. Met andere woorden, het is een natuurlijk voorkomend laagdimensionaal materiaal. Door zowel de waterstof als titaan atoomkolommen zichtbaar te maken in afbeeldingen van het atomair scherpe grensvlak tussen titaanhydride en titaan zoals verkregen met iDPC-STEM, is de kristallografische puzzel van de grensvlakstructuur ontrafeld, iets wat onmogelijk is met de traditionele beeldvormingstechnieken zoals HAADF-STEM en ABF-STEM, aangezien de waterstofatomen dan niet zichtbaar zijn.

Het in beeld brengen van atomen van lichte elementen en hun dynamiek in verschillende technologisch relevante materialen, toont aan dat het hele periodiek systeem nu grondgebied is van de elektronenmicroscopie. Dit maakt onderzoek mogelijk naar onontgonnen materiaalsystemen die lichte elementen bevatten, wat kan leiden tot cruciale inzichten in de fysica van materialen die bijdragen aan technologische vooruitgang. Dit omvat bijvoorbeeld metaalfasen die zuurstof, stikstof of koolstof bevatten welke een centrale rol spelen in metallurgie, of complexe dunne oxide lagen voor volgende generatie micro-elektronica, en ook lithium-gebaseerde batterijen of materialen voor waterstofopslag voor duurzame energieslagtoepassingen. Ten slotte, ondanks dat het niet is onderzocht in dit proefschrift, is het de verwachting dat de combinatie van iDPC-STEM met (de momenteel revolutionaire) elektronenenergieverliesspectroscopie in de nabije toekomst een belangrijke rol zal gaan spelen in de materiaalwetenschap, door de rijke fysica en chemie van materialen te ontrafelen op de atomaire schaal.

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Acknowledgements

This is it. Four years of PhD research have come to an end. Although it is incredible to study and discover the beauties of nature, what really makes it fun and worthwhile is doing it together. So, now is the time to thank everyone who made the past years so enjoyable for me. Bart, without a doubt, you are the best teacher and best mentor anybody could wish for. On the road we may be ‘natural enemies’, you on your racing bike and I on my motorcycle, but clearly we share the same passion for materials science and electron microscopy. It was great to explore the potential of the institute’s new microscope together. I vividly remember our discussions every time we got new exciting results. I’m particularly grateful that you always put personal development in front of the scientific ones. George, what can I say, you do science like you work on your car and talk to your family over the phone. That is with dedication and with passion. Thank you for your scientific input, specifically for the hydrogen storage project that started during my masters and which we also continued during my PhD. Gert, my roommate, or at least that’s how it feels like after sharing an office for all these years, we had a great time. First of all, thank you for training me the basics and making sure everything just works. More importantly, thank you for making coffee all the times I arrived shortly after you (which was obviously carefully planned, I’ll admit that now), the relaxed atmosphere and the many discussions about many different topics, as long as it was about a certain president. Also, we must not forget that we probably have set an unofficial world record together for the inauguration of our microscope. *Fansels ek tige tank foar it meitsje fan mien fyts.*

Of course, many thanks to my colleagues and everybody else that contributed to the success of my PhD. Jamo, we were the lucky ones receiving training in Eindhoven to use our high-end microscope. Naturally the training sessions were exciting and useful, but the cold beers afterwards and chatting with you and also Pavan were the best. Xiaotian, we really connected as soon as I met you at the start of our PhD project. I enjoyed our chats about cultural differences, future careers, family, and also the ones about our research projects. Majid, we met near the end of my PhD, but we had a very good time together. Most of it we spend either pushing the microscope, or brainstorming about new exciting possibilities, even leading to groundbreaking results together with Pavan and others. I still have to laugh when I think

about our ‘spying session’, as I called it, during the virtual conference that we attended. Daniel, you know what I mean when I say that it was great to have somebody on ‘our side’ in the office. Thank you for the fun atmosphere in the office. And thank you Heng, Xukai, Laura, Paul, Weiteng, Razi, Bin, Julien, Atul, Jesse, Zahra, Lijuan, Panos, Jefta, Talieh, Alexey, Julian, Minpeng, Niko. Also, I’m very thankful to Tom, Lena, Rohill and Christiaan, which are the bright students that I was lucky to supervise, which have made valuable contributions to my research project. Several guys from Thermo Fisher have been crucial for this project, thank you Erik, Hassan, Ronald, Ricardo, Ivan, Eric, Arno, Christoph, Sorin. Without your training sessions, guidance and long travels all the way to the north to bring the microscope in top notch condition, this research would simply not have been possible. Also, many thanks prof. Kooyman, prof. Pei and prof. Mayer for your useful comments and suggestions to improve this thesis by participating in the assessment committee.

Heit, mem, thank you for your hard work that gave me the opportunity to do whatever I like, and thank you for always showing interest in whatever I did. Janny, thank you for combining your artistic talent with my science results, which lead to the winning poster at the largest physics conference in the Netherlands and also the cover of this thesis. Beppe Janny, pake Folkert, ome Siep, Jitske, Mark, Folkert, Janny, Hidde, Herman, Baukje, Gerben, Marc, Robin and Hannah thank you for listening (or at least pretending to) whenever I tried to explain once more what I was doing or when I tried to share exciting results. Lastly, Lieske, my soulmate, thank you for your love and continuous support. What a journey it has been.

Thank you

Sytze