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**Localized triatomic self-assembly:
Unveiling long-range chemical anisotropy in
exfoliated black phosphorus**



A thesis submitted
by

Anuj S. Pokle

Supervisor: ***Prof. Valeria Nicolosi***

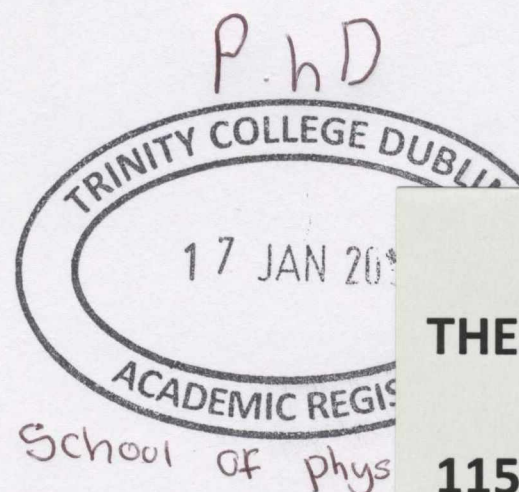
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to

The Department of Physics
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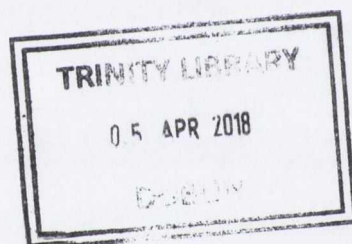


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Declaration

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A

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“Science is a wonderful thing if one does not have to earn one's living at it.”

... Albert Einstein

*Dedicated to my mother **Seema**, father **Subhash**, brother **Vijay**
and of course whoever finds it inspiring!*

“Intent of science and human intelligence is to know; technology is just a fallout. Unfortunately, today no one would fund science if it's not useful.”

... Anonymous

Acknowledgments

“We see past time in a telescope and present time in a microscope. Hence the apparent enormities of the present.”

... Victor Hugo

It is hard to believe that with every word I write, my four years at Trinity College Dublin is drawing to an end. Being in Trinity feels your mind with joy, after all, it is Dublin’s main tourist attraction. You do get used to it in three years’ time. Am not sure what made me quit my three-years job as a service engineer and pursue a PhD. However, I must say it was worth it and pretty exciting, for which I have many people to thank. So here I go...

First of all, I would like to express my gratitude to my supervisor, **Prof. Valeria Nicolosi** for giving me the opportunity to pursue a PhD in her group. I have been really lucky to have Valeria as my mentor. If and when I leave this group, it would be hard to adjust elsewhere. She is very receptive and wise in providing solutions. I had unlimited freedom to explore and experiment ideas and not to forget the support and encouragement received. Although the group exploded like a big bang before I realised, she still made best efforts to give enough time from her busy schedule. A bit guilty of taking holidays now and then, but I guess she was fine with it! I would like to particularly thank **Drs Andrés Seral** and **Joao Coelho** for providing me with amazing samples during my initial PhD days and also for being my travel buddies (I am the one remaining to organise the next big trip, I know!). Being in the same EU project **Dr Sonia Metel** is a lady, being wise and overloading us with her amazing cheesecakes and delicious dinner. Also, not to forget **Ms Carol McCaffrey** for being so helpful and cheerful even when she was piled up with invoices. As they say, a smile goes miles.

Diverting my attention from CRANN to AML which I think is the coolest place away

from the campus. Allow me to thank some real people here who helped me throughout my PhD without which it would not have been possible. First of all, I would like to thank **‘The Clive Downing’** (who is the heart and soul of the AML facility). I would describe him as the jack of all trades and master of all, on top of that he is very kind. Secondly, **Mr Dermot Daly**, the dual beam expert, having an excellent sense of humour which sometimes I do take time to understand. Mentioning of FIB, I cannot leave out **Ms Megan Canavan** (alias MeV) being the AML queen and an expert in preparing the bestest lamellas ever. I know you are not proud of it, but we are!

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would always remember the fun time I had with **Dr Naren Karthi, Pandiaraj (Pandi baba)** and **Sridhar Krishna**. Because of them I never felt being away from Goa. I must confess not being a good student in learning Tamil and further disappointed now, forgetting even little that I knew. I always miss my childhood friends, particularly the epic entrepreneurial conversations with **Prasad, Bhagvant** and **Kiran**. I really cannot think as big as they do, hats off to these guys. We think doing research is everything but the main goal is to make it accessible to the public domain. Like everyone else, my school days were the best with **Heramb, Vaman, Vinayak, Allister, Ashwin, Kunal, Sagar, Pooja, Neha, Pramatha, Divya**, and the list goes on. Nevertheless, for having a great craic, I would always miss **Sainath, Milind, Mithun, Drexel, Bharat, Shane**, and **Salim's** company during my graduation. We just act like kids when we meet up. Being from Goa (The Konkan Paradise) how could I not mention Chaturthi-Diwali-Christmas-New year celebrations with my neighbourhood friends. I have a lot to owe my childhood memories to **Hubert, Charles, William, Cletus-Caji** (twin bro's), **Debbie, Bernadette**, and again the list is enormous. All you guys rock.

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धन्यवादः

(*Dhanyawadaha*)

सगळ्यांचे बरे जाऊ

(*Saglyanche bare jau*)

go raibh maith agat go léir

Thank you all!

Abstract

“We’re running the most dangerous experiment in history right now which is to see how much carbon dioxide the atmosphere can handle before there is an environmental catastrophe.”

... Elon Musk

With the emergence of the two dimensional (2D) materials, the feasibility of mass-scale production has been proven by performing Liquid Phase Exfoliation (LPE), Chemical Vapour Deposition (CVD), Plasma Laser Deposition (PLD), Molecular Beam Epitaxy (MBE), etc. Proving to be excellent in the device, optical, battery and various other applications, the main challenge is to characterise these materials. Scanning/Transmission Electron Microscopy (S/TEM) has proven to be a very powerful technique which simultaneously allows you to investigate the structure and its local physical-chemical properties (using Electron Energy Loss Spectroscopy - EELS) at the atomic scale. With the current development in the field of electron microscopy, in-situ experiments have changed the way we used to think about the material response towards electrical, strain, heat etc.

This thesis is devoted to the study of 2D material especially Black Phosphorous (BP) or also referred to as Phosphorene. BP was synthesised (bulk form) hundred years ago, but it is just recently in 2014 that it was reintroduced from a perspective of a layered thin film material. Many previously unidentified properties have arisen which attracted tremendous interest from material scientists, semiconductor industry, chemists to condensed matter physicists.

My work applies the microscopic approach in investigating BP interaction with other metals (Cu in this case as prime importance). For this purpose, Transmission Electron Microscopy (TEM) technique has been undertaken. Various in-situ heating and electrical measurements are performed to study the kinetics and electrical properties. The main perspective used in this work is that of High-Resolution Scanning Transmission Electron

Microscopy (HR-STEM) imaging and Electron Energy Loss Spectroscopy (EELS). The localised tri-atomic self-assembly observed in BP with Cu was also further investigated by first principle calculations using density functional theory (DFT). Finally, simulations are also performed using two different multi-slice algorithms (namely QSTEM and MUTEM) which agreed with the experimental results.

This is a first step towards observing chemical anisotropy in black phosphorous and probably one of its kind to fabricate the thinnest metal (or semiconductor or insulator) wire in a two-dimensional semiconductor by self-assembly. The work aims to offer a new outlook what 2D system has to offer to the variety of disciplines. Complete understanding of the self-assembled atoms (which is purely naturally occurring bottoms-up approach) would open up new possibilities for other materials, future integrated circuits and in the field of condensed matter physics.

Acronyms

1D – One Dimensional

2D – Two Dimensional

3D – Three Dimensional

AC-STEM – Aberration Corrected Scanning Transmission Electron Microscopy

ADF – Annular Dark Field

BP – Black Phosphorus

BF – Bright Field

BFP – Back Focal Plane

CCD – Charge Coupled Device

CFEG – Cold Field Emission Gun

CTEM – Conventional Transmission Electron Microscopy

CVD – Chemical Vapour Deposition

DF – Dark Field

DFT – Density Functional Theory

DOS – Density of States

EBL – Electron Beam Lithography

EDX – Energy Dispersive X-ray Spectrometry

EELS – Electron Energy Loss Spectroscopy

EFTEM – Energy Filtered Transmission Electron Microscopy

ELNES – Electron Energy Loss Near Edge Structure

EXELFS – Extended Energy Loss Fine Structure

FEG – Field Emission Gun

FET – Field Effect Transistor

FFT – Fast Fourier Transform

FIB – Focused Ion Beam

HAADF – High Angular Annular Dark Field

HRS/TEM – High Resolution Scanning/Transmission Electron Microscopy

IPA – Isopropyl alcohol

LPE – Liquid Phase Exfoliation

MAADF – Medium Angle Annular Dark Field

MBE – Molecular Beam Epitaxy

MEMS – Microelectromechanical systems

MIBK – Methyl isobutyl ketone

PIPS - Precision Ion Polishing System

PLD – Plasma Laser Deposition

PMMA – Poly(methyl methacrylate)

Q-ADF – Quantified Annular Dark Field

QSTEM – Quantified TEM/STEM Simulations

RDF – Radial Distribution of Neighboring Atoms

SAED – Selected Area Electron Diffraction

SEM – Scanning Electron Microscopy

SI – Spectrum Imaging

S/TEM – Scanning/Transmission Electron Microscopy

TDS – Thermal Diffuse Scattering

TMD – Transition-Metal Dichalcogenides

XPS – X-ray Photoelectron Spectroscopy

List of Publications

1. J. Coelho, **A. Pokle** *et al.*, “Lithium Titanate/Carbon Nanotubes Composites Processed by Ultrasound Irradiation as Anodes for Lithium Ion Batteries,” *Scientific Reports*, vol. 7, no. 1, p. 7614, Aug. (2017).
2. **A. Pokle** *et al.* EELS probing of lithium based 2-D battery compounds processed by liquid phase exfoliation. *Nano Energy* **30**, 18–26 (2016).
3. Seral-Ascaso, S. Metel, **A. Pokle** *et al.* Long-chain amine-templated synthesis of gallium sulfide and gallium selenide nanotubes. *Nanoscale* **8**, 11698–11706 (2016).
4. B. Mendoza-Sánchez, J. Coelho, **A. Pokle**, & Nicolosi, V. A study of the charge storage properties of a MoSe₂ nanoplatelets/SWCNTs electrode in a Li-ion based electrolyte. *Electrochimica Acta* **192**, 1–7 (2016).
5. D. Hanlon, C. Backes, E. Doherty, C.S. Cucinotta, N.C. Berner, C. Boland, K. Lee, A. Harvey, P. Lynch, Z. Gholamvand, S. Zhang, K. Wang, G. Moynihan, **A. Pokle** *et al.* Liquid exfoliation of solvent-stabilized few-layer black phosphorus for applications beyond electronics. *Nature Communications* **6**, 8563 (2015).
6. B. Mendoza-Sánchez, J. Coelho, A. Pokle & V. Nicolosi. A 2D graphene-manganese oxide nanosheet hybrid synthesized by a single step liquid-phase co-exfoliation method for supercapacitor applications. *Electrochimica Acta* **174**, 696–705 (2015).
7. J. Coelho¹, B. Mendoza-Sánchez¹, H. Pettersson, **A. Pokle** *et al.* Manganese oxide nanosheets and a 2D hybrid of graphene–manganese oxide nanosheets synthesized by liquid-phase exfoliation. *2D Mater.* **2**, 25005 (2015).

*“Everything we call as real is made of things that cannot be
regarded as real.”*

... Neils Bohr

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Chapter 1

Motivation and Thesis Outline

“What could we do with layered structures with just the right layers? What would the properties of materials be if we could really arrange the atoms the way we want them...”

... Richard Feynman

In the world of computation, our brain is the best inspiration, which uses few watts of power to carry out computation equivalent of today's supercomputers. Comparing to a Silicon (Si) based computing system, it uses about million times less energy per computing operation, not to forget the immense data storage (~ 2.5 petabytes) and brain activity (~ 1 exaFLOP). Each one of us has a live system which manipulates hundreds of trillions of different pathways signal. This what or should drive us in designing and exploring new materials for the next generation computing. Unfortunately, we do not have the technology yet in building neuron-like entities connected with tens of thousands of wires (synapses) to each other. For now, we would have to rely on conventional materials designed and connected in two-dimensional arrays. To our disappointment, even the Si-based microchips are nearing the quantum limit, and the search for a replacement is on. Realizing, Richard Feynman's prediction on isolating individual layers,[1] Robert Frindt attempted thinning down MoS_2 [2][3] by adhesive tape and Li intercalation. Although several synthesis, characterization and theoretical modelling were carried out over two-dimensional (2D) layered materials, it was not until 2004 that the true novel transport properties were experimentally proven.[4] 2D materials have gained worldwide attention and are heavily researched in the field of transistors,

photodetectors, DNA detection, sensor fabrication, memory devices, lithium-ion batteries, photovoltaic devices and much more.[5][6][7]

1.1 – Challenges in the field of IC's

Size of the Transistor: Until now (and in the near future) electronic industry has shown a rapid rate of innovation to meet the consumer demand for an improved capability which has driven the industry in an upward spiral. But the question is whether we would be able to keep up with Moore's Law? The prediction made in 1965[8] still holds good but not for much longer. It is not just a question of heat generated due to more transistors packed together but the feature size itself. Once you start reducing the transistor size quantum effects, come into play. The drain-source distance is too narrow to stop electron tunnelling.

Intel has come over this by introducing tri-gate FinFETs (Fin-Field Effect Transistors) used for most 22 nm and below chip design technology. It could probably go down to 7 nm node. The newly launched GAAFET (Gate All Around-FET) by IBM has 5 nm chip design and may go down to 3 nm node, but after that, no one has a clue what to expect. Due to the change in technology to achieve the 10 nm node size and below only a few major companies would be able to afford it.

The Interconnects: Apart from the transistor node size, scalability is another factor, which is combining of transistors on a single chip. Currently, we can have more than 100 million transistors in each square millimetre of a chip. This certainly depends on how the transistors are wired. Unfortunately, on-chip interconnects are not scaling as fast as the transistors and pose as another limiting factor. The Cu interconnects are used for this purpose after it replaced Aluminum (Al) in 1997. Current technology limits the copper interconnects used in the integrated circuits to ~ 10 nm in width. Due to electromigration and sidewall scattering the resistance of the copper interconnects jumps up drastically.[9][10][11]

New capabilities enabled by graphene, CNT's (Carbon Nanotubes) and other materials are being investigated. In scaling up interconnects, reliability is important because it is another challenge which we still need to find a proper solution, if we to replace the conventional materials. Various other techniques have been used to fabricate atomically thin 1D structures. This includes encapsulating Te atoms inside carbon nanotubes,[12] using molecular structure directing agents,[13] angstrom-sized electron probe in the STEM,[14] and by scanning tunnelling microscopy (STM).[15] However, such techniques are not scalable or easily implementable for large-scale production.

1.2 – Aim of the Project: An Outline

To address the physical limitations of the Silicon Valley, 2D materials such as graphene, hexagonal boron nitride, transition metal dichalcogenides (TMD) and phosphorene has captured the imagination of the electronic community. This includes advance applications in nano and optoelectronics. Search for the ideal material is very appealing. However, to replace an age-old material like silicon, we have to keep in mind that the reality of defects/ impurities and durability in the 2D world is also a factor to consider. This demands more understanding of the 2D materials. This project aims at characterizing the copper (Cu) diffusion into black phosphorous (BP) with the help of an aberration-corrected electron microscope. Both these materials are interesting as one (Cu) is used as interconnects in the microchips, and the other (BP) is a two-dimensional high charge carrier mobility semiconductor.[16]–[20] Combining the two may provide us with the answer to having a matrix of semiconductor-metal (or a semiconductor heterojunction) system which can be tailored to our needs on a single sheet. Finally, engineering control at such atomic scale (but simultaneously applicable to mass scale) would open up an exciting field of research across different disciplines.

This thesis can be divided into four main parts;

The first part comprised of chapter 3, will look into the theoretical background of microscopy but later more importantly into the technical part undertaken in carrying out

my work. This includes the instruments that have been used, synthesis of the material and the software used for analyzing the structure and carrying out the simulations. The instrument section introduces to the newly installed aberration corrected STEM which is a dedicated Scanning Transmission Electron Microscope, namely the UltraSTEM 200. Equally important is the setup described to carry out in-situ electrical measurements inside SEM (Scanning Electron Microscope) and TEM (Transmission Electron Microscope).

The second part (Chapter 4) investigates the interaction between BP and metal (Cu, in this case, to be of prime importance). In particular, it deals with the structure of pristine BP followed by the self-growth process of Cu atoms via BP layers. This is carried out using in-situ as well as ex-situ approach inside TEM. Here we will see for the first time how chemical anisotropy in black phosphorous towards copper results in a localized self-assembly observed inside TEM in real time.

The third Section which is chapter 5 goes into the aberration-corrected high-resolution STEM (HRSTEM) imaging with Electron Energy Loss Spectroscopy (EELS), used to get structural and chemical information respectively at the atomic level. To get a precise number of BP layers, counting the number of atoms (in an atomic column) is performed using Quantified STEM. This is followed by HAADF image simulations (using QSTEM and MULTEM multislice algorithms) to compare the theoretical and experimental results. The theoretical models are obtained by first principle calculations using DFT (Density Functional Theory).

The final part which is represented by chapter 6 explores the application of BP with Cu triatomic wires. Apart from using the conventional device measurements over Si wafer, an attempt has been made to modify the heating holder MEMS chip to behave as electrical device measuring tool. Due to the atomic size of the self-assembled Cu atoms (3 atoms wide), this section tries to investigate the electrical properties in-situ inside TEM and SEM.

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Chapter 2

Introduction and State of the Art

Background

“Is there no way to make the electron microscope more powerful?”

... Richard Feynman

‘Resolution is just a part of the puzzle.’

2.1 – Nanoworld of 2D

Two-dimensional materials comprise of substances with a thickness of few nanometers. The two-dimensional plane restricts the motion of electrons in the third direction. Unlike other three-dimensional silicon or germanium based semiconducting materials, lowering the lattice symmetry induces various types of anisotropic properties. This includes electrical, optical, chemical, heat etc.[1][2] The interesting part is, one can tailor their properties depending on their composition, crystalline structure, stacking sequence of layers etc. They exhibit diverse properties like being true metals (NbS_2), superconductors (NbSe_2), semimetals (WTe_2), insulators (Titania nanosheets), semiconductors (MoS_2) and even charge density waves[3][4][5]. Also, depending on the phase the same material exhibits different behaviour. For example, 1T- MoS_2 is metallic whereas 2H- MoS_2 is semiconducting[6]. 2H- MoS_2 in bulk possesses an indirect band gap, but when exfoliated into monolayers it exhibits direct band gap. These interesting properties have sparked a huge research investment.

Substantially, layered compounds cover all range of electronic properties. Due to increase in the surface area, they have wide potential applications, including nanocomposites, energy storage, field effect transistors, photocatalysts, quantum oscillations, etc.[7]–[11] To explore the 2D nanoworld boundaries recent development in the heterostructures are remarkable. Heterostructures refer to the combination of two or more semiconductors with different energy bandgaps. This has opened up a whole new range of applications in the field of valleytronic devices[12][13], solar cells[14], flexible and semitransparent electronics[15] etc.

2.2 – Experimental Motivation

2.2.1 Materials to wonder-synthesis

Graphene has proven to be great stimuli to generate a lot of interest in other 2D materials. For the various applications mentioned, there are many methods for synthesizing such materials. In 2004 Novoselov successfully demonstrated single-layer nanosheets of various 2D structures such as graphene, NbSe₂, MoS₂ and Bi₂Sr₂CaCu₂O_x[16][17]. These were synthesized by mechanical exfoliation method. The samples obtained are of good quality however the size (and amount) is quite small (~ tens of microns) which limits its use in device fabrication. In order to get a large amount of single or few-layer nanosheets, liquid phase exfoliation method can be used. This method was first implemented over clay materials,[18] which was then successfully implemented over various layered materials[19][20]. It does not change the hexagonal symmetry or introduce phase change in the material unlike in the case of lithium intercalation[21][22].

However large-scale growth is required to apply TMD's to real devices. Chemical vapour deposition (CVD) method does achieve large-area growth, however, is expensive compared to the previous two methods. Also, there are difficulties in controlling the thickness of the metal oxides compromising the film uniformity. Other techniques like

Atomic Layer Deposition (ALD) have demonstrated to give better control over material composition and thickness.[23][24] In such techniques the substrate used to grow the material is crucial.[25][26] As a result, the transfer from the original substrate possesses a challenge causing contamination. Nevertheless, depending on the application, appropriate synthesis route is desired. This thesis will exclusively deal with mechanically exfoliated black phosphorous.

2.2.2 Shedding electrons

Following comprehensive research development on 2D materials and devices, various micro/nanoscale characterization techniques are employed. Such as transmission electron microscopy (TEM), scanning tunnelling microscopy (STM), scanning electron microscopy (SEM), helium-ion microscopy (HIM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, photoluminescence etc. Due to the boom in the so-called 'Zoo of 2D materials' characterizing such materials has become even more challenging. The work referred into this thesis would see more of TEM than any other technique. Especially STEM (Scanning Transmission Electron Microscopy), EELS (Electron Energy Loss Spectroscopy) followed by in-situ experiments (heating and electrical). First principle calculations using density functional theory (DFT) has been carried out in order to obtain the theoretical model. Further modelling and simulations are performed using Crystal maker, QSTEM and MULTEM software. In the case of device fabrication EBL (Electron-Beam Lithography) and FIB (Focused Ion Beam) techniques are used. Other characterization techniques such as XPS and Raman spectroscopy are also undertaken to get a better insight into the sample properties.

2.3 – Black Phosphorous: The comeback kid

After tremendous research put into Graphene and two-dimensional Transition Metal Dichalcogenides (2D TMD), BP was regarded the new graphene, not only because it is 2D, but also its band gap can be dialled from 0.3 to 2.0 electron volts depending on the number of layers with high charge carrier mobility.[27]–[29] This bridged the gap between Graphene having no band gap to the 2D TMD like MoS₂ having band gap from 1.0 to 2.5 eV. By choosing the metal contacts the on/off, states can be controlled in BP by tuning the Schottky barriers at two contacts. This also allows BP to be ambipolar, i.e. it behaves as n-type as well as p-type field effect transistor. Whereas, in the case of MoS₂, the Fermi level is pinned near to the conduction band edge at MoS₂ – metal interface.

BP has more to offer in the field of condensed matter physics.[11] Superconductivity in pressure-induced BP was studied since 1968,[30]–[33] where the best found onset T_c was near 9.5 K at 30 GPa. BP transforms from being orthorhombic (semiconductor) to rhombohedral in the pressure range of around 7 GPa at 21 K. Above 10 GPa which is at around 16 GPa it crystallizes into the cubic structure (metallic behaviour) at 21 K. Recently, independent transition temperature in black phosphorous was discovered exhibiting superconductivity at around 3.8 K by intercalation.[34]

This shows BP has a lot of potential in the two-dimensional system but it suffers from major degradation issues in the ambient environment.[35]–[39] To tackle this issue, many groups have performed first principle calculations and have made experimental attempts in doping it with metal adatoms,[40]–[43] which also changes the property of BP. This thesis would explore the regime of BP-Metal interaction and how it could shape the future of the two-dimensional implementation in the world of Moore's Law.

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Chapter 3

Theoretical and Experimental Techniques

“Theorists write all the popular books on science: Heinz Pagels, Frank Wilczek, Stephen Hawking, Richard Feynman, et al. And why not? They have all the spare time.”

... Leon M. Lederman

3.1 – Transmission Electron Microscopy

The first Transmission Electron Microscope (TEM) was designed in 1932 by Max Knoll, and Ernst Ruska followed by the first Scanning Transmission Electron Microscope (STEM) constructed in 1938 by Manfred von Ardenne. Even though the two techniques are an integral part of the same instrument today, the motivation behind developing each one of them was different. The motive behind TEM was purely from optical microscopes to push the resolution further. Whereas the idea of having scanning transmitted beam (i.e. STEM) originated from Scanning Electron Microscope (SEM). Max Knoll in 1935 produced the first SEM images, but it was Manfred who designed the first SEM in 1933 but due to the patent application, was not out in public. From this point, Manfred's motivation of scanning transmission began as he realized that unlike in TEM chromatic aberration won't be a problem and there is no need to refocus the electrons to form high-resolution micrographs once it scatters via the sample.

Rapid advancement in this analytical science regarding noise cancellations, lenses, aberrations, field emission source, detectors etc. has allowed us to see and perform chemical analysis at atomic scale simultaneously. TEM is a powerful technique where the information limit critically depends on the microscope's resolving power (currently

below 1 A for TEM and STEM), energy spread of the electron beam (currently 0.3eV native energy spread), thickness, stability and composition of the sample.[1][2] This particular chapter will be focused on the theoretical and experimental aspect of my thesis work.

3.1.1 Electron trajectory

Controlling the electron trajectory is what lies at the heart of a microscope. So, let us see how an electron behaves in a magnetic field. An electron travelling down the centre region of the magnetic lens experiences a Lorentz force which can be described using cylindrical coordinates. From the invariance of the conservation of momentum under Lorentz transformation, and Newton's law, in the form of $\mathbf{F} = dp/dt$ where $p = mv$.

$$\frac{dp}{dt} = \frac{d(mv)}{dt} = -|e| [E(r, t) + v * B(r, t)] \quad 3.1$$

Equation 3.1 where; $\mathbf{F}$ = force acting on the electron, m = mass of the electron, v = velocity of the electron e = charge of the electron, E = electric field strength, r = radial component, t = time constant, B = magnetic flux density.

Consider the gun to the viewing screen as the z-axis so that we can have two components for the electron motion. When an electron passes through a radially symmetric lens, the z-component of the velocity couples with the radial component of the field to produce an azimuthal force, which makes electron rotate. This new azimuthal velocity component couples with the z-component of the field to produce a radial force, which brings the electron closer to the lens axis. A circular magnetic lens always produces focusing action; divergent round magnetic lens doesn't exist. Figure 3.1 shows radial and azimuthal plot of the electron trajectory. It also illustrated the dependence of focal length on accelerating voltage. The combination of lenses produces a series of crossovers along the column of the microscope.

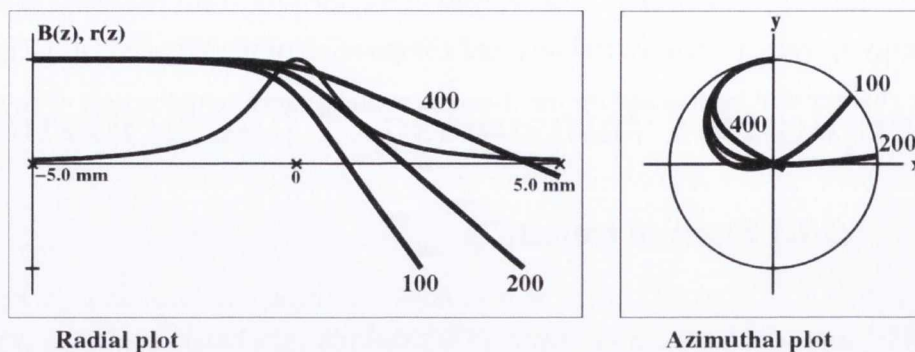


Figure 3.1 Radial and azimuthal trajectories for accelerating voltage 100, 200 and 400 kV.[1]

3.1.2 Basic Instrument Structure

Primarily there are two modes in TEM; The Conventional TEM (CTEM) and STEM. In the first technique, the whole area of interest is flooded with close to parallel electron beam. The image is formed by the objective lens situated just after the specimen slot. Whereas in STEM mode a lens prior to the specimen is used to form a fine probe. The probe is scanned across the specimen (raster scan) addressing each pixel in the series. The image resolution in CTEM is primarily determined by aberrations in the objective lens. In the case of the STEM, the probe forming lens (the condenser system) is limited by aberrations. So, in STEM the spherical aberrations need to be corrected before the beam hits the sample. This results in a reduction of beam tail so that fine beam positioned over atom columns does not flow into neighbouring atoms (though technically there is a channelling effect). This has huge consequence in identifying elements just with their contrast (Z contrast) using the high angle annular dark field (HAADF) detector. Imaging and EELS analysis has a lot to gain from the STEM. This significantly reduces the need for image simulations.

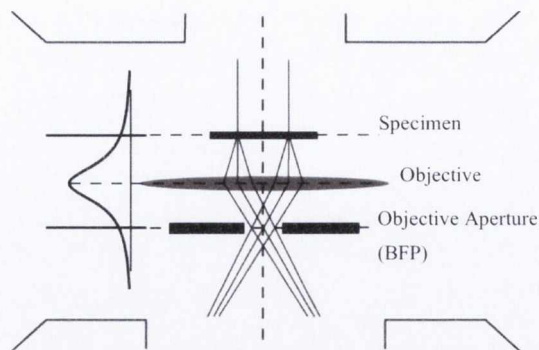


Figure 3.2 Asymmetric objective lens showing high contrast objective lens. Angles between the rays and optical axis are only a few milliradians (exaggerated in the diagram). The back focal plane (BFP) lies at the objective aperture.[1]

Most of the TEM instruments today come with both parallel and convergent beam mode. The objective lens is the heart of TEM. Condenser lenses determine how the specimen is illuminated. Asymmetric lenses do not allow a fine probe as shown in figure 3.2. Also, introducing another mini condenser lens (MC) as shown in figure 3.3, the beam mode can be controlled from TEM to STEM.

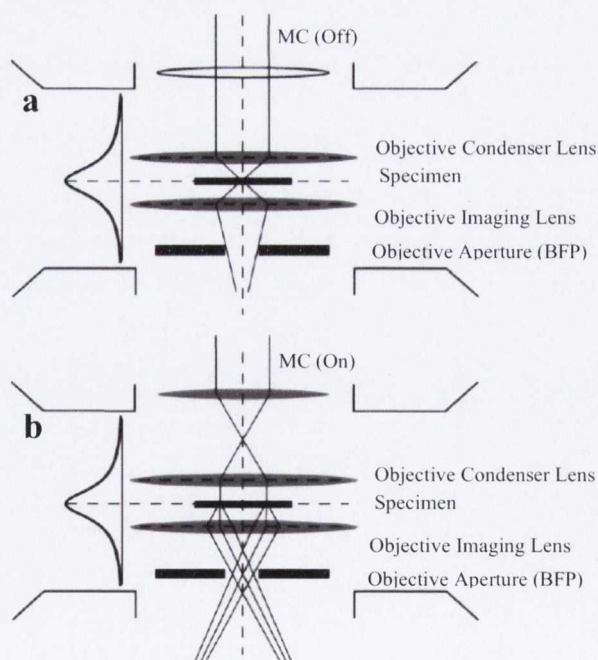


Figure 3.3 Symmetric objective lens illustrating (a) Nanoprobe mode and (b) Microprobe mode when the MC lens is off and on respectively.[1]

After objective and condenser, the next important part is the intermediate (diffraction) lens which is the first lens of the projector system. The other lenses play a role in magnifying the image. There are the whole set of lenses dedicated to image formation once the beam passes through the specimen.

3.1.3 Imaging and Contrast Modes

In TEM there are basically two modes (other than STEM) imaging and diffraction. The system could work with a parallel or convergent beam mode which is illustrated in figure 3.4. The electron can change both its amplitude and phase as it goes through the specimen. This gives rise to contrast, and by choosing certain conditions, one of them dominates.

If you use the objective aperture to select the diffracted or the central beam you either get a dark field (DF) or bright field (BF) respectively as shown in figure 3.4. This gives the amplitude contrast. The phase contrast is when you allow the whole beam to pass through the back focal plane of the objective lens and allow them to interfere. The Z-contrast is exploited in STEM mode which will be dealt in detail in section 3.4.

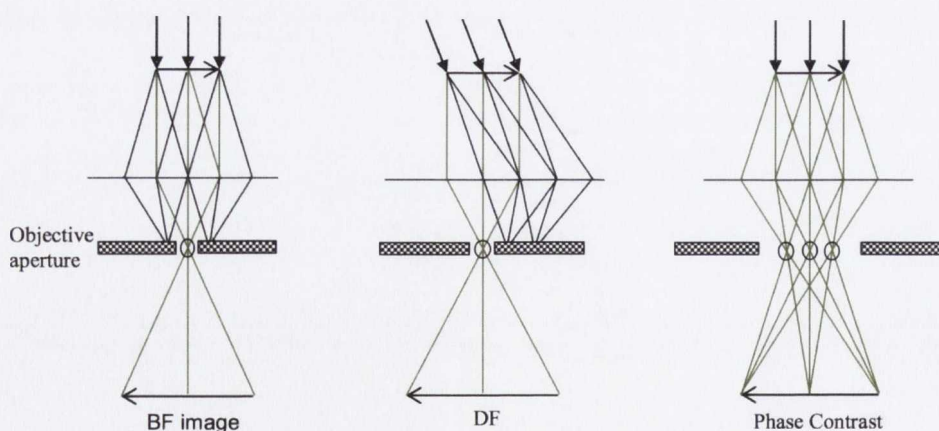


Figure 3.4 Illustrating amplitude contrast (BF and DF) and phase contrast imaging.

$$C = \frac{(I_1 - I_2)}{I_1} = \frac{\Delta I}{I_1} \quad 3.2$$

Amplitude contrast is the difference in intensity between two different areas, and there are two types; mass thickness contrast and diffraction contrast, which assumes incoherent electron scattering and coherent electron scattering respectively. In the former one, any scattered electron could be used to form the DF images. The latter needs at least two beams to get strong contrast in both BF and DF images.

Mass thickness contrast arises from incoherent elastic scattering (Rutherford Scattering). It is thickness (t) and atomic number dependent (Z). Whereas, the diffraction contrast is nothing but the Bragg diffraction contrast which takes into account the coherent elastic scattering, crystal structure and orientation of the sample.

Transmitted and diffracted waves travel different distances in crystal, so each diffracted wave has its own phase representing different solutions to the Schrodinger solution. Thickness, orientation, astigmatism, focus value and scattering factor contribute to the phase shift. The phase image is nothing but a 2D interference pattern formed when you allow many waves to interact.

3.1.4 Reciprocal Space

In this thesis, due to some work carried out in the field of electron diffraction, it is important to mention about the electron diffraction geometry.

The d-spacing from the diffraction pattern is calculated as follows;

$$r = \frac{\lambda L}{d} = \lambda L g \quad 3.3$$

Where λL = camera constant

And L = camera length

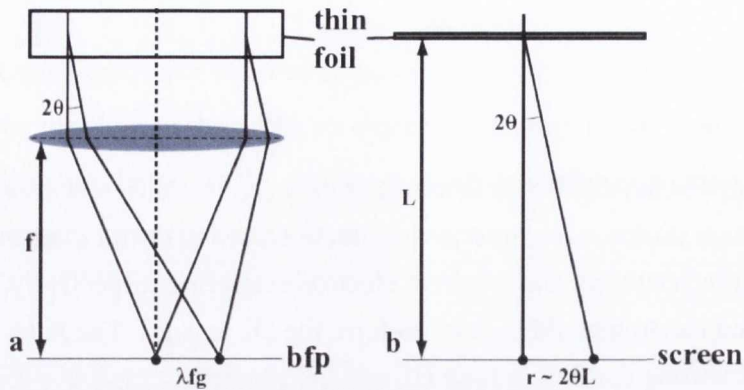


Figure 3.5 (a) Schematic representation of diffraction geometry, (b) definition of the diffraction camera length, L . [3]

The back focal plane of the objective lens contains the planar section of the reciprocal lattice. Electrons scattered in a particular direction by the crystal foil (Figure 3.5), are focused by the objective lens into a point at a particular location with respect to the optical axis. For electrons diffracted by planes with interplanar spacing d , the distance between the optical axis and the point where the electrons are focused is equal to g (reciprocal lattice vector corresponding to this plane). The distance between the optical axis and the location where electrons are focused in the back focal plane of the objective lens corresponding to the origin of reciprocal space since those electrons have not experienced a significant momentum change. [3]

The Ewald sphere is tangential to the back focal plane of the objective plane (Figure 3.6). A “relrod” represents the shape of the reciprocal lattice point of a real, finite size crystal. The figure represents the spatial relationship between the Ewald sphere and a plane in reciprocal space. In (a) the plane is tangent to the sphere, and the relrods corresponding to reciprocal lattice points intersect the sphere. When reciprocal lattice point is tilted around an axis in the plane, the intersection of this plane and the Ewald sphere becomes a circle via the origin, Laue circle indicated by the white arc. With increasing tilt angle, the circle becomes larger (Figure (b), (c) and (d)).

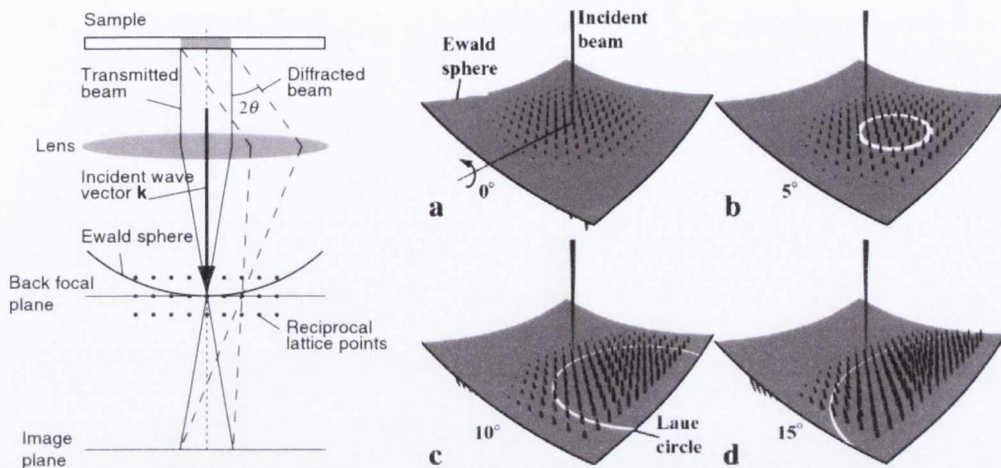


Figure 3.6 Diffraction geometry superimposed over the lens drawing. (a) plane tangent to the sphere, (b) to (d) shows Ewald sphere increasing with the tilt of the beam.[3]

3.2 – Electron Scattering

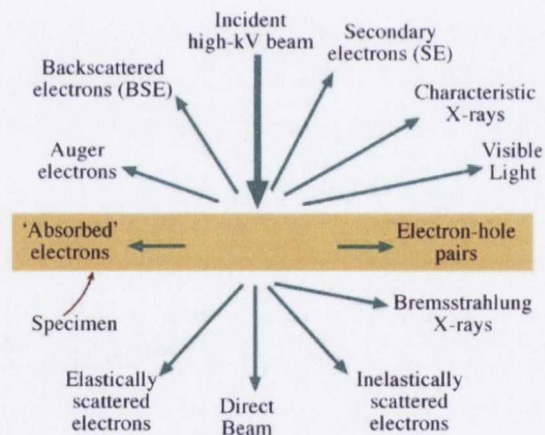


Figure 3.7 Types of signal generated when a high-energy electron beam interacts with a thin sample.[2]

The primary electron is a single high-energy electron beam which passes through the TEM specimen generating numerous outgoing signals as shown in figure 3.7. Now let us discuss different electron scattering mainly elastic, inelastic, plasmon scattering and inner shell ionization.

Elastic scattering shows no energy (detectable) loss and is represented by the zero-loss peak described by the Rutherford scattering. Low angle elastic scattering (having spatially coherent nature) provides the atom position. Diffraction techniques also use the same electrons. Talking about elastic scattering, it is important to note that in TEM dynamical scattering is prominent over kinematical scattering due to large interaction with matter. Multiple scattering occurs in a dynamical regime with multiple beams within the specimen resulting in interference. This results in loss of intensity or generation of new unwanted intensities which makes interpretation of the intensities difficult quantitatively.

In inelastic scattering, most of the primary electrons which have passed through the specimen lose less than few tens of eV and are highly energetic. Due to the short mean free path, the inelastic scattering events result in phonons which until recently were out of reach of microscopists[4]. But typically, phonon scattering contributes to the background of images and diffraction pattern and cause of specimen heating. Interaction of probe electrons with pre-existing phonons gives rise to thermal diffuse scattering (TDS) which are indistinguishable from the phonons. Both these effects contribute to background noise. Unless the specimen is cooled down, the two effects cannot be separated, i.e. where only TDS reduces.

Plasmon scattering is a collective oscillation of free electrons induced by the incident electron beam. It is a non-localized event and dissipates energy in the range up to 30 eV. They usually overlap in energy with signals due to the transition of single electrons between outermost bands of electron energies. Here the mean free path depends on the specimen (thickness ~100 nm) At higher energies, the combined valence electron scattering contributes to the background of EEL spectrum.

Ejection by the primary electron of a localized bound electron from a sample atom gives rise to inner shell ionization. Although its cross-section is small, the energy loss is quite sharp and characteristic of element and state of bonding. Their mean free path is often $>1 \mu\text{m}$. Significant information about the density of empty states (DOS). Analyzing the near-edge fine structure (ELNES) and extended fine structure (EXELFS) bonding within the specimen can be deduced.

3.3 – Spectroscopy

3.3.1 EELS v/s EDX

EDX and EEL spectroscopy can be obtained in TEM as well as in STEM mode. However, one of the main advantages in STEM mode is the ability to use a highly-focused probe to undertake elemental analysis at high spatial resolution. As mentioned in section 3.2, incident beam interacts with sample elastically as well as inelastically. EELS is an absorption spectroscopy in which energy loss of the incident electron is measured. For elemental analysis, such inelastic processes like phonon, plasmon scattering, single electron excitation and direct radiation losses are significant. Whereas in the case of EDX emission spectroscopy which is the secondary emissions are taken into consideration. Following the inner shell ionization (as discussed in section 3.2) the atom will relax after ionization emitting characteristic X-ray or Auger electron. During the electron sample interaction, the energy or wavelength of the emitted X-rays is monitored. EDX provides a quick elemental composition of the sample. Unlike EELS the requirement of the sample thickness is not profound.

EELS provides not only elemental information but also the binding energy of the electron. This consists information regarding the chemical environment of the elemental species. This is complementary to XPS technique. However, X-ray photoelectron spectroscopy (XPS) is a surface sensitive technique where the X-ray beam is used to irradiate the sample while simultaneously measuring the kinetic energy of the electrons knocked out of the material. The various energy losses observed in a typical EELS signal is shown in figure 3.8. In brief, specimen information provided by EELS are as follows;

- Zero Loss peak – specimen thickness
- Plasmon peaks – valence/conduction electron density
- Low loss distribution – polarization response (complex dielectric function)
- Near zero loss features – hints about band structure (interband transitions)
- Core loss regions – elemental composition

- Near edge fine structure (ELNES) – hints about band structure (density of unoccupied states)
- Extended fine structure (EXELFS) – atomic specific radial distribution of neighbouring atoms (RDF)

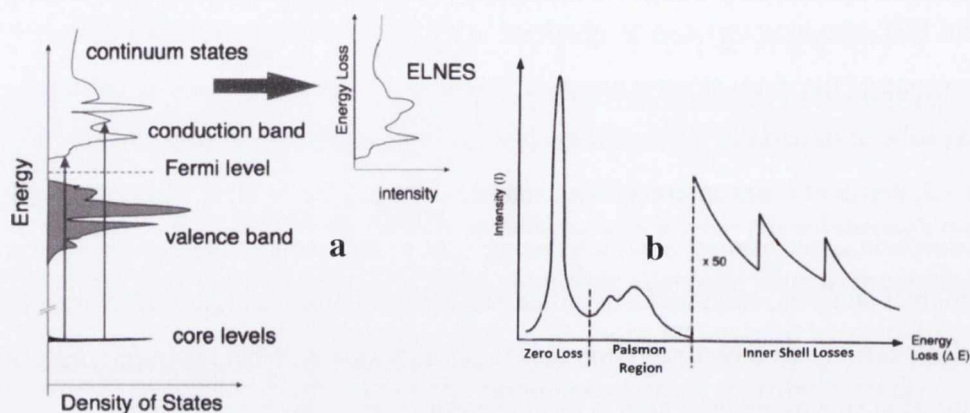


Figure 3.8 (a) Illustrating the electronic transition involved in ELNES in a solid (occupied states shaded) and (b) overall EEL spectra.[4]

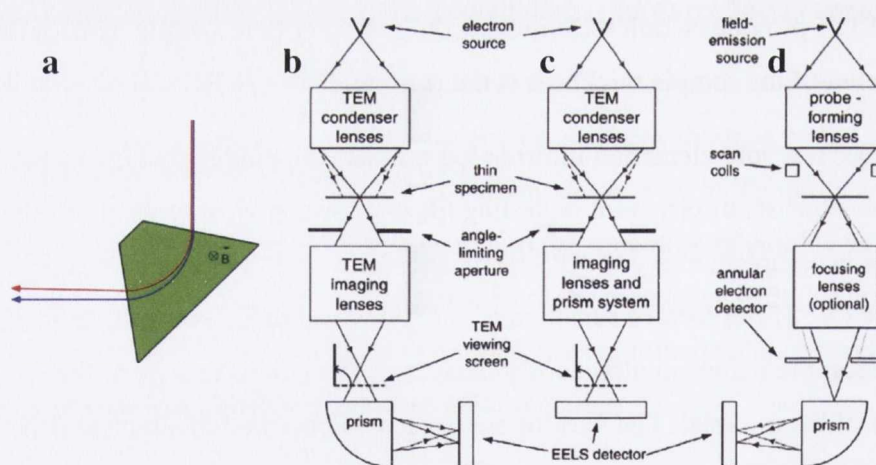


Figure 3.9 (a) Schematics of an EELS detector showing a magnetic prism (green) to separate out different electron beam energies. (b), (c) and (d) shows three methods of using EELS; conventional TEM with magnetic prism spectrometer, in-column imaging filter and STEM system respectively. [2]

Figure 3.8 shows how the density of states (DOS) term is reflected in the ELNES. The ELNES intensity above the edge threshold (i.e. the fermi level marked in figure 3.8 (a)) reflects the unoccupied DOS probed by an inner-shell electron excited from core level.

A simple illustration of an EELS detector is shown in figure 3.9. Core and valence electrons ejected from their initial energy level can subsequently scatter with the potential of the crystal or exit the sample depending on their energy. The minimum energy required by the primary electron to eject the core electrons corresponds to a first approximation to the ionization potential of the excited atom in the specimen. This ejected core electron could also probe the first unoccupied bound state of the crystal. So, its final state and allowed energy level will strongly depend on the overall electronic structure and thus structural and chemical environment of the atom excited by the incident electrons.[5][6]

3.4 – Nion: UltraSTEM200

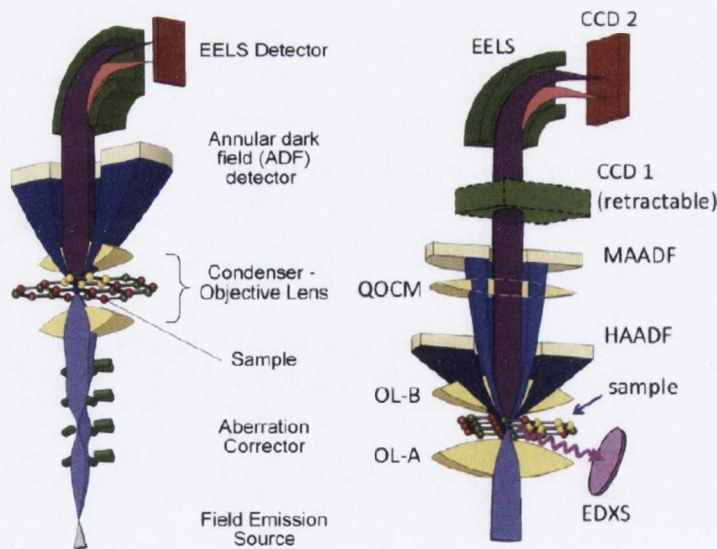


Figure 3.10 (a) STEM Schematics (b) shows actual HAADF detector design.

Evolution of STEM was slower even though it was developed about the same time as TEM. In STEM the lenses are adjusted to create a focused convergent electron beam. This probe is then scanned across the sample. An important concept in the STEM is electron channelling. In a crystal, the electron is confined by the attractive, periodic potential of the atom when electron probe is positioned over an atomic column. In TEM there are chromatic aberrations as there is an objective lens below the sample and electrons of different energies get focused at different positions.[8][9]

STEM offers significant benefits in dark field operation HAADF (High Angle Annular Dark Field) imaging where the beam convergence angle (inner angle) is around 30 milliradians (mrad). The image is formed from an elastically scattered electron as the Bragg diffracted electrons are avoided due to such large angles. Unlike TEM the HAADF signal is directly proportional to the density and thickness of the material. This makes it possible to interpret the image in terms of thickness and Z contrast imaging. Z-contrast images are formed from incoherent scattering and do not reverse contrast with a change in focus or sample thickness. So, there is no phase problem avoiding various simulations. Direct interpretation of different elements in TEM is not possible except when focal series reconstruction is carried out.

In STEM mode, using energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS), elemental mapping can be performed. Having high spatial resolution provides a composition and electronic structure information at atomic resolution.

Having a probe size smaller than an atom makes STEM a powerful technique for determining the structure and composition of matter. The above figure 3.10 (a) illustrates a pre-sample area showing cold field emission gun, followed by gun and three condenser lenses (not shown), corrector and the objective lens. The post sample optics (Figure 3.10 b) consists of HAADF and EELS detector with four projector lenses (not shown).

The 200 kV Nion UltraSTEM system elements have various modules described from bottom to top. Beginning with the gun which is a **CFEG** (Cold FEG), the magnetic **gun lens** consists of 4 quadrupoles and four sextupoles. The beam blanker provides fast blanking which can help to minimize sample damage. The beam blanker interface also

functions as a thermal separation between the gun (baked at 240 °C) and the column (which is baked at 140 °C). 120 °C air is circulated within this interface to keep the gun region isolated during baking.

The three **condenser lenses** allow the probe convergence and current (source demagnification) to be varied. Prior to the corrector, there are different ports namely **VOA**, **gate valve** and **pumping module**. The VOA (Virtual objective aperture) defines the electron beam. The aperture could be centred electrically with four sets of alignment coils.

The C₃-C₅ **corrector** introduces pre-aberrations in the electron wavefront so that after the beam passes through the first objective lens, it is free of geometric aberrations up to 5th Order. The corrector uses three strong octupoles, each combined with a quadrupole and 16 weaker quadrupoles. One of the advantages of these correctors over sextupole is having much greater tolerance to sideways misalignments of their individual components.[10]

QLM, which is the Quadrupole lens module couples the corrector electron-optically into the objective lens to take care of the 5th order aberrations. It works in accordance with the exit quadrupole of the corrector and allows the beam in the last correcting elements of the corrector to be elliptical leading to lower C_c for the electron passing via the corrector.

The **Objective lens** windings are split into lower and upper half which splits the heat load. Coils symmetrical arrangement also helps in minimizing the tendency of the outer magnetic circuit of the lens to saturate.

The **sample stage** vacuum is normally in the 10⁻⁹ Torr range, and an anticontaminator (similar to a cold finger in TITAN) is used to avoid moisture gathering. There are four major ports used for sample introduction, pumping, TV camera mounting and for attachments such as X-ray spectrometer. A sample load lock is present holding up to 5 sample cartridges into a sample magazine. The pressure in the load lock is usually in the order 2 x 10⁻⁷ Torr. It becomes better and reaches 10⁻⁸ Torr after a day or so. The **sample**

exchange arm is pneumatically driven to pick up a sample cartridge from the magazine, detaches it in the stage and then mechanically detaches from the cartridge.

The **projector Lenses** couples the appropriate angular ranges into the various detectors of the UltraSTEM. To keep the poorer vacuum detector section separate, the projector pumping module evacuates the projector section of the column. This makes sure that gas is not guided by the projector beam tube right to the objective lens and the sample. This also contains magnetic shielding designed to minimize coupling of the magnetic fields of the projector lens to the pre-field of the objective lens.

The **upper gate valve** is similar the other pumping module in which it isolates the detector vacuum from the rest of the column. This is useful when the detector needs to be vented. In the Nion column, each scanned image detector uses fixed Photo Multiplier Tube (PMT) and a movable scintillator tray. The HAADF detector (**Detector I**) usually detects electrons from about 80 mrad half-angle to about 300 mrad. The range of angle incident on the detector can be easily changed by changing the camera length, changing the excitation of the projector lens.

To adjust the height of the entrance crossover seen by the EELS spectrometer and also to take care of the electrical adjustments for third order spectrum aberrations a **QOCM** (Quadrupole-octupole coupling module) is used. It consists of three combined QO layers and four layers QOCM. It is able to do the first order optics roughly equivalent to one round lens and to correct the third order aberrations that would otherwise show up in energy loss spectra.

Detector II (BF/ABF/MAADF) is located after the QOCM. While using the EEL spectrometer, QOCM gives the right height of the EELS entrance crossover, but cannot be used to change the MAADF/HAADF ratio of camera length at the same time. Different positions are assigned to insert the detectors. In the EELS regime, the MAADF detector detects electrons from about 50 mrad. If the HAADF is in the range only extends up to 65 mrad. It spans from 50 mrad to 200 mrad otherwise. When the camera length on the HAADF is increased by two times using the projector lenses, it acts like a MAADF with the inner cutoff angle of about 40 mrad. It should be noted that ABF

(Annular Bright Field) imaging is a phase contrast imaging mode, and the interpreting ABF images without doing extensive simulations can be misleading.

Ronchigram CCD is mounted above the detector II. It is a 1k x 1k CCD chip with separate readout area having 10 MHz readout rate. The whole image detected by the CCD is first shifted into the readout area and then read out.

Above the CCD there is the **EELS aperture** having four pneumatically controlled positions. The beam then enters into the **EELS** (Electron Energy Loss Spectrometer). The Gatan Enfium (Quantum) records spectra at a fast rate with a wide range of dispersion values. The spectrometer has electrical adjustments for optics which are corrected to higher orders.[11], [12]

3.5 – In-situ Experiments in TEM

3.5.1 Device Fabrication

Standard device fabrication technique was used to design simple transistors over the Si wafer and the DENS MEMS chip. A positive resist Poly (methyl methacrylate) PMMA was drop-cast over the Si wafer or the MEMS chip and rotated at 3000 rpm for 2 min. The chip was then transferred onto a hot plate kept at 180°C for 3 min.

Before designing the contacts, pad markers were made. 60 μm aperture, high current at 15 kV electron beam was used to perform the lithography. The dose used was 450 $\mu\text{C}/\text{cm}^2$. This was then developed in cold MIBK/IPA (1:3 ratio) for 45 seconds followed by in IPA for 5 sec. For markers, any form of metal can be deposited by Temescal (metal e-beam evaporator) which is around 5-20 nm. For contact pads 30 μm aperture is used at 15 kV with 450 $\mu\text{C}/\text{cm}^2$ of dose. Ti/Au (10/50 nm) metal was deposited using Temescal. The metal is then lifted out by using acetone (The chip is immersed into acetone solution until the metal from the unexposed resist region gets removed). The lithography was

carried out using Carl Zeiss SEM Supra 40. A schematic of the procedure is given in figure 3.11

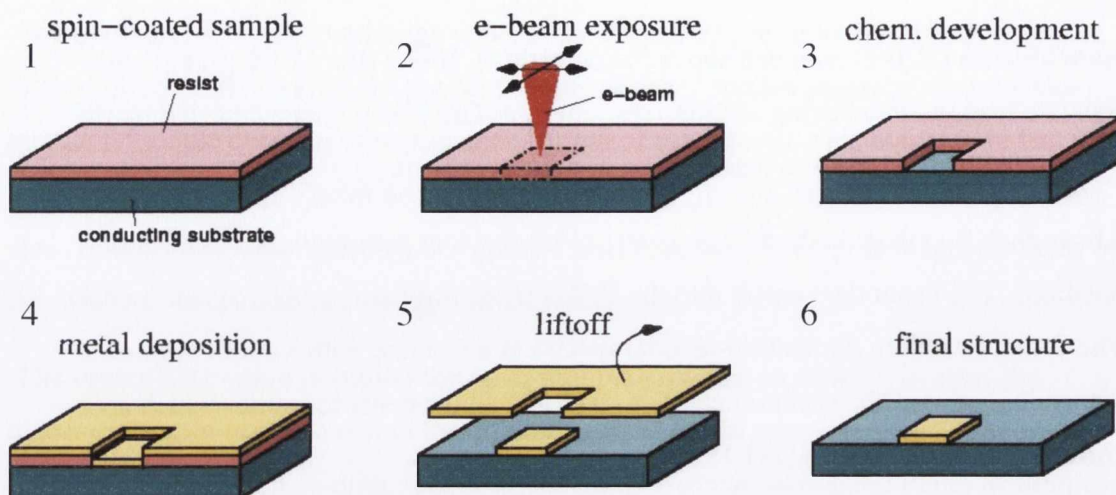


Figure 3.11 Schematic of the e-beam lithography procedure (1-6) wherein a positive resist (PMMA) is spin coated followed by e-beam exposure. This is then chemically developed to deposit respective metal. The e-beam unexposed region will then be removed (lift-off) using acetone giving the final device. [Ref.: Nano-Optics Graz Methods]

3.5.2 Heating and Electrical Measurements

The DENS Wildfire TEM holder is used to conduct the electrical measurement. Even though it is used for heating purposes only, it can be modified to carry out electrical measurements. Molybdenum is used for conduction in the MEMS chip due to its high melting point and at ease with which it can be deposited. However, due to its oxidation above 300°C silicon nitride is deposited on it.[15] The first step in fabricating a device is to etch the SiN layer from the required region of contact to get to the conducting layer of Mo. This is achieved by using FIB (Figure 3.12).

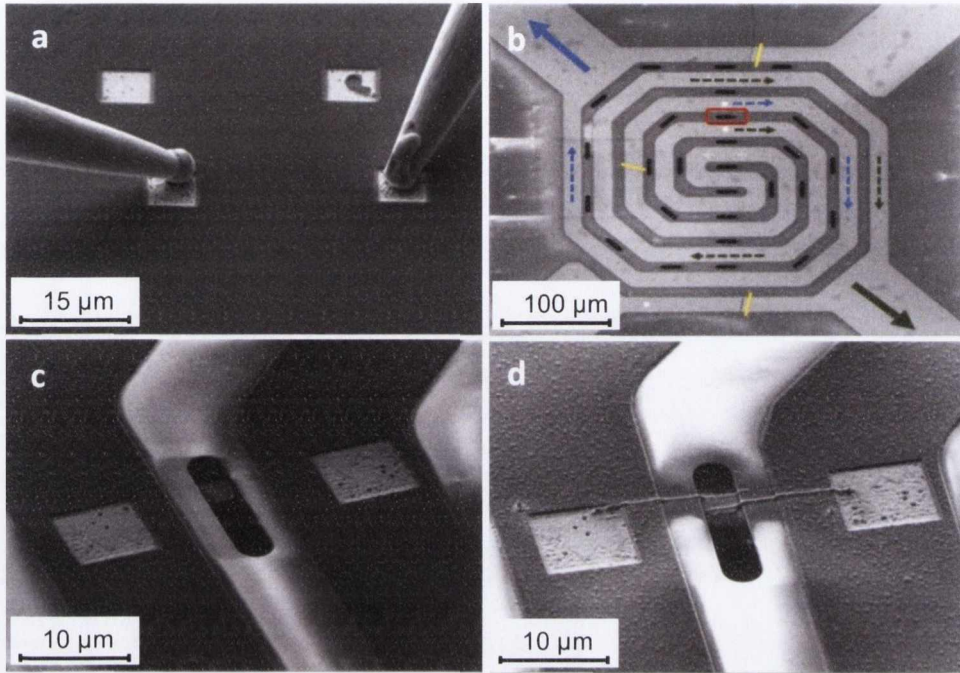


Figure 3.12 Describing the etching procedure for the MEMS chip using FIB technique. The two micromanipulators are shown in (a) to check for the conductivity. The yellow lines in (b) are the fully etched regions in order to get two contact points marked in green and blue arrows. The red rectangle shows the nanosheet position. (c) is the zoomed in region where the electrical measurements need to be carried out followed by Pt deposition in (d).

In-situ electrical measurements were carried out in SEM (Carl Zeiss Ultra) and TEM (TITAN 80-300). The in-situ measurements in SEM were carried out either on Carl Zeiss Auriga or Carl Zeiss Ultra. The figure 3.13(a and b) shows the schematic and the actual set up respectively using the Carl Zeiss Auriga, wherein both the micromanipulators are controlled by the Kleindiek system and the tip 1 and 2 (T1 and T2) goes to the Keithley system (source multimeter). The setup inside the SEM is demonstrated in Figure 3.14 showing the MEMS chip placed over two carbon tapes followed by both the tips. The second tip (labelled as Tip 2) is the same tip used for FIB lamellae preparation.

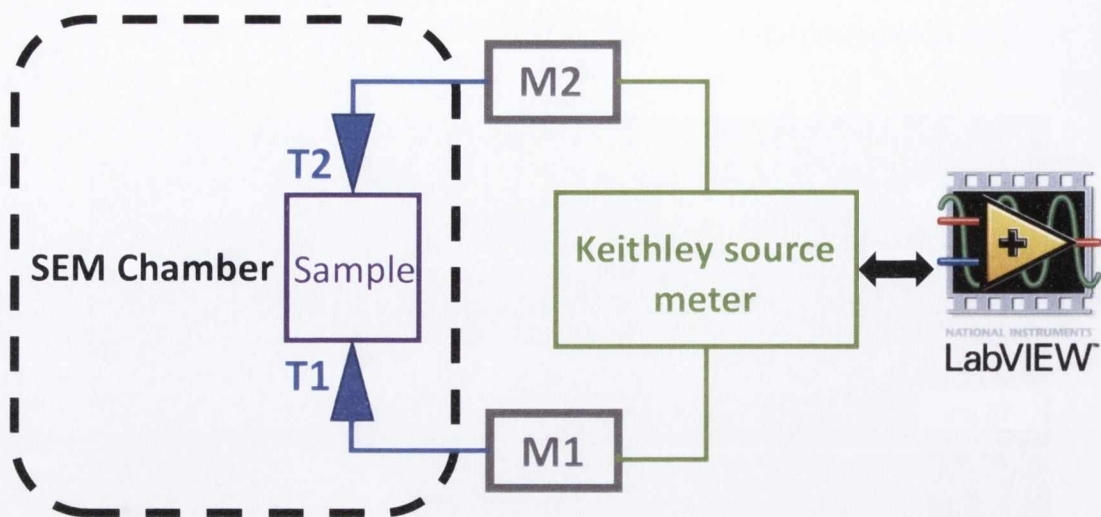


Figure 3.13 (a) Schematic of in-situ electrical measurement setup for SEM. Where T1 and T2 are the two tips controlled by the micromanipulator (M1 and M2). The electrical measurements are controlled using the LabVIEW program.

The TEM setup varies from the SEM as the output is channelled out from the holder directly into the Keithly source meter using an adaptor (switching board) as shown in figure 3.5 (a). The numbers in the figure 3.15 (b) indicate the following;

- 1 – TEM system – monitor
- 2 – Switching Board
- 3 – MEMS Chip (SEM image) showing the two contacts used
- 4 – Lab View
- 5 – Keithley System

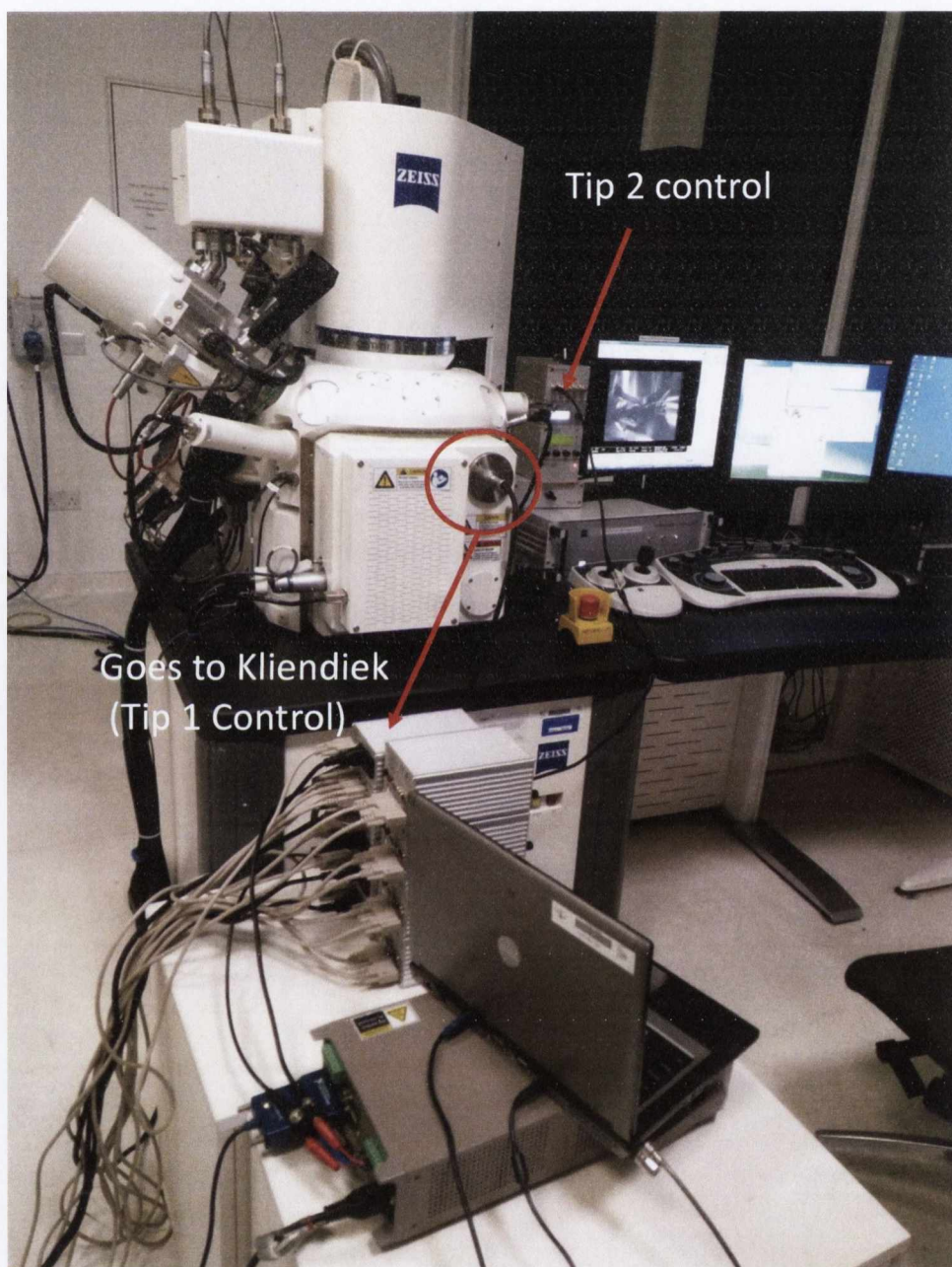


Figure 3.13 (b) In-situ electrical measurement setup for SEM in which the two tip controls are indicated.

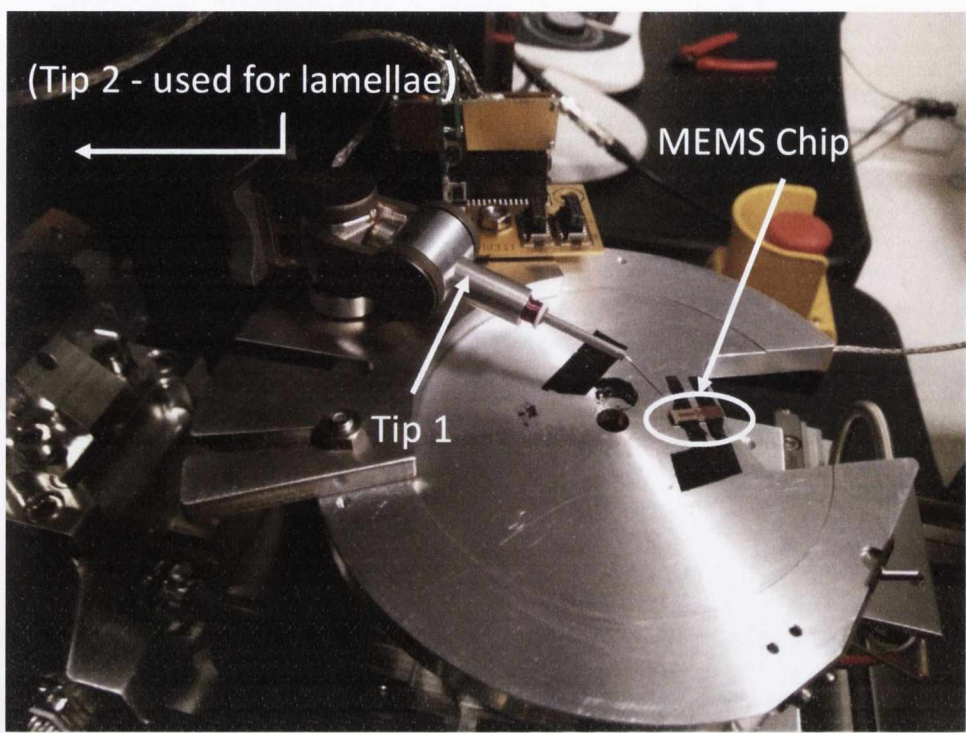


Figure 3.14 Illustrates the set up inside the SEM where MEMS chip is glued over a carbon tape.

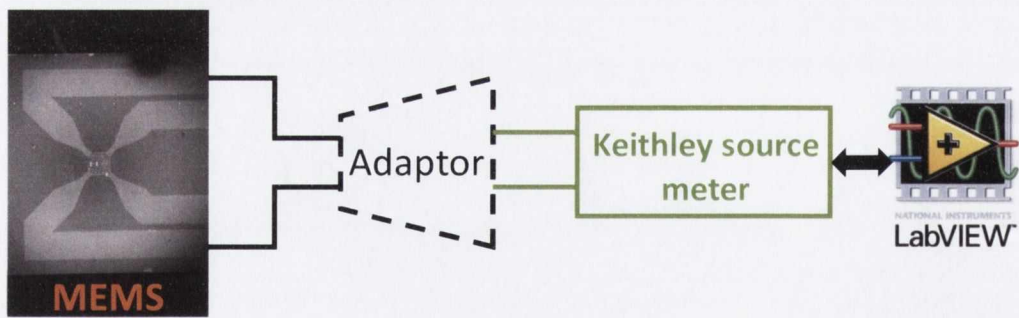


Figure 3.15(a) Scematic for in-situ electrical measurement set up for TEM using the heating holder MEMS chip.

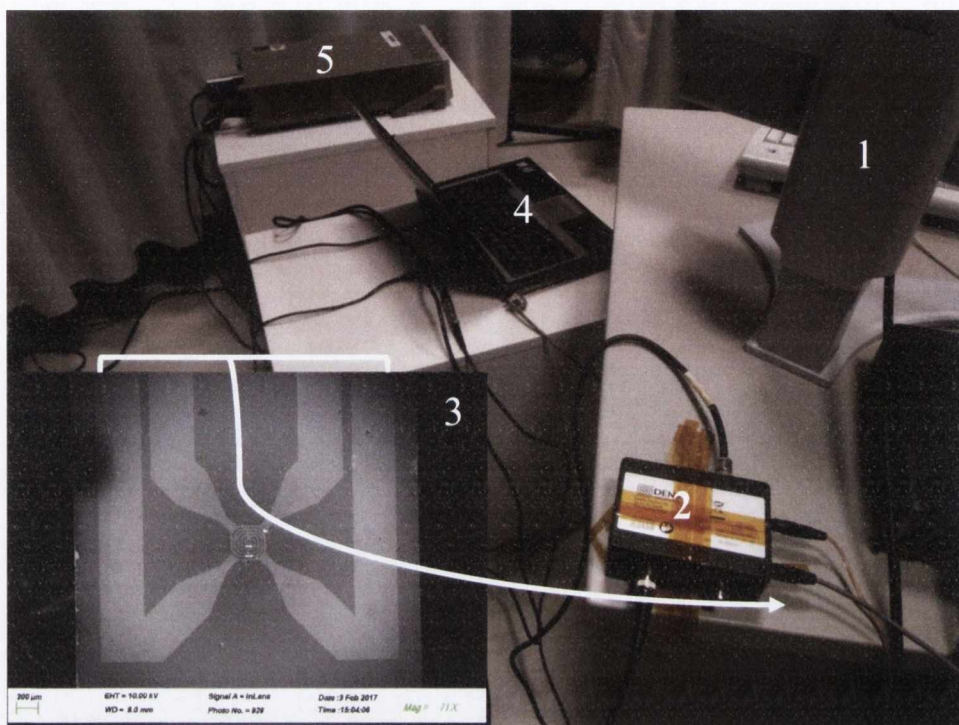


Figure 3.15(b) In-situ electrical measurement set up for TEM using the DENS wildfire holder MEMS chip.

3.6 – Image Simulations and Quantification

QSTEM (Quantitative TEM/STEM Simulations) software was used to simulate the STEM images using multislice algorithm (qstem.org). The structural coordinate file (.xyz) obtained by DFT calculations and Crystal Maker needs to be converted to a configuration file (.cfg). The Thermal Diffuse Scattering (TDS) is also included while simulating the images. The images generated by QSTEM are in a binary format. Apart from using Crystal Maker for modelling and QSTEM for simulations, the rest of the work like DFT calculations, Quantified STEM and MULTTEM simulations were done by collaborators already mentioned in the Acknowledgement section.

The STEM quantification was performed by imaging carried out over a calibrated annular dark-field (ADF) detector. Here the intensity of a large number of identical atomic columns is statistically decomposed into their underlying grouping followed by

ICL (Integrated Classification Likelihood) analyses of the intensities. The sensitivity response of the detector is evaluated for various performance metrics including detector response linearity.[16] Statistical estimation theory was applied over the whole image using StatSTEM. In this method, each column is modelled as a Gaussian peak. This was then compared to the model (In this case Black Phosphorus) under the experimental setting to enable quantitative analysis. The thickness of the BP layers was estimated by using the total scattered intensity of each phosphorus column. The measured scattering cross-section from the experimental image was matched to the simulated values done by using MULTTEM multislice algorithm software.

3.7 – Sample Preparation and Experimental details

In the BP-Cu studies, the black phosphorus was purchased from Smart Elements (Art. Nr. 003933). Crystals were stored in the glove box (MBraun) to avoid degradation. The mechanical exfoliation was carried out using the NITTO blue tape (BT-150E-CM) inside the glove box. Liquid-phase exfoliation was carried out using IPA solvent and sonicated using the sonic tip (Fisher Scientific) for 4 hrs at 60% amplitude. The exfoliated sheets were deposited over TEM holey carbon 200 mesh Cu grids purchased from SPI Supplies. Initially, the wire growth was achieved by thermally treating these TEM grids in a vacuum oven (2×10^{-3} mbar) kept at 110°C for five days. Similar results were also obtained by using other metal grids (Au and Ni 200 mesh holey carbon grids) when Cu nanoparticles (Sigma Aldrich 774111-5G) were deposited over the exfoliated BP nanosheets.

Preliminary studies on BP metal interaction were carried out using TITAN 80-300 non-aberration corrected S/TEM instrument. The TEM holey carbon Cu grid (400 mesh - Agar) is baked in Precision Ion Polishing System (PIPS). EELS spectra collected with a GIF Tridiem 863 EELS Spectrometer, Gatan, Inc., attached to a FEI TITAN field emission microscope operating at 300KV. EELS spectra obtained in TEM as well as in STEM mode. The energy dispersion set as 0.1 eV/ch. The full width at half maximum of

the zero-loss peak in vacuum was 0.8-0.9 eV. The collection angle for the EELS spectra was ten mrad with a convergence semi-angle of 21 mrad. X-ray photoemission spectroscopy analysis was carried out using an Omicron UHV XPS analysis system, with photoelectrons excited using a monochromated Al K α X-ray source ($h\nu = 1486.6$ eV) at a base pressure of 1×10^{-10} mbar. An electron energy analyser (pass energy of 20 eV) was used, yielding a combined instrumental resolution of ~ 0.45 eV.

Aberration-corrected HAADF STEM and EELS were carried out on a NION UltraSTEM200, operated at 60 kV. This microscope is fitted with a Gatan Enfium spectrometer for EELS. *In-situ* heating and electrical measurements were performed on a FEI TITAN300, operated at 300 KV. In-situ heating was carried out using a DENS Wildfire holder which is based on Micro-Electro-Mechanical System (MEMS). It controls the temperature environment locally on the device by 4-point-probe. The temperature was initially varied from room temperature to 300°C at 50°C interval and kept at 300°C for 65 min. The temperature was then raised to 500°C with 50°C interval. The mechanically exfoliated BP were placed over the MEMS electron transparent windows and Cu nanoparticles were drop cast over it.

Quantified STEM imaging was carried out using an aberration-corrected FEI-TITAN operated at 120 KV with detector angles ranging from 46 to 215 mrad. The counting of the number of atoms was performed using statistical parameters estimation theory using StatSTEM.[17]

Digital Micrograph was used to perform the EELS and STEM imaging analysis. Modelling and STEM image simulations were carried out using Crystal Maker and QSTEM[18] software, respectively.

DFT calculations were performed using the CP2K program. The density functional theory (DFT) approach was applied as implemented in the CP2K code (www.cp2k.org). The CP2K Kohn and Sham orbitals were expanded in a mixed Gaussian (double- ζ plus polarization, DZVP) and plane-waves basis set. A 600 Ryd energy cut-off was used for the plane-wave expansion of the electronic density. Tether and Goedecker-type pseudopotentials were used for all atoms, and BZ integration was restricted to the Γ -point. The geometry was relaxed until the maximum force on each atom was less than

0.01 eV/Å. PBE[19] exchange and correlation functional with a Van der Waals correction at the Grimme-D3 level[20] were used.

For the controlled growth study, two different approaches were used. In the first approach, Cu nanoparticles are dropped cast on a SEM stub and then lifted them by Coulomb interaction using a fine needle (Picoprobe - GGB Industries controlled by Kleindiek-nanotechnik) in a Carl Zeiss Auriga FIB, operated at 5 kV. In this way, the Cu nanoparticles are easily transferred over exfoliated BP flakes deposited on a Silicon wafer (Purchased from the University Wafer). Cu wires are then grown by simply heating the system over a hot plate (IKA RCT basic) in the glove box as discussed above. The TEM grids/Si wafers with BP were transported to the microscopes using a vacuum desiccator to avoid any appreciable degradation.

The second methodology involved first exfoliating the BP nanosheets and transferring them onto a Silicon wafer as described above, followed by lithography using the e-beam lithographer (Carl Zeiss Supra 40), followed by e-beam metal evaporation using Temescal. Cu wires could then be grown by simply heating the system over a hot plate (heated at 300°C for 5 min) as discussed above in a glove box. SEM images of the controlled growth study were acquired using a Carl Zeiss Ultra operated at 5 kV.

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Chapter 4

Localized long-range translational ordering in 2D Black Phosphorus

“Science is essentially international. It is only through lack of a historical sense that national qualities have been attributed to it.”

... Marie Curie

4.1 – Introduction

In this chapter, we will explore another dimension of anisotropy in material, in this case, chemical anisotropy. Anisotropy refers to a directionally dependent feature; it can be either the mobility of the charge carriers, phonons, photons etc. Due to the restrictions in the z-direction, materials like graphene, boron nitride, 2D TMD's, black phosphorus and its analogues etc. exhibit unique properties in which the electrons, phonons and their interactions with photons behave anisotropically. However, there was never chemical anisotropy observed before. The discovery of anisotropies (like electrical, optical etc.) has enabled us to engineer the actual concept of utilizing strong anisotropies for novel optoelectronic devices[1], [2].

Apart from all the anisotropies found, what if we could chemically dope a material in the desired direction, locally and at the atomic scale. This will solve all our high-tech instrumentation requirements issues, which are needed to precisely dope the materials, especially in the field of spintronics and quantum designing. The phenomenon of chemical anisotropy investigated here in BP towards metallic Cu is naturally occurring. It will be remarkable if this can be implemented in other materials (at different scales) by exploiting their diffusion trigger. Then it may be an array of atomically thin wire tracks to carry current, site-specific doping for quantum confinement or heterojunction

structures.[3]–[7] This diffusion mechanism can also provides a solution for contact resistance (metal-semiconductor interface) in device fabrication, which is a major concern in 2D material implementation in real applications.[8]

4.2 – Black Phosphorous - Structural Insight

In BP, phosphorous atoms join together to form a two-dimensional puckered sheet and have an orthorhombic structure. Its high charge mobility of the order of $10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and tunable band gap from 1.51 eV to 0.59 eV for a monolayer and five-layer sample respectively makes it a strong contender for semiconducting industry[9].

To get an insight into the structure, we have to look at its stacking difference. BP usually has four different types of stackings namely; AB, AB', AA and AA'. [10], [11] We will be specifically looking at the AB stacked BP which is the case in our experiments. A simple schematic representation of the unit cell is represented in figure 4.1. In this work, the cross-sectional view which is [100] view was never obtained experimentally as it was not possible to tilt the sample 90° .

4.3 – Chemical Anisotropy towards Cu: Accidental Growth

Anisotropy refers to the property of a material exhibiting variation in the physical (or optical, electrical etc.) properties along different molecular axes. This is seen in crystals and even in liquid crystals. In isotropic materials (amorphous materials) like glass, no long-range order exists and the properties are identical in all directions.

Due to restriction in the z-direction and having a unique puckered sheet structure in layered BP, it exhibits various anisotropies. In this section, we will look into the interaction between BP and copper (Cu). Surprisingly, the interaction between another form of phosphorus allotrope with metal solutions has been investigated since the 15th

century.[12][13] It was found that when yellow phosphorous is placed in copper sulphate solution, a black film of copper phosphide is formed followed by metallic copper. It was concluded that salts of metals below copper in electrochemical series showed no action provided that solution was not alkaline.

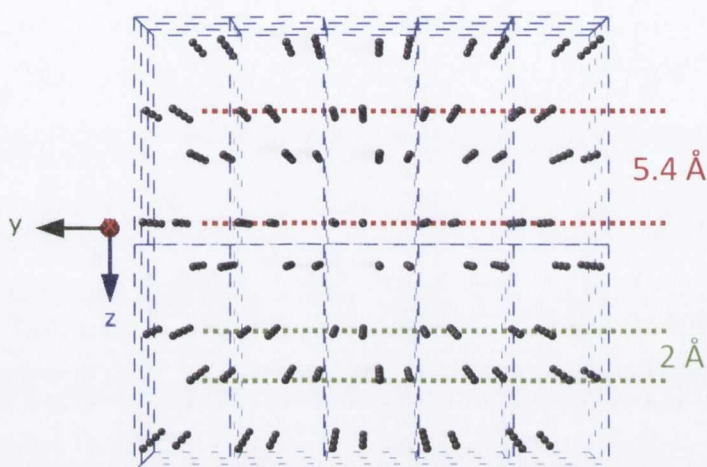


Figure 4.1 Pristine BP model (cross-sectional view) with the unit cells marked in dotted blue rectangles. The red and green markings show the respective atomic parameters in the z-direction where interlayer spacing is found to be around 5.4 Å. Here X-axis can also be denoted by zigzag (ZZ) and Y-axis as Armchair (AC) direction.

It is worth to note that the reducing action of phosphorous over Cu (forming copper phosphorous (Cu_xP_y) alloys or copper phosphide (Cu_3P)) was used in the copper industry as deoxidant, alloying agent and brazing purposes.

Interestingly copper phosphide (Cu_3P_2 or CuP_2) is also a semiconductor used in high-power, high-frequency applications and in laser diodes,[14], [15] and readily available from American Elements. The stabilizing and semiconducting property of the composite also enhances BP's energy storage and water splitting capabilities.[14], [16]–[19] This makes it an interesting candidate for electron microscopy. Here we will investigate BP interaction via in-situ heating with various metals (inside TEM), degradation studies (with Cu) followed by optical measurements. The interaction between BP and copper seems to be far more interesting at the atomic scale which is dealt with more details in chapter 5.

The initial investigations were carried out using the TEM Cu grid (Figure 4.2), the same results were obtained by the use of Cu nanoparticles and thin film Cu deposition by e-

beam evaporation. Number of BP layers governs the thickness of these triatomic wire structures which are unaffected by the step layers (dealt in chapter 5).

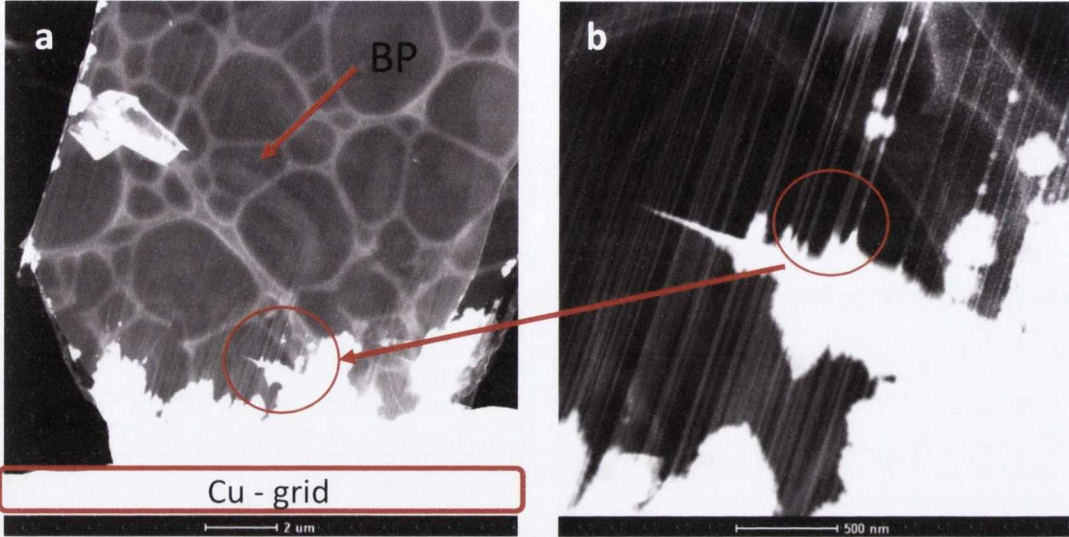


Figure 4.2 Panels (a) and (b) clearly show copper from the grid getting diffused over BP, forming highly directional lines. Figure (b) is the magnified region marked with red circle in (a).

Figure 4.2 illustrates the uncontrolled ex-situ experiment wherein black phosphorous (BP) was mechanically exfoliated onto a TEM Cu grid (having lacey carbon film) and was kept in a vacuum oven for seven days at 110 °C. As can be seen from the figure, the copper diffuses over the BP flakes from the grid, forming what appear to be large wires. Due to the small feature size of the wires over BP, it was impossible to use SAED (Selected Area Electron Diffraction) to get relevant information. Figure 4.3 shows nano-diffraction technique applied over a multilayer BP. The diffraction was carried out at 10 nm step with a dwell time of 0.5 seconds across the 1 μm line profile. The relevant diffraction regions have been marked in coloured spots in figure 4.3. Comparing the green spot (taken over pristine BP) with blue and red (taken over wires) shows a perfect hexagonal pattern for pristine BP whereas smeared spots for the diffraction over the bright lines (the nanosheet was not oriented in any particular zone-axis). This suggests that the interaction of BP with Cu has not changed the entire BP structure.

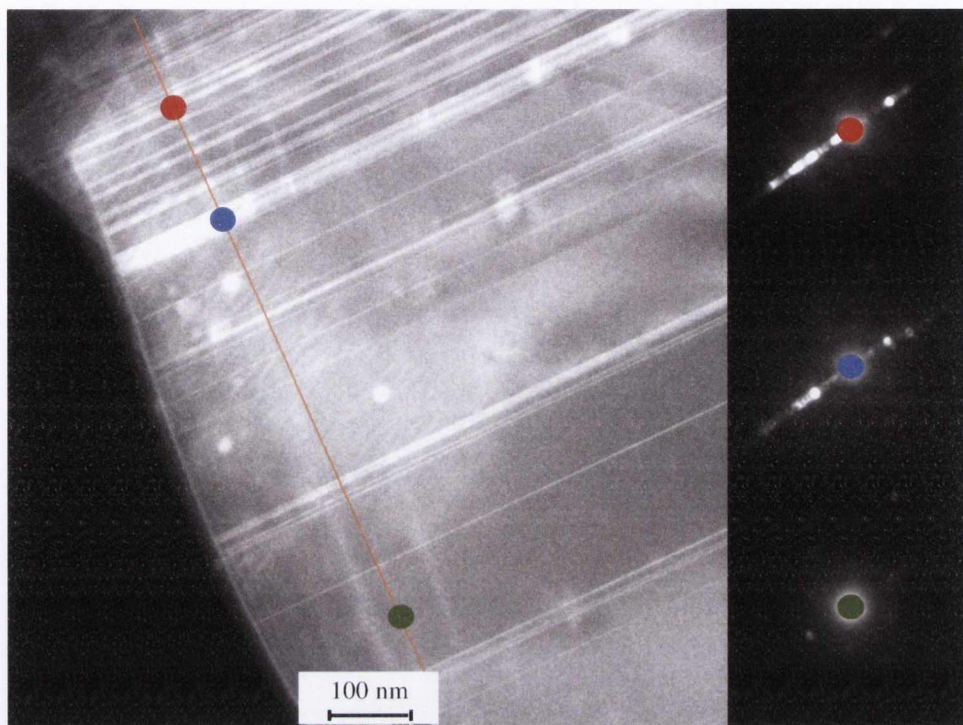


Figure 4.3 Nano-diffraction performed at various points over the orange line. The relevant diffraction micrographs are illustrated on the right with respective position colours. The DP over pristine BP (green spot) gave typical hexagonal pattern whereas over the wires (red and blue spots) the DP spots are grouped in orderly manner suggesting localized long periodic ordering.

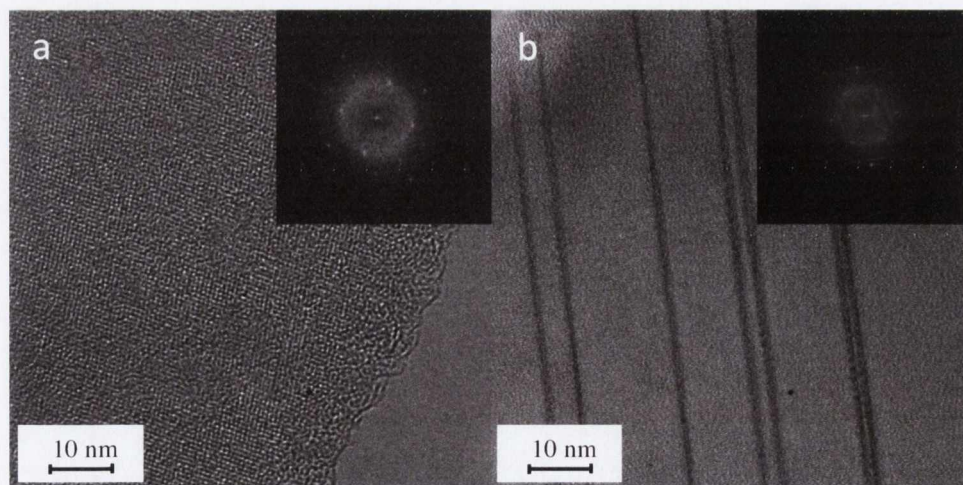


Figure 4.4 HRTEM of pristine BP (a) and BP with wires formed from Cu interaction (b). The inset shows corresponding FFTs. Imaging at 300 kV at high magnification resulted in beam damage.

This proves that the wires are indeed showing localized long-range crystal ordering. Similar results are also obtained in HRTEM (High-Resolution Transmission Electron Microscopy) analysis. When a pristine BP FFT (Fast Fourier Transform, figure 4.4 (a)) is compared to the FFT of BP having the wires (Figure 4.4 (b)) it showed preferred orientation at wire regions (rather than the typical BP hexagonal pattern). The sample was extremely sensitive at high magnification at 300 kV, and the edges were getting amorphized quickly (Figure 4.4 (a)). To get accurate interpretation imparting less beam damage HRSTEM (High-Resolution STEM) at 60 kV was performed in NION UltraSTEM microscope which will be dealt in the next chapter.

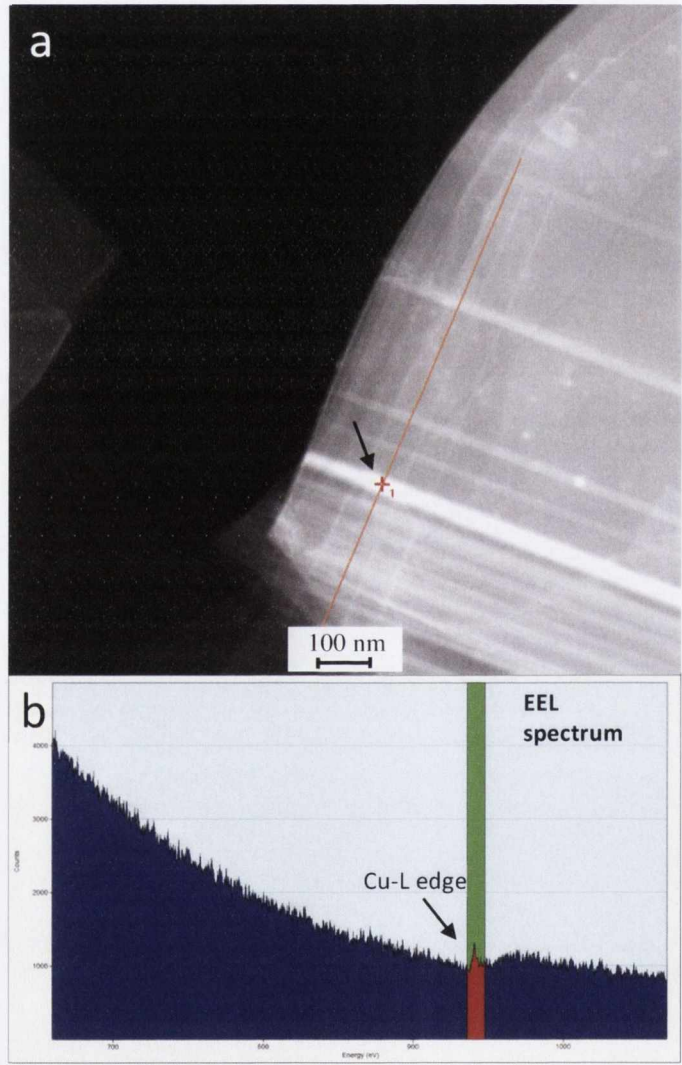


Figure 4.5 EEL spectrum line profile carried out across the orange line in (a), the Cu-L edge (b) was visible only at the wire regions ((a) – pointed by a black arrow)

To prove that the wires were indeed made of Cu atoms EELS and EDX were performed. Figure 4.5 (a) illustrates a line profile carried over the orange line. The EEL spectrum shown in (b) is taken from the region marked using a black arrow in (a). The EELS always showed a peak at ~ 934 eV whenever the beam hovered over the wires in STEM mode. This was further proven by undertaking simultaneous EELS/EDX mapping analysis as shown in Figure 4.6.

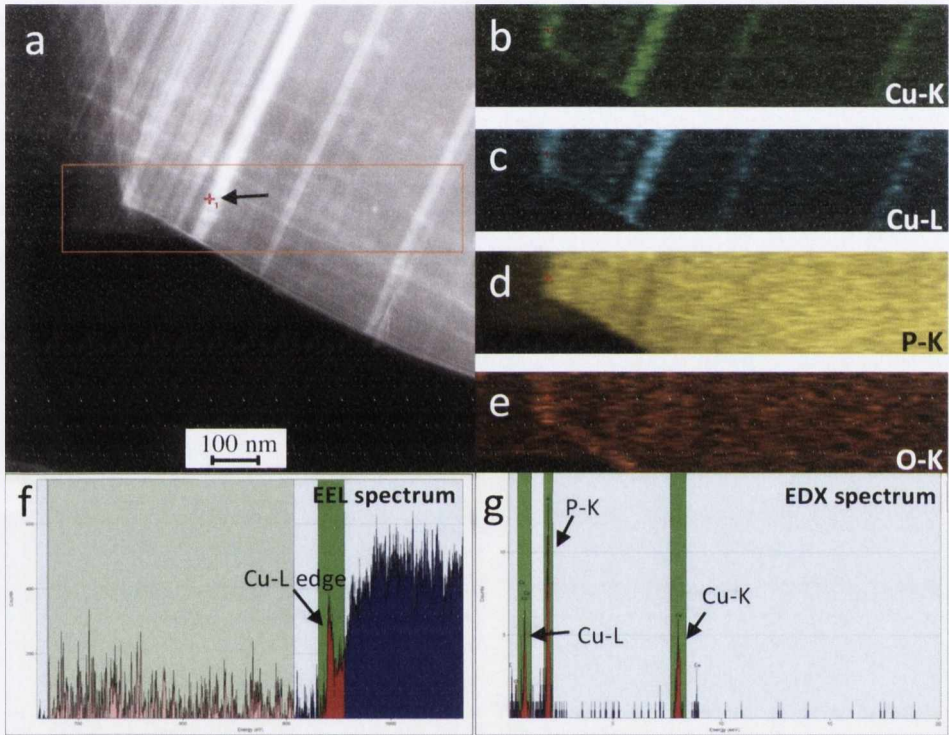


Figure 4.6 EDX mapping carried out across the region marked in orange rectangle in (a). Figure (b), (c), (d) and (e) represents elemental mapping generated from Cu-K, Cu-L, P-K and O-K edges respectively. The EDX spectrum is shown in (g). EELS with back ground subtraction is illustrated in (f) confirming presence of Cu simultaneously.

Figure 4.6 (a) shows a HAADF image over which EDX mapping and EELS were conducted. The elemental mapping across the orange rectangle was carried out with 0.1 sec dwell time on a frame size of 50 X 50 pixels to lower the beam damage to the sample. The EDX spectrum is shown in (g) which was used to extract the Cu-K, Cu-L, P-K and O-K edge to get the elemental maps are shown in (b), (c), (d), and (e) respectively. Cu presence is clearly visible at the bright lines (observed in HAADF image figure 4.6 (a)) represented in (b) and (c) EDX elemental maps. The phosphorus (d) is present uniformly, and oxygen is more concentrated at the edge which is expected

due to edge effects (edges undergoing oxidation). Collecting simultaneous EELS signal further confirmed the results by detecting the Cu-L edge (with background subtraction applied) shown in figure 4.6 (f).

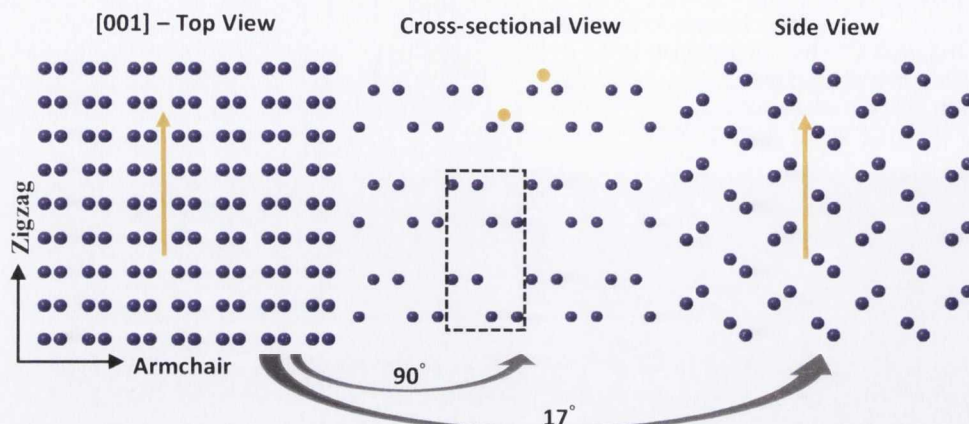


Figure 4.7 A simple atomic structure model of multi-layer BP illustrating different orientations [001], [100] and [101] respectively. Copper can either take the hollow or top site which is marked in orange circles. The arrow (represented in orange) shows the direction of the wire growth which is in zigzag (ZZ) direction. The unit cell is marked in dotted rectangle in the cross-sectional view.

Until now, microscopic level studies in investigating the BP-Cu (or with other metal ad-atoms) interaction has only been carried out by first principle studies. As per some of the computational studies done on metal ad-atoms,[20]–[22] it is seen that the hollow and the top site (marked as orange circles in figure 4.7 and 4.8) are the most probable sites that could be occupied by a metal ad-atom. Through DFT calculations it was found that growth of Cu atoms in BP was also viable interstitially as well as substitutional which is dealt in detail in the next chapter.

Figure 4.7 and 4.8 shows a simple model to understand the direction of the wire growth. The view along [101] direction gives herringbone type of a structure[23]. The growth of these wires is along a zigzag direction. The arrow (orange) in figure 4.7 and 4.8 shows the direction of the wire growth. This is further confirmed by aberration corrected STEM (AC-STEM) discuss in the following chapter. The pristine BP sample obtained from Smart Elements had AB or AB' stacking. In the [001] projection (Top View), due to the same elemental species (P-atoms), it is extremely difficult to distinguish between the two

stacking orders.[11], [24] A monolayer can be distinguished with the bilayer, but as the number of layers increases, it becomes indistinguishable (Figure 4.8).

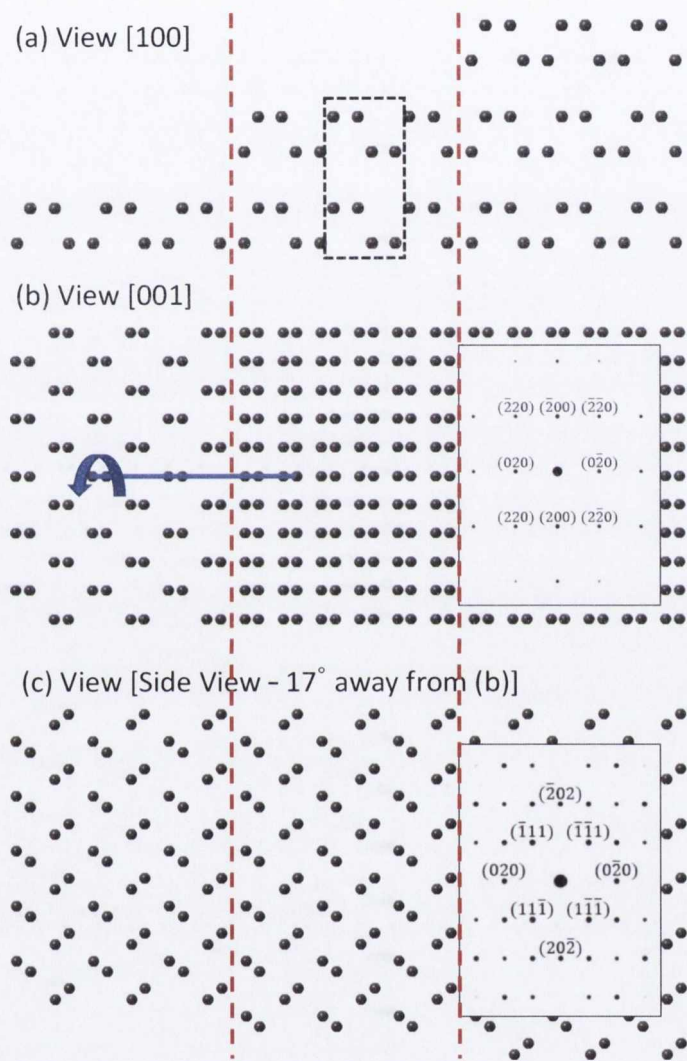


Figure 4.8 (a) (b) (c) Stepped trilayer BP along different orientation [100], [001], [Side View] respectively. Rotating the crystal along the vector marked in blue (b) which is [001] gives different zone axis. The inset in (b) and (c) are their respective diffraction patterns. BP unit cell is marked with dotted rectangle in (a).

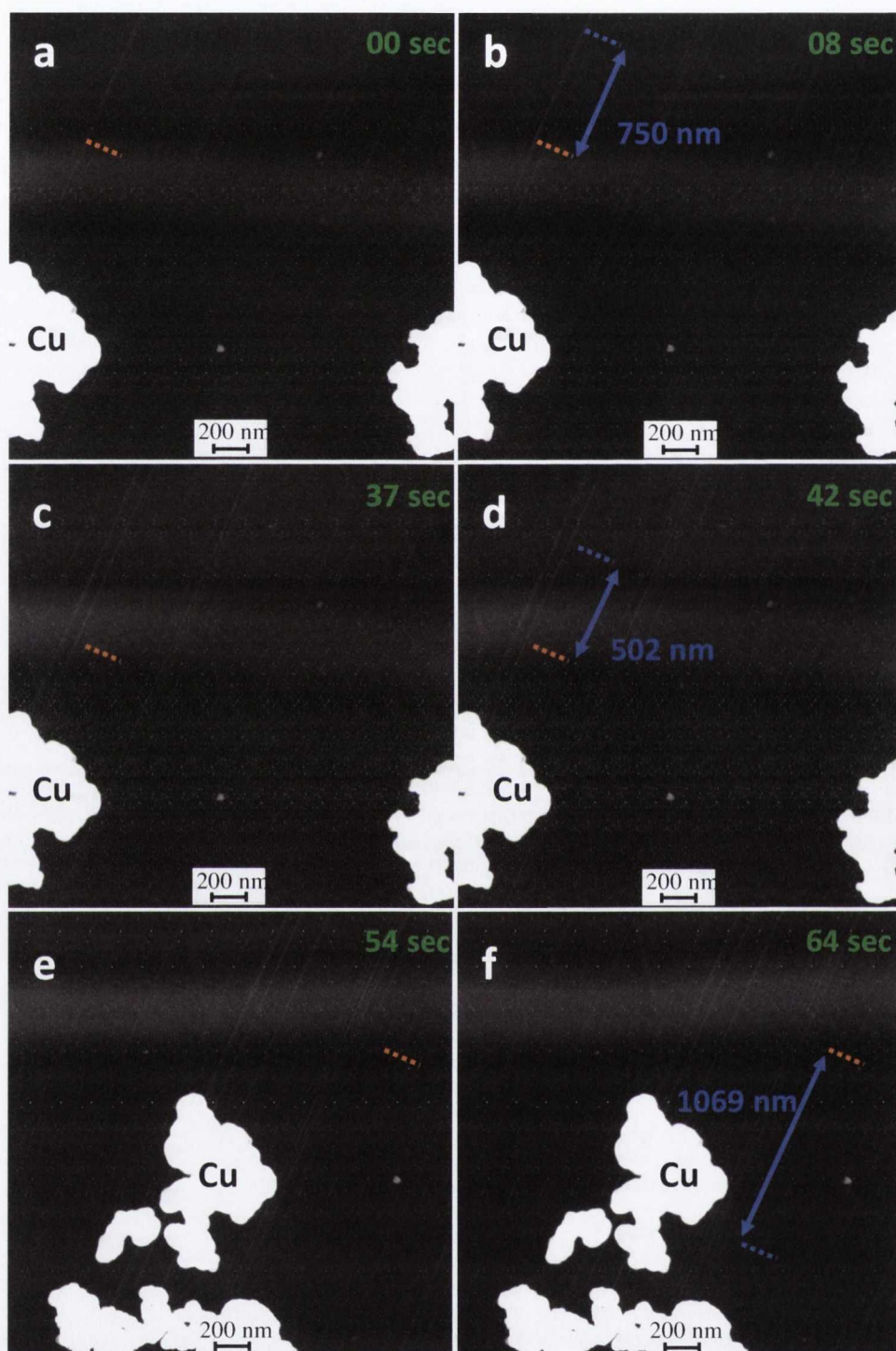


Figure 4.9 Sequence of three different wire growth measurements from figure (a) to (f). The images were captured at different intervals to calculate the speed of the self-assembly. The orange dotted line represents the starting point from where the measurements were done until the blue dotted line.

4.4 – In-situ investigation and growth kinetics

To further investigate the growth process, controlled *in-situ* heating inside TEM was performed. For this experiment, BP was mechanically exfoliated and transferred onto a MEMS chip. Cu nanoparticles were dispersed in isopropyl alcohol (IPA) were dropped cast carefully onto the BP flakes placed over the transparent window chip.

The growth kinetics were observed by thermal interrogation via *in-situ* TEM (Figures 4.9). It was found that ballistic self-assembly occurs at 300 °C along [010] direction. The diffusion of the copper atoms is starting from the Cu nanoparticles. Using this data speed of the assembly growth was calculated at 300 °C. Three different wire growths were observed giving similar results. The results are explained below;

- Figure 4.9 (a and b) – 750 nm in 08 sec = 93.75 nm/sec.
- Figure 4.9 (c and d) – 502 nm in 05 sec = 104.4 nm/sec.
- Figure 4.9 (e and f) – 1069 nm in 10 sec = 106.9 nm/sec.

This gave an average speed of ~ 101 nm/sec. The orange dotted line in figure 4.9 represents the point from which the measurements were taken until the blue dotted line (orange and blue assigned as the starting and the end point for the growth respectively). The variation in the speed calculations could be because of the ripples or bending of the BP nanosheet (occurring in the z-direction at high temperatures) which explains the anomalies in measurements.

Continuous heating of the sample at 300 °C (for 65 min) results in the formation of more wires throughout the whole region (Figure 4.10 (a)). Further ramping of the temperature to 500 °C for 60 seconds (Figure 4.10 (b)) results in copper diffusing throughout the flake. After ~120 sec at 500 °C (Figure 4.10 (c)), the BP nanosheet starts deteriorating, and holes start appearing in the flake as the experiment progresses to ~ 130 sec (Figure 4.10 (d)). After ~140 sec, the same trend is continued until the copper starts covering the BP surface (Figure 4.10 (e), (f)). In metals like Cu, Au etc. compared to the bulk the melting at the surface occurs much at lower temperatures.[25] The hereby seen thermally

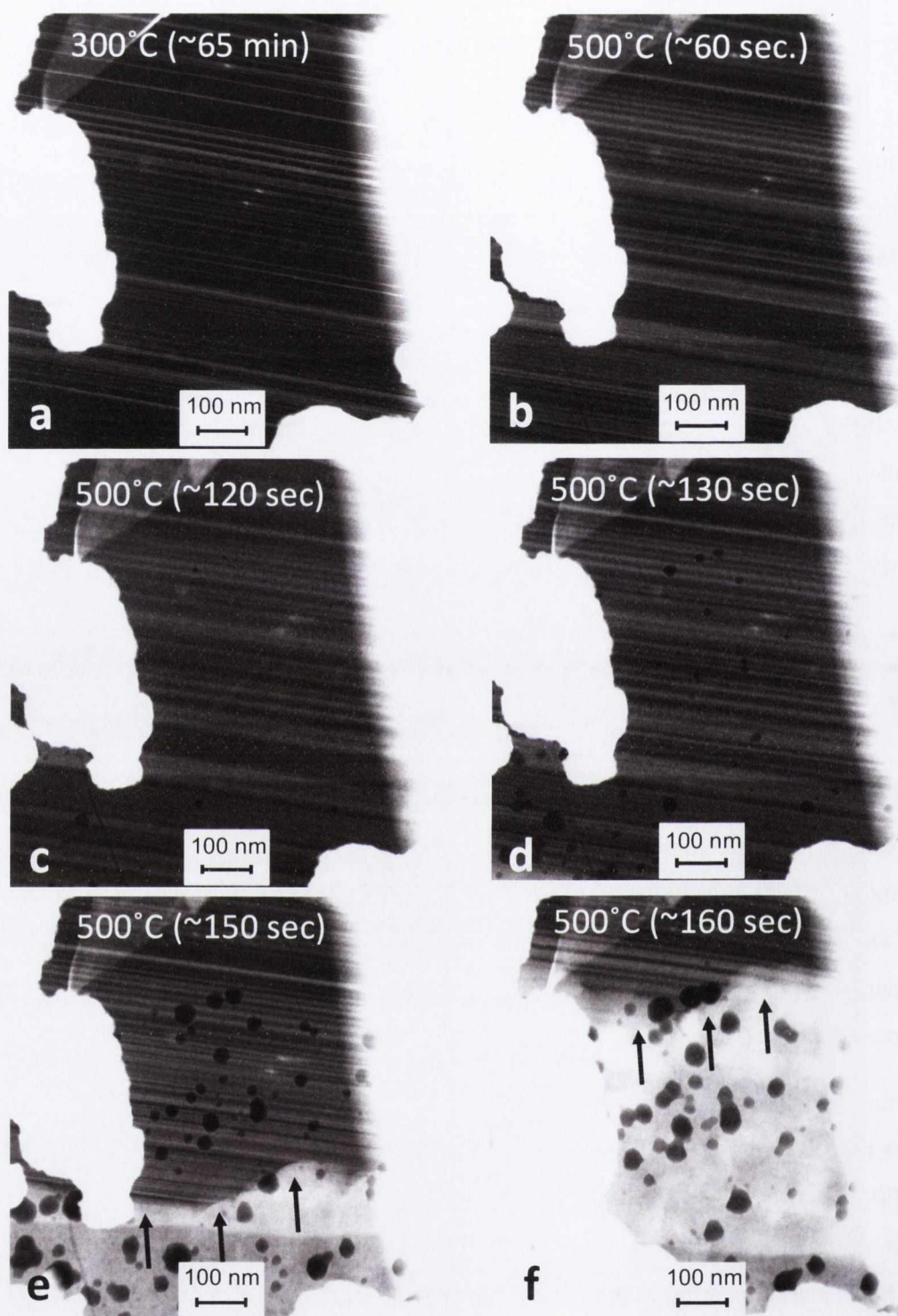


Figure 4.10 In-situ TEM heating carried out for longer duration of time on a MEMS chip heated at 300 °C (a) and then up to 500 °C (b) to (f) for 60, 120, 130, 150 and 160 seconds respectively. It is clearly observed that more wires keep forming, and as the temperature is ramped up to 500 °C, a copper film starts spreading over the whole BP and starts deteriorating, indicated by the black arrows in figure (e) and (f).

4.5 – Growth of wires from different metals

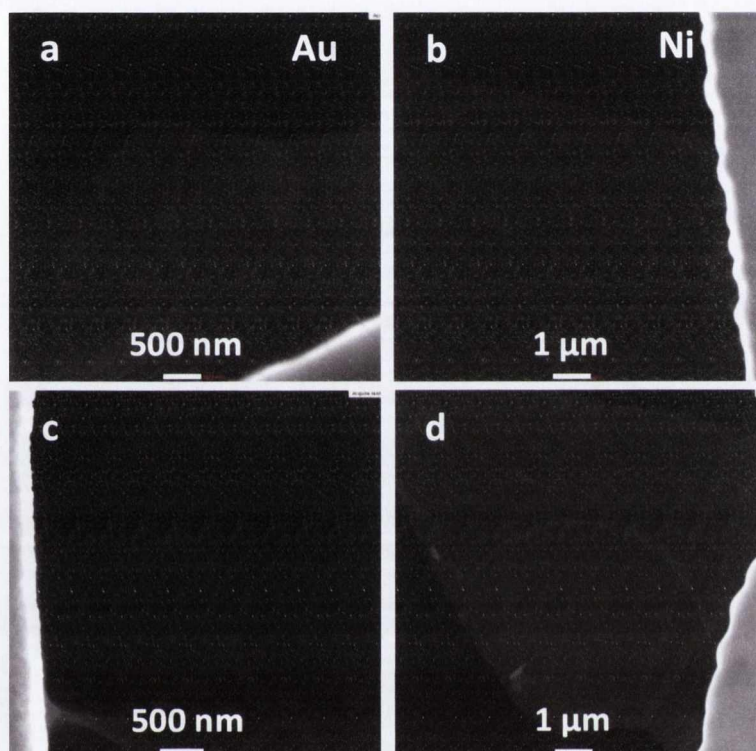


Figure 4.11 BP exfoliated over Au and Ni grid shown in (a) and (b) respectively. After heat treatment, no interaction is observed as seen in (c) and (d). This was after 6 days of baking at 100°C in a vacuum oven.

This phenomenon of self-assembly of metal atoms was not observed when the experiment was carried using Au, Ni grid (Figure 4.11) and using Ag and CuO nanoparticles over BP as illustrated in figure 4.12.

Figure 4.12 (a) shows multilayer BP over which Ag nanoparticles are dropped cast. As the temperature is ramped up to 300 °C, the Ag starts reacting with BP with no sign of self-assembly. Figure 4.12 (b) shows multilayer BP with CuO nanoparticles. The temperature was increased to 500 °C until BP got amorphous, but again no self-assembly was observed.

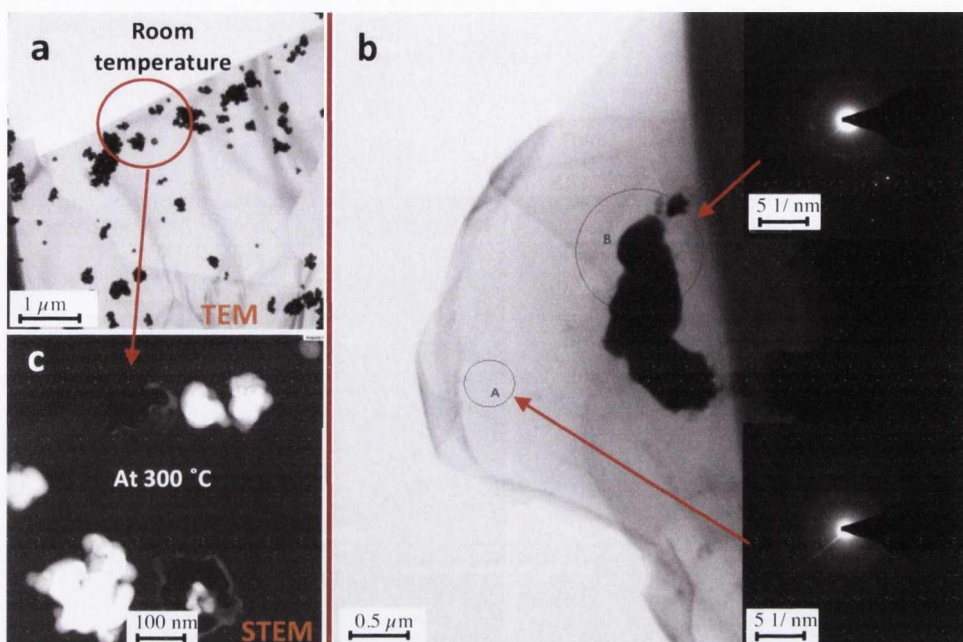


Figure 4.12 (a) and (b) shows TEM of an in-situ heating experiment carried out over a MEMS chip where no formation of any wires was observed when Ag or CuO nanoparticles were dropped cast over BP and heated step by step up to 500 °C. At this temperature, BP turns amorphous as shown in the SAED pattern taken on region A. In case of Ag nanoparticles; the BP started reacting and getting deteriorated at 300 °C as shown in (c) in STEM mode

4.6 – Degradation test

Pristine BP is known to go under quick degradation.[10] Interestingly, it was found that the Cu-P interactions have a secondary, nonetheless very significant, effect of rendering the BP sheets more resistant to degradation, prolonging their lifetime in ambient conditions from hours to weeks (Figure 4.13). The above samples were prepared by depositing 20nm Cu metal using e-beam metal evaporator (Temescal) over Si/SiO₂ chip. BP was then mechanically exfoliated over it. It was found that BP kept under vacuum without heat showed the formation of bubbles over the surface and in 2 months most of the BP had totally oxidized.

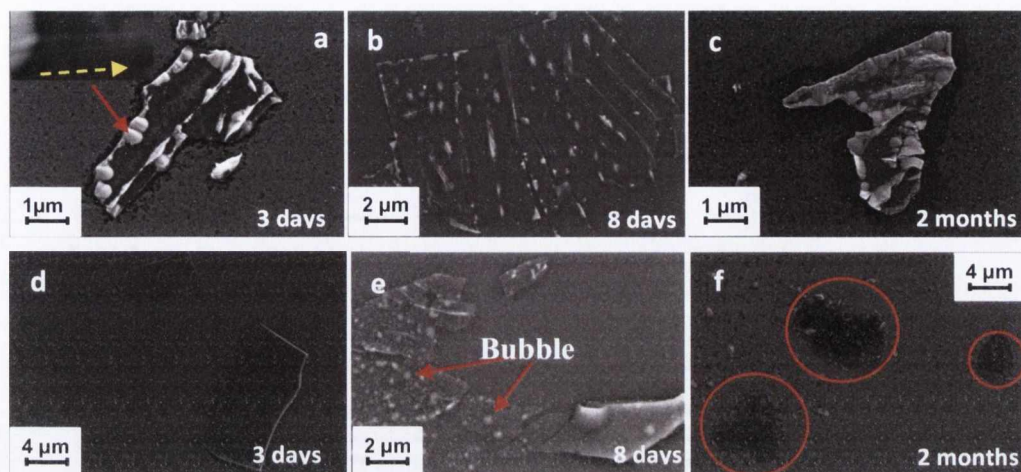


Figure 4.13 (a), (b) and (c) shows the sample kept in a vacuum oven at 100°C whereas (c), (d) and (f) kept under vacuum at room temperature. Figure (e) indicates the bubble formation and the regions marked in circle in (f) shows complete degradation of BP after two months. The inset in (a) shows the wire formation indicated in yellow dotted lines.

4.7 – Optical Anisotropy

Among various anisotropies, BP displays optical anisotropy. This can be studied by performing Raman spectroscopy which is used to probe the vibrational modes in a crystal. In black phosphorus A_g^1 , B_{2g} and A_g^2 are strongly active vibration modes which are used to study optical properties. As per the previous discussion, the wire formation is a local phenomenon and does not change the BP structure except where the wires are formed. The whole BP structure remains intact and crystalline as shown in the high-resolution EM images. Raman carried out on the BP and BP/Cu sample did not show any difference as copper is Raman inactive. To investigate the optical anisotropy of these systems, polarized Raman was carried out over pristine BP (Figure 4.14), and Cu treated BP (Figure 4.15). To avoid the confusion whether the lines were formed or not, Cu nanoparticles were dropped cast over two identical BP samples: one batch was heated as described above, whilst the other was kept at room temperature. Given the very small (i.e. width of three atoms) feature size of the Cu lines it was not possible to know how many copper wires were formed on the thermally treated sample. Further work needs to be carried out to study the change in the Raman response as a function of the number of

layers and number of copper wires present respectively. Comparing figure 4.14 and 4.15 there is no evidence of the optical anisotropy of BP being affected by the Cu treatment.

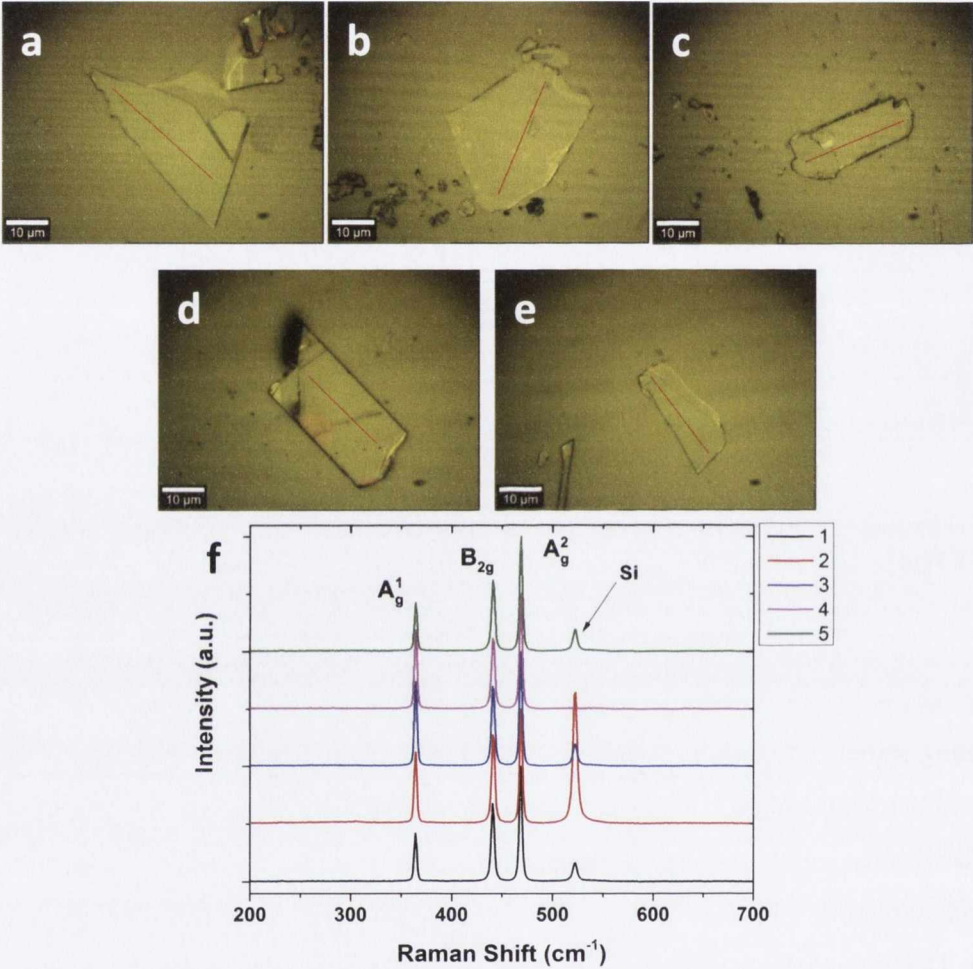


Figure 4.14 Raman carried out on pure BP. Figure (a) to (e) shows Raman spectra carried out on five different flakes. The corresponding spectra are illustrated in figure (f) showing the typical Raman intensities for A_g^1 , B_{2g} and A_g^2 followed by a Si peak.

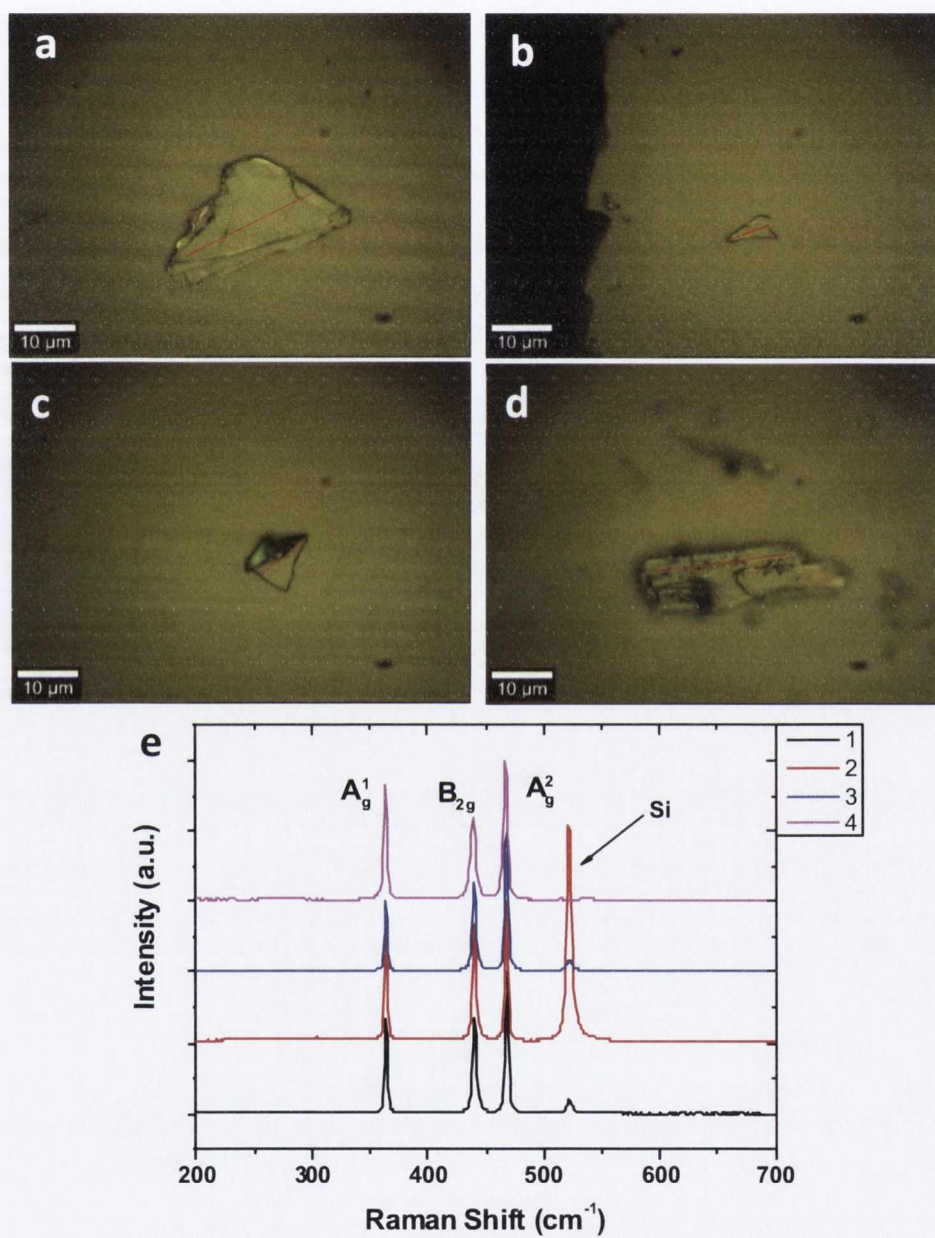


Figure 4.15 Raman carried out on BP/Cu treated sample ((a) to (d) flakes) showing its corresponding spectra in the plot (e). BP was heated on a Cu foil heated up to 300 $^{\circ}\text{C}$ for 15 min.

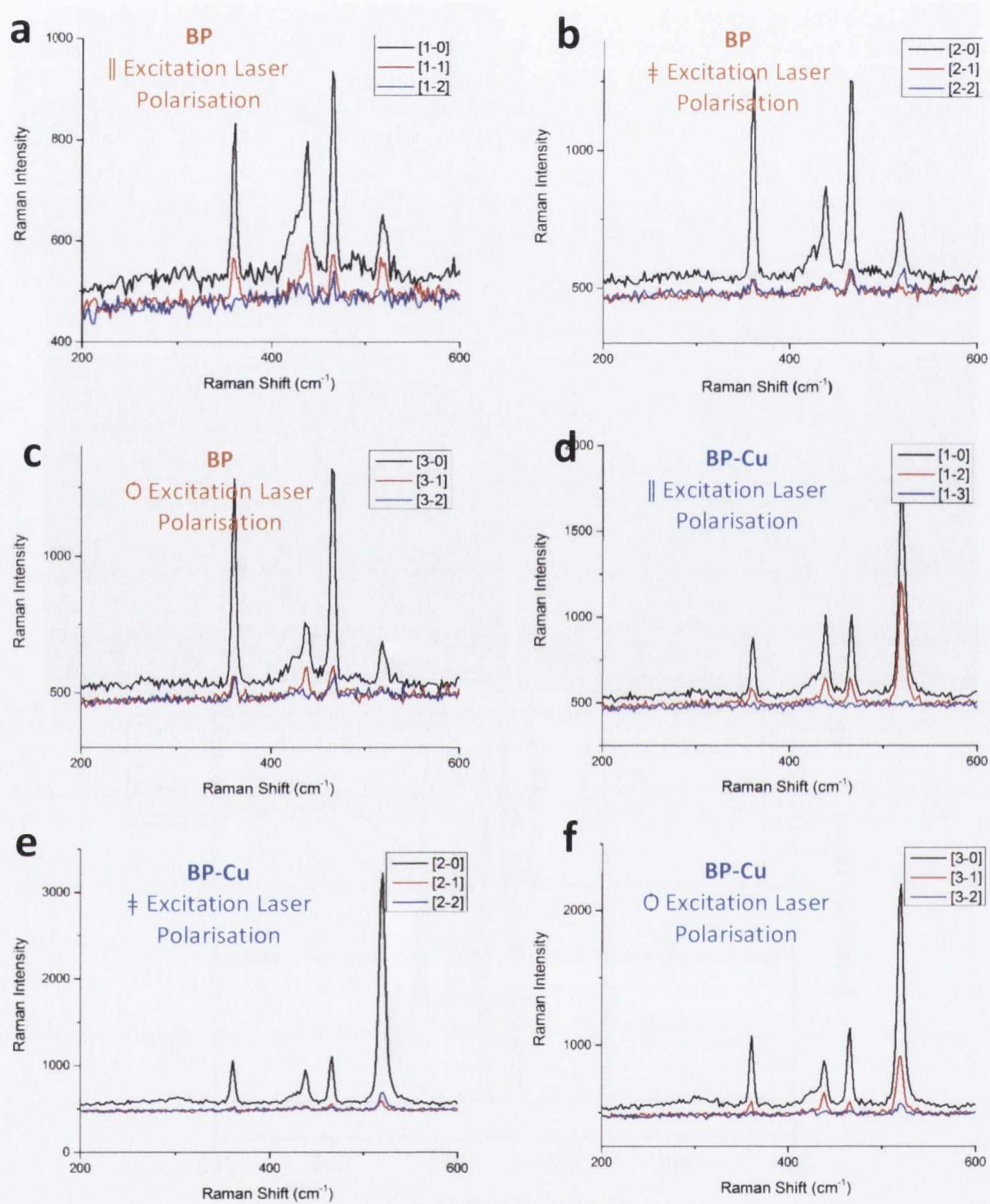


Figure 4.16 Polarized Raman carried out on pure BP (a) to (c) and Cu treated BP (d) to (f). As seen from the BP-Cu plots the sample gives similar response to the laser excitations compared to the pristine BP samples.

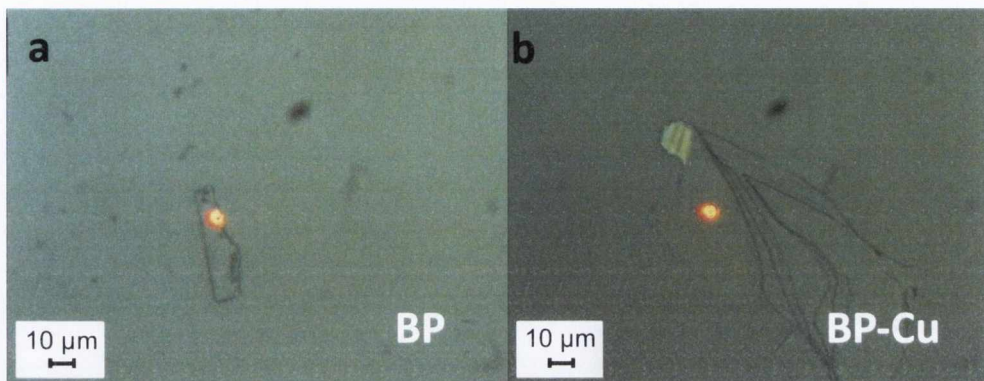


Figure 4.17: Optical images of the polarized Raman shown in figure 4.16, where (a) and (b) represents the flakes used to obtain (a) to (c) and (d) to (f) plots in figure 4.16 respectively.

Since BP is an anisotropic material, it shows a unique optical response which is highly polarization dependent. The Raman spectroscopy carried out in figure 4.14, and 4.15 respectively did not show any change in the BP and Cu treated BP sample[27]. As the polarized Raman spectroscopy will give more insight into the optical anisotropy of BP, similar sample preparation procedure was followed. In polarized Raman, two parameters were changed. Excitation laser polarization and emission polarization. Raman plots shown in figure 4.16 (a), (b), (c) and (d), (e), (f) are done on BP and BP-Cu sample respectively. $\parallel$ means the polarization was parallel to the direction of the laser, $\perp$ perpendicular and O means circularly polarized. Keeping the excitation laser polarization parameter constant, emission polarization was varied in each plot. The black line is when no emission polarization was applied followed by red (parallel emission polarization) and blue with emission polarization being perpendicular. Figure 4.17 shows one of the BP (a) and Cu treated BP (b) nanosheet from where the signal was collected.

Even after copper interaction the anisotropy in BP was preserved and did not show any changes as compared to the pristine BP counterpart. As can be seen whenever the emission polarization was not polarized (i.e. $[1-0]$, $[2-0]$ or $[3-0]$) the sample showed all three intensities namely A^1_g , B^2_g and A^2_g in both samples. However, when it was varied, the intensities showed a variation which was consistent in both samples. This is expected as BP is known to be optically anisotropic so it would behave differently depending on the excitation of the laser polarizer. In this experiment, the N^a nosheets were randomly

placed and the orientation was not known. The Raman intensities are not only dependent on the polarization angle but also on the BP orientation.[28] So if the flake orientation (either zigzag or armchair) can be kept parallel to the scattered light, some difference in the A^2_g intensity could be expected.

4.8 – Summary of the findings

In conclusion, in this chapter, we have observed for the first time how chemical anisotropy in BP enables the fabrication of localized, highly-directional wire-like structures by a very simple and reproducible approach. The growth method is extremely simple and controllable. Importantly, we find that the BP-Cu interactions are highly localized and not affecting the overall BP structure. Ex and in-situ experiments were conducted to study the kinetics of the wire growth. However, the experiments also need to be reproduced for different temperature raises to get the activation energy. Further heating the sample resulted in degradation and Cu diffusing all over the surface. The wire growth was found to be very specific for Cu metal and did not occur for Ag, Ni, Au and even CuO nanoparticles. Nonetheless, further investigation should be made for various other metals and BP analogues.

BP-Cu interaction was found to have a profound effect on its degradation. This will help in reducing the oxidation issues while fabrication BP device. Also, looking at the optical properties analysed by polarised Raman, the optical anisotropy of the BP and BP-Cu interacted sample remains same. This will allow fabricating novel devices of Cu diffused BP to work as electronic as well as for optoelectronic applications simultaneously.

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Chapter 5

Structural and Spectroscopic

Characterization using AC-STEM

“One can be fooled by appearances, which happens only too frequently, whether one uses a microscope or not.”

... Voltaire in Micromegas

5.1 – Metal or a composite?

In this chapter, we present an extensive study on the structure and spectroscopic properties of the Cu diffusion over BP using aberration-corrected scanning transmission electron microscopy (AC-STEM), electron-energy-loss spectroscopy (EELS) and X-ray photoelectron spectroscopy (XPS) in combination with first principle calculations followed by quantified image simulations.

In-situ investigation of the Cu diffusion over BP (discussed in the previous chapter) has opened up many questions as to what the wire-like structures are composed of. Ballistic self-assembly of Cu over the semiconductor can have considerable implications in the field of integrated circuit (IC) interconnects. This demands proper examination to reach a definite conclusion. Currently, due to the presence of electromigration and sidewall scattering the resistance of the copper metal increases drastically[1][2][3]. The possibility of growing atomically-thin wire-like structures directly bound into the semiconductor material will open up new horizons beyond Moore’s Law.

Tremendous literature review on the interaction between BP and Cu points out to the fact that the wire structure is likely to be a composite rather than being pure metallic Cu.[4]–

[6] Reducing action of Phosphorus over Cu metal is well known. Though in this scenario the diffusion is seen from Cu metal towards BP nanosheets. By using electron, energy loss spectroscopy at atomic scale chemical nature of these wire structures is probed and confirmed by undertaking first principle calculations. The density functional theory (DFT), section 5.4 and quantified ADF (Q-ADF) imaging, section 5.6 was carried out by collaborators at the School of physics (Trinity College Dublin) and EMAT (Antwerp, Belgium) respectively as mentioned in the acknowledgement.

5.2 – High-Resolution HAADF Imaging

To study the BP-Cu interaction at the atomic scale, aberration-corrected STEM (AC-STEM) was used. The imaging was done at 60 kV to minimize the beam knock-on damage. Figure 5.1 shows atomically resolved STEM images of Cu like wires on multi-layered BP, revealing that the formation is indeed highly localized and does not impact the entire BP structure. Interestingly, self-assembling Cu atoms exhibit a long-range translational ordering, overcoming the effect of Landau-Peierls thermal fluctuation instabilities.[7] In this case, such instabilities seem to be suppressed by the interactions with the BP substrate.

The high-angle annular dark field (HAADF) STEM micrograph in figure 5.1 (a) shows the as-grown multi-parallel triatomic Cu wires in the [001] BP projection. The zoomed in wire marked using a green rectangle is displayed in figure (c) indicating the width to be 3.6 Å. Figure 5.1 (b) shows a biparallel wire assembly on a multilayer BP sheet in [101] projection (which is 17 degrees with respect to the [001]). Whilst the micrographs in (d) and (e) were acquired zooming in on the region marked in orange and blue rectangles respectively.

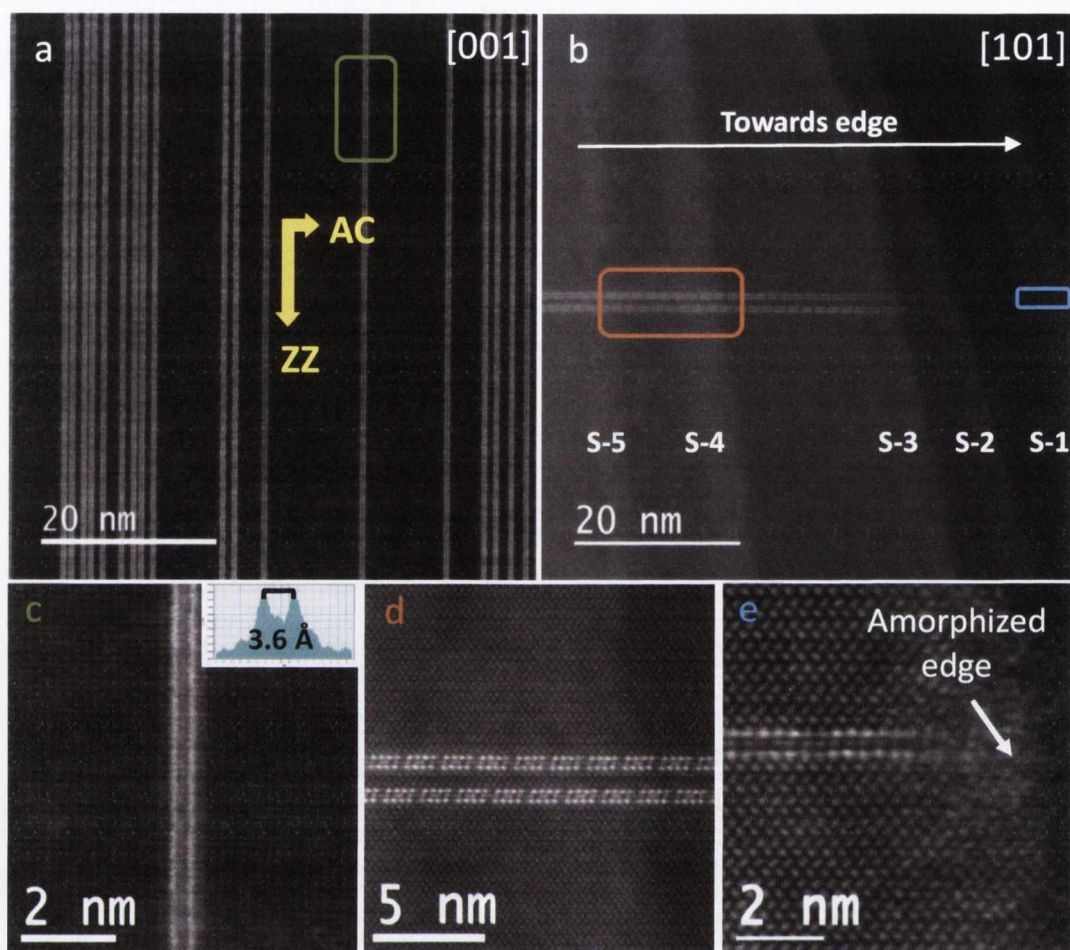


Figure 5.1 Experimental HAADF images showing highly localized Cu atom ordering on multilayered BP. (a) and (b) show [001] and [101] projections respectively. The yellow arrows in (a) show the different flake orientations: armchair (AC) and zigzag (ZZ), respectively. (c) high-magnification image of a single 1D structure (from the region marked in green in (a)). This structure shows a width of 3.6 Å (intensity profile in the inset). (d) and (e) show high-magnification images of the regions in figure 1(b) marked by the orange and blue rectangles respectively. Both of these clearly illustrate that the growth remains uninterrupted throughout the BP layers and across steps and that the wire-structure remains intact until it approaches the nanosheet's edge.

Looking at figure 5.1 (b), clearly illustrates that the growth remains uninterrupted throughout the BP layers (another example given in figure 5.2) until it approaches the edge, where the flake is amorphized (Figure 5.1 (e)) due to oxidation.[8]

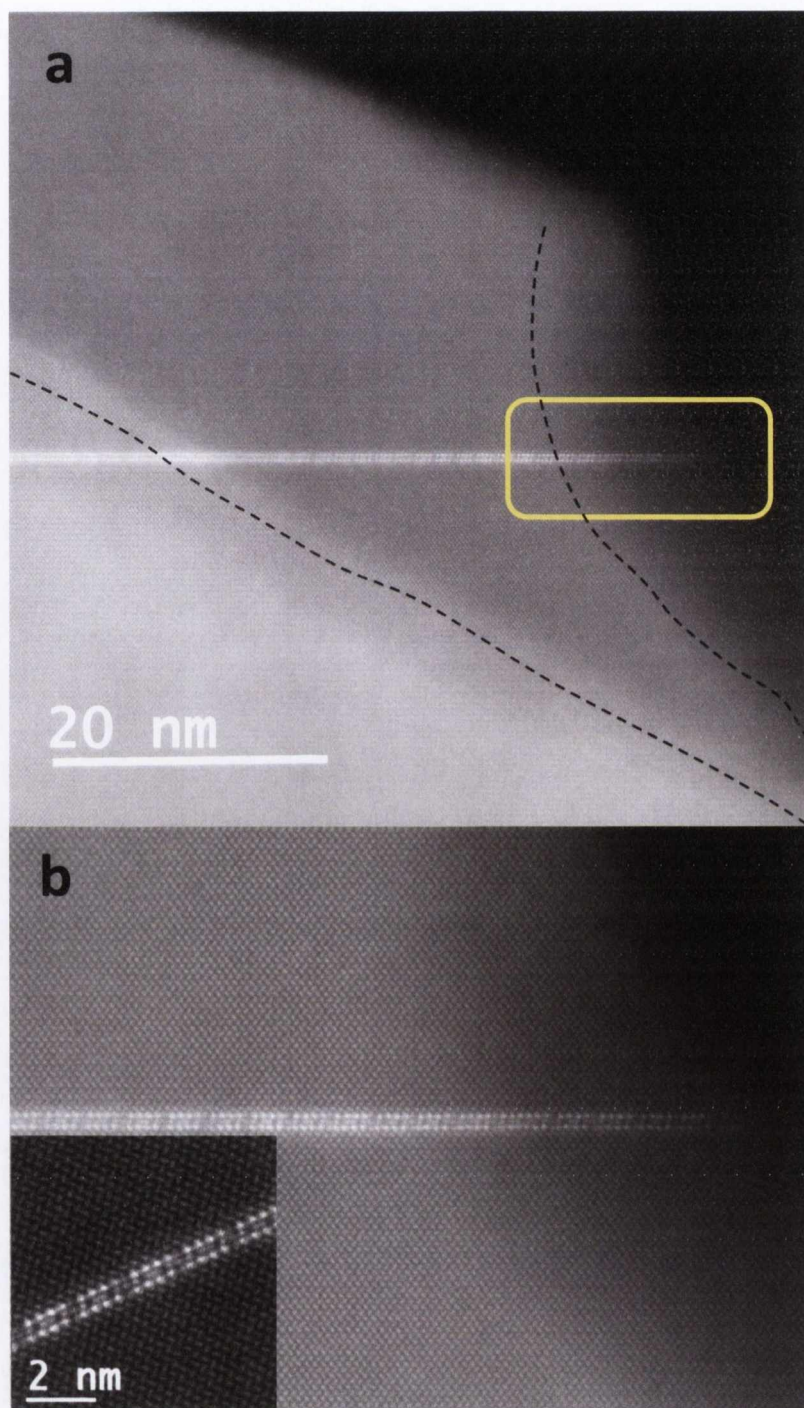


Figure 5.2 Another example of Cu uninterrupted self-ordering through the BP multilayers. (a) HAADF STEM of a Cu wire structure/multilayer BP flake. The dotted lines mark the step-edges. (b) zoomed-in part of the region marked with a yellow rectangle in (a). The inset shows an atomically resolved wire processed using smart align plug in.

5.3 – EEL Spectroscopy and XPS

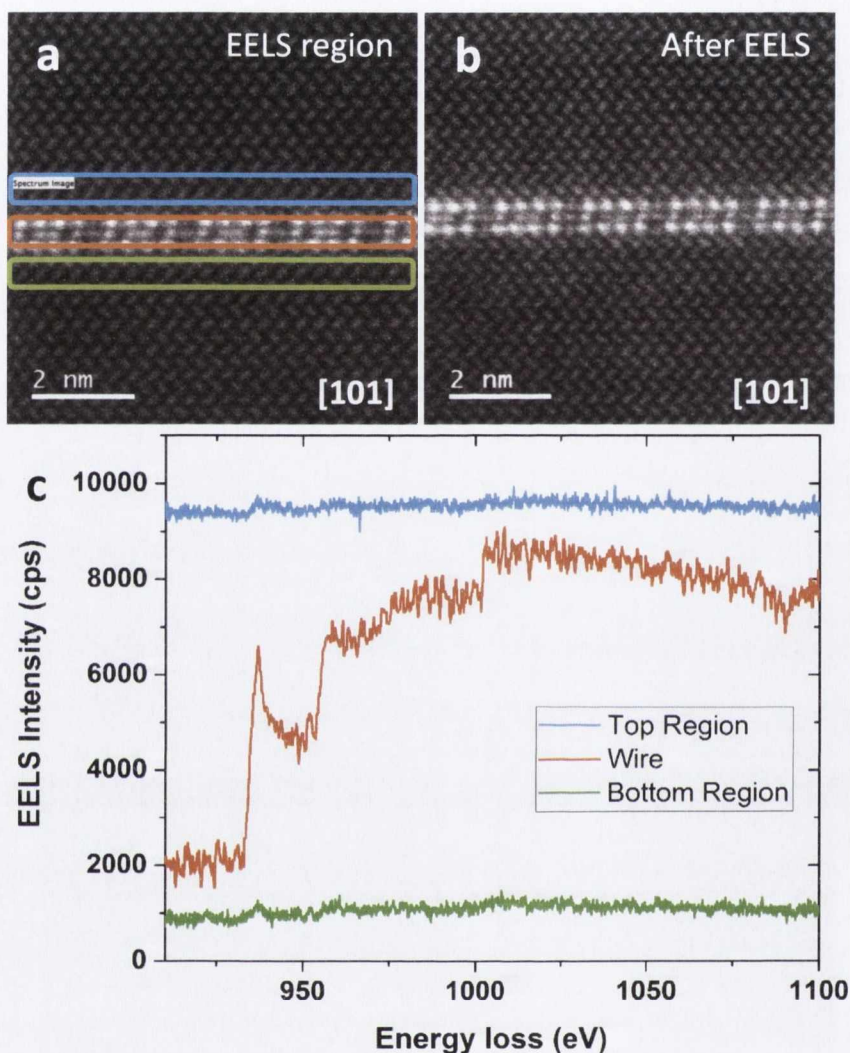


Figure 5.3 HAADF-STEM Images of the wires before and after recording the EELS spectra shown in figure (a) and (b) respectively. EELS spectra acquired over the wire (orange rectangle) shows the Cu L-edge at ~936 eV. The spectra taken over the blue and green region in (a) did not show any Cu presence.

The chemical nature of the tri-atom assembly was investigated via Electron energy loss spectroscopy (EELS). Core-loss spectra were acquired along the wires, proving the presence of copper (Figure 5.3 (c)). Spectra collected from the top and bottom region (blue and green region) did not show any presence of Cu. This further confirmed that the growth is highly localized where the Cu-L edge is only observed at the wire regions (orange rectangle in figure 5.3 (a)). A combined X-ray photoelectron spectroscopy (XPS) and

electron energy-loss near-edge structure (ELNES) study were performed to gain insights on the nature of the bonding occurring between Cu and P atoms and reveal the valences of the copper in the structure. Figure 5.4 (a) and (b) show the XPS spectra of pristine BP and Cu-BP nanosheets respectively. Importantly, both the exfoliated pristine BP and the Cu-BP spectra exhibit the sharp 2p phosphorous component (~ 129.5 eV and ~ 130.5 eV), indicative of pristine BP, demonstrating that the thermal treatment does not have any detrimental effect on the underlying BP flakes. The spectrum in figure 5.4 (b) also shows a weak peak centred at 133.7 eV (green component marked as P-O, P=O) which is usually associated with phosphate.[9][10] A further peak centred at 128.8 eV (C1 in blue) was also observed in the copper phosphide (Cu_3P) reference sample shown in figure 5.5 (c).

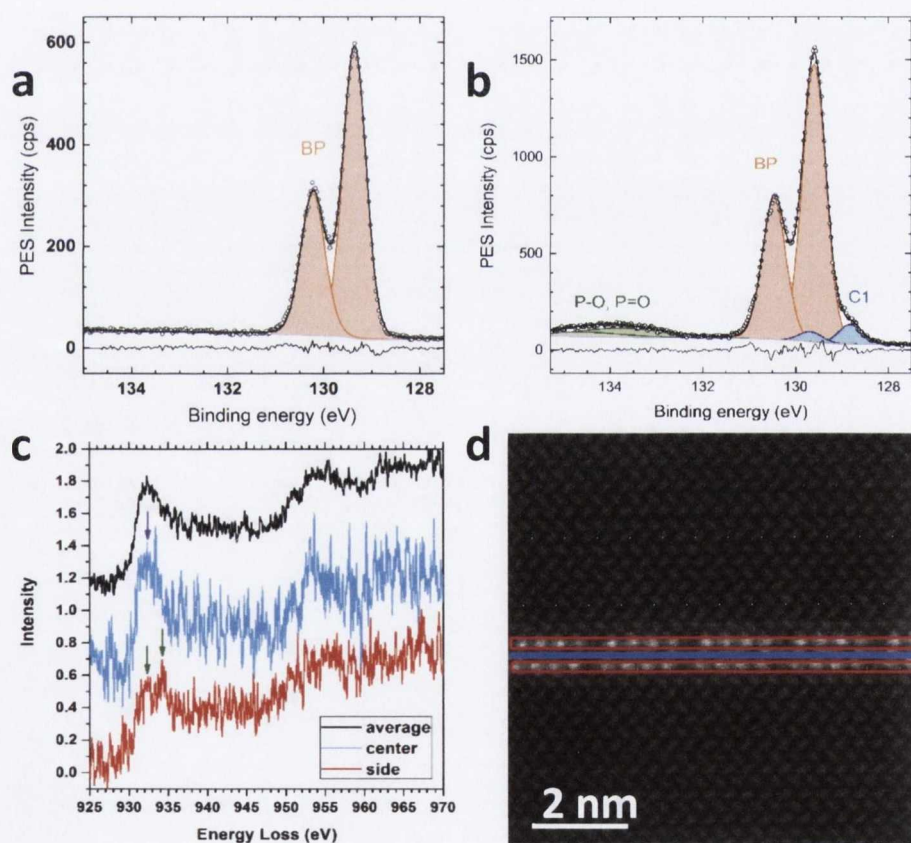


Figure 5.4 (a) and (b) XPS spectrum of a pristine BP sample and Cu interacted BP sample respectively. The Shirley background was removed from such spectra. Fit lines are labelled as CuP, BP, and C1, (c) Cu L-edge EEL spectra taken from the red region (sides) and the blue region (centre) confirming different Cu oxidation states. The green arrows show the peak doublet formed compared to the single peak marked with the black arrow. (d) Atomic-resolution HAADF STEM image showing the region from which the EEL spectra were acquired.

Figure 5.4 (a) shows the XPS 2p phosphorous spectrum in pristine, unprocessed BP; clean and well-defined $2p_{3/2}$ and $2p_{1/2}$ peaks are visible in this spectrum. Figure 5.5 (d) shows the Cu 2p component completely absent in pristine, unprocessed BP. Spectra in 5.5 (b) and (e) show the P and Cu spectra in the BP-Cu wire system. Spectra in 5.5 (c) and (f) show the P and Cu spectra in reference Cu₃P sample. In figure 5.5 (b), the 2p phosphorous component remains sharp. However, several additional contributions are now appearing. Noticeable Cu 3s peaks at 122 and 125 eV (enlarged in the inset) with no Cu²⁺ shake-up, and prominent peaks at 133.7 and 128.8 eV (in agreement with the structure seen in the Cu₃P reference material), as well as very broad phosphorous 2p signal with the $2p_{3/2}$ at 133.2 eV.

In figure 5.5 (e) the Cu signal shows two components corresponding to Cu¹⁺ or Cu⁰. For the reference Cu₃P material (f) we find a mixed valence within a strong 2+ shake up signal and two main Cu components at 932 and 935 eV. Both the sample without and with copper in figure 5.4 (a), (d) and (b), (e) respectively were thermally treated at 300 °C for 5 minutes.

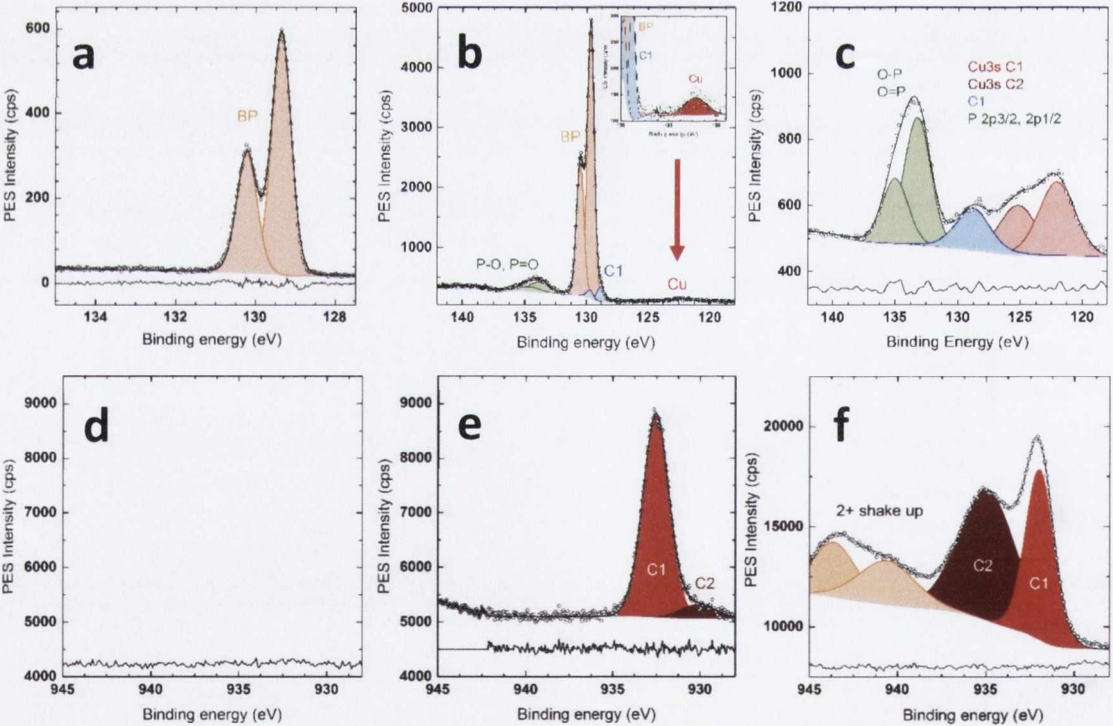


Figure 5.5 Comparative XPS study of phosphorous 2p and Cu 2p components for pristine BP (a) and (d), respectively, BP with Cu wires (b) and (e) respectively and Cu₃P as a reference (c) and (f), respectively. The inset in figure (b) shows the Cu-3s peak enlarged.

To gain further insight into the nature of the Cu-P bonding, fine structure analysis of the Cu L2,3 spectrum (acquired with high spatial resolution) were performed across the wire structures represented in figure 5.4 (d). Spectra were acquired from the sides of the 1D Cu-P structure (red areas in figure 5.4 (d) where the bright Cu containing columns are clearly visible) as well as its central region (blue area in figure 5.4 (d) where the Cu containing columns exhibit relatively lower intensities). These are shown in figure 5.4 (c) as red and blue spectra respectively. Interestingly, the Cu located at the structure's edge (red region) showed different oxidation states when compared to the Cu located at the centre (blue region). Whilst the side of the Cu-P structure (red) exhibited only the typical Cu^{2+} peak at ~ 932 eV (purple arrow), Cu located at the centre of the Cu-P structure (blue region) showed a doublet at ~ 932 and ~ 934 eV (green arrows). Confirming the presence of mixed oxidation states, namely Cu^{2+} and Cu^{1+} . [11][12]

5.4 – Growth Mechanism: Density Functional Theory

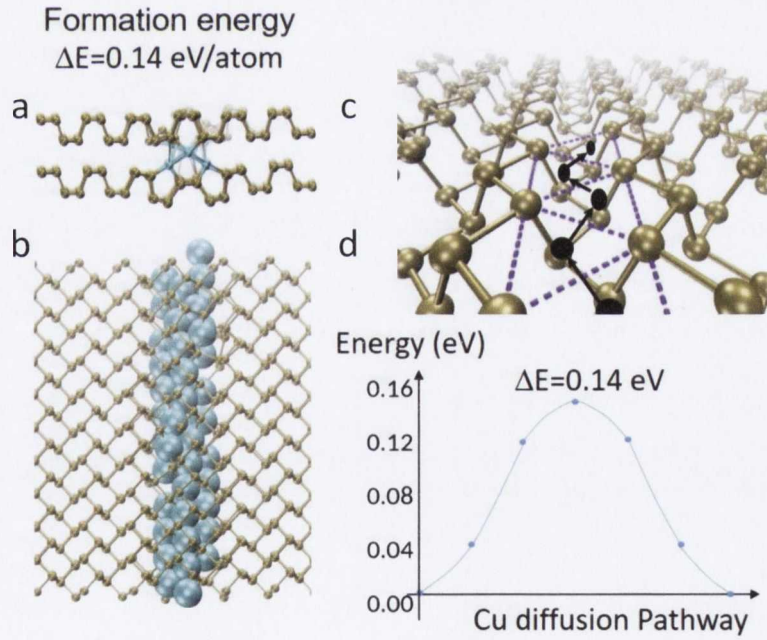


Figure 5.6 (a) Side view along [100] direction of illustrating the structure of the most stable interstitial Cu wire (b) [101] view Cu atoms along the wire are adsorbed between adjacent zig-zag P rows forming the lower and upper surfaces of the BP layers above and below the wire, respectively. (c) Cu diffusion path through surface adsorption sites, highlighted by black dots at the centres of the triangles connecting adjacent surface zig-zag rows. (d) energy profile along diffusion pathway.

BP interaction with metals has been theoretically investigated using first-principles calculations[13][14]. Out of all the metals, copper has proven to be the most interesting one. In BP, phosphorous atoms join together to form a two-dimensional puckered sheet with natural channels along (010) direction with P atoms forming adjacent hexagonal chairs. The unit cell is orthorhombic. Its high charge mobility of the order of $10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and tunable band gap (ranging from 1.51 eV to 0.59 eV as the thickness of the sample goes from one to five layers) make it a strong contender for semiconducting industry[15].

Different Cu structures can be adsorbed on BP.[14], [16], [17] The most stable configuration we found was a three-atom-thick intercalated Cu 1D structure, intercalated between BP layers with an exothermic formation energy of 0.3 eV/Cu atom. This intercalated structure formed along the natural BP growth channel in the (010) direction,[18]–[20] with a triangular cross-section (pentagonal was also found to be stable, figure 5.7), shown in figure 5.6 (a). The ultimate structure featured hexagonal Cu_3P -like motifs, as shown by the similarity of the respective Cu-P radial distribution functions at short distances. Cu-Cu interatomic distances were about $2.55 \pm 0.3 \text{ \AA}$, and the overall width of the 1D Cu structure was $3.8 \text{ \AA}$. This is extremely close to the experimental value of $3.6 \text{ \AA}$ (Figure 5.1 (c)).

The DFT calculations suggested that the formation of a Cu wire is also kinetically viable, revealing that the diffusion of a Cu atom on a BP surface occurs interstitially, along with a zigzag pathway between centres of adjacent BP hexagonal chairs (Figure 5.6 (c)). The activation barrier for such Cu diffusion barrier amounted to 0.14 eV.

In addition to diffusing interstitially, different metastable Cu 1D structures were found adsorbed on the BP surface. Notably, motifs with the symmetry of the experimentally observed 1D wire were found for both interstitial, and surface structures when the size of the supercell used to model the BP was consistent with this symmetry and not all the available hexagonal sites were occupied.

DFT also showed that Cu structures preferably form at exposed BP edges. The chemisorption of a Cu atom at the BP (010) edge, (a likely point to initiate growth), was exothermic by 0.02 eV after a dissociative process leading to the release of a P atom. Even though, the Cu-BP interactions appeared to be thermodynamically unfavourable for short

1D surface structures, these became progressively more favourable for increasing lengths. The adsorption energy cost ranged from 0.81 eV to 0.17 eV/atom by increasing the number of Cu atoms composing the 1D structure from 1 to 40. The formation of a surface 1D wire generally appeared more favourable when Cu atoms sat in substitutional positions on sites previously occupied by P atoms which were released from the surface.

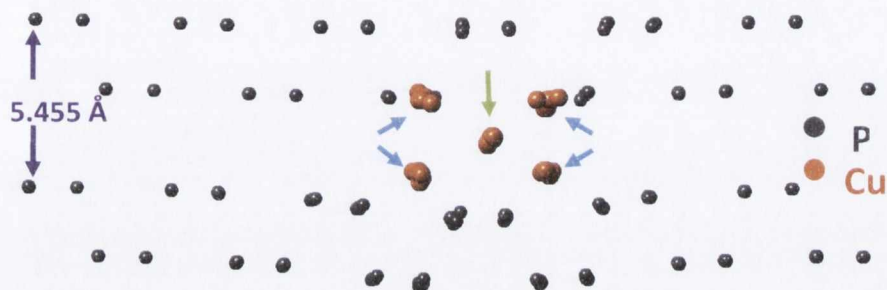


Figure 5.7 [100] view of BP-Cu structure showing Cu being in different chemical environment at the centre (orange arrow) and sides (green arrows)

Figure 5.7 is a DFT calculated model which helps in understanding the different oxidation states obtained from the STEM-EELS pattern shown in figure 5.4 (c). As discussed earlier, at the centre of the wire (represented by the green arrows), we find a single peak in the Cu L-edge, which represents Cu being in a +2 state; a mixed valency ($\text{Cu}^{+2}/\text{Cu}^{+1}$) is instead encountered at the wire edges, represented by the blue arrows. The length of the Cu-P bonds at the sides of the wire also appears different to the ones at the centre of the wire. For the Cu atoms situated at the sides of the wires, we encounter a charge transfer from 'P' to 'Cu', resulting in the occupancy of Cu-3d states. This leads to a mixed Cu valency at the edges when compared to the Cu atoms at the centre of the wire.[21][11] Electron transfer from Cu to P cannot be ruled out. Simultaneous ELNES of P L2,3 and Cu L2,3 or O K edge (with EELS simulation) may answer the question.

5.5 – Comparing Experimental and Calculated model Qualitatively

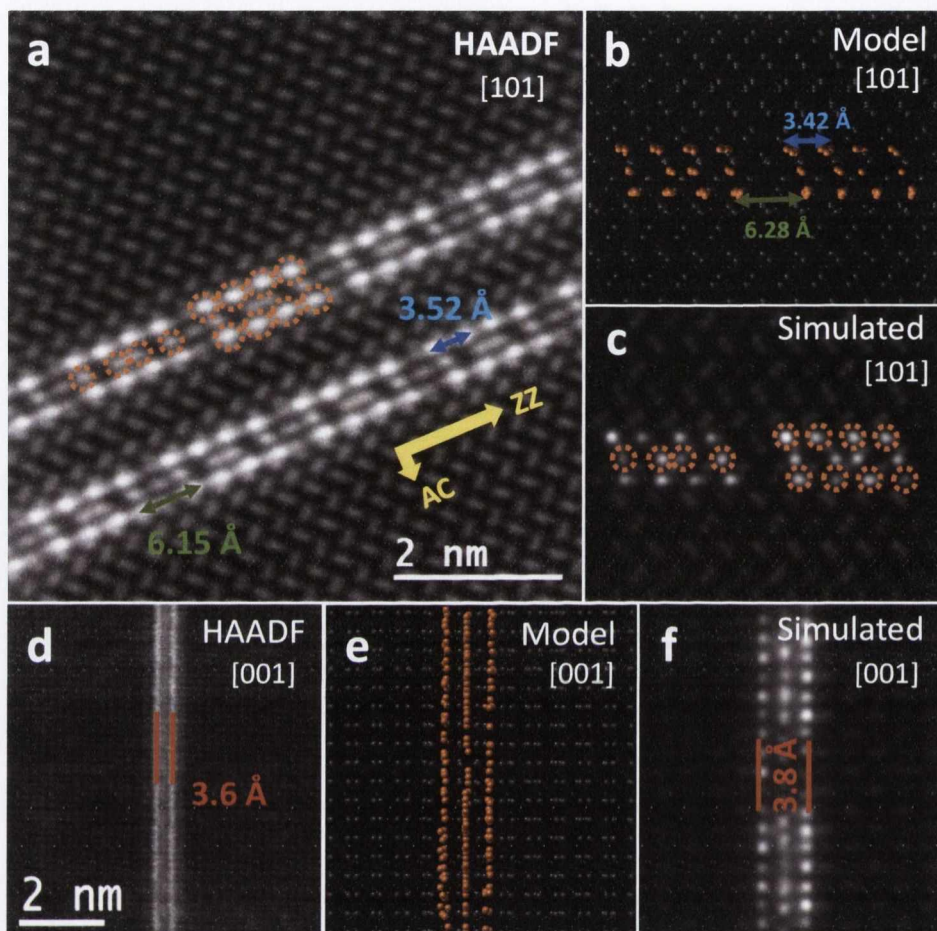


Figure 5.8 (a) Smart Aligned atomic resolution STEM image representing two Cu based wires grown on BP. The orientation of the flake underneath is [101]. The arrows marked in yellow show the flake's orientation - armchair (AC) and zigzag (ZZ). The major intensities marked in orange circles were redundant in the QSTEM image shown in figure 4(c) which was simulated from the model shown in figure 4(b). The micrograph was taken in [001] direction (d) was also compared with the simulated image taken from the model figure (e), showing a good agreement as can be seen from the figure (f). The interatomic distances marked in figure (a) and (d) closely matched with the DFT calculated modelled represented in (b) and (e) respectively (via Crystal Maker). Figure (d) and (f) illustrates the width of the wire calculated to be 3.6 Å and 3.8 Å respectively.

In order to reduce sample beam damage and correct for experimental scanning distortion, a series of fast scanned images (12 images acquired with 1024×1024 pixels and a 10 μs /pixel dwell time) were successively recorded, aligned, non-rigid registered and were averaged following the smart align method.[22] To add further robustness to

the stage-drift, a 90° scan rotation was incremented between the frames during acquisition.[23] Figure 5.8 (a) shows an image of two nanowires grown on BP on its [101] projection after applying such image processing routine. The major intensities of Cu-atoms (dotted circled in figure 5.8 (a)) were then matched with the simulated STEM-image (Figure 5.8 (c)) to find a good agreement.

Also, the interatomic Cu distances calculated in the experimental micrograph in [101] projection (Figure 5.8 (a)) $6.15 \text{ \AA}$ and $3.52 \text{ \AA}$ showed a close match with the DFT calculated model with $6.28 \text{ \AA}$ and $3.42 \text{ \AA}$ respectively (Figure 5.8 (b)). The HAADF image simulated by QSTEM for the [001] projection (Figure 5.10 (f)) showed a straight firm wire structure with a similar width of $3.8 \text{ \AA}$ as compared to $3.6 \text{ \AA}$ in the experimental image (Figure 5.8 (d)). In brief, the simulated [001] projection gives rise to a straight wire, whilst the [101] direction generates a similar periodic structural motif as to the one seen in the experimental STEM images. Figure 5.8 (b) and (e) are models generated using crystal maker software. Further quantitative analyses over the area of interests were conducted by applying statistical estimation theory. The quantified intensity profiles for experimental and simulated images (performed using MULTTEM) gave a close match (Figure 5.10). This demonstrates that the tri-atomic wire-like structures are indeed made of copper phosphide.

5.6 – Counting the Atoms: Quantified STEM and Simulations

A precise knowledge of the thickness or the number of layers is required to simulate the HAADF STEM images obtained experimentally. In order to do so, accurate STEM quantification was performed, wherein imaging was carried out over a calibrated annular dark-field (ADF) detector. In this manner, experimental images can be quantified by a direct comparison with simulated images. Here, image simulations of black phosphorus have been performed by using the MULTTEM software[24], [25]. Source size broadening has been included to incorporate for partial coherence. By using the StatSTEM software[26], statistical parameter estimation theory has been used to model the intensity

distribution of each BP column as a Gaussian peak. Due to the scattering cross-section, the total intensity of electrons scattered by an atomic column, increases monotonically with thickness. The thickness was estimated by matching the experimentally measured values to simulated values of the BP model. For the system in figure 5.9, it was found that, on average, the thickness in both BP regions of images a and b is about 9 unit cells or around 5 nm. By using this specimen thickness, it has been found that the copper penetrates through the full thickness of the sheet, as is shown in figure 5.10 (c).

Using the DFT calculated bilayer structure, aberration-corrected HAADF STEM images were simulated for a 9-unit cell thick BP in the [101] and [001] projections respectively. A 9-unit cell (~5nm) thick model was chosen to match the experimental thickness (figure 5.9). Due to the stacking difference in BP[27]–[29] the copper-based wire forms closely packed structure with increasing number of BP layers.

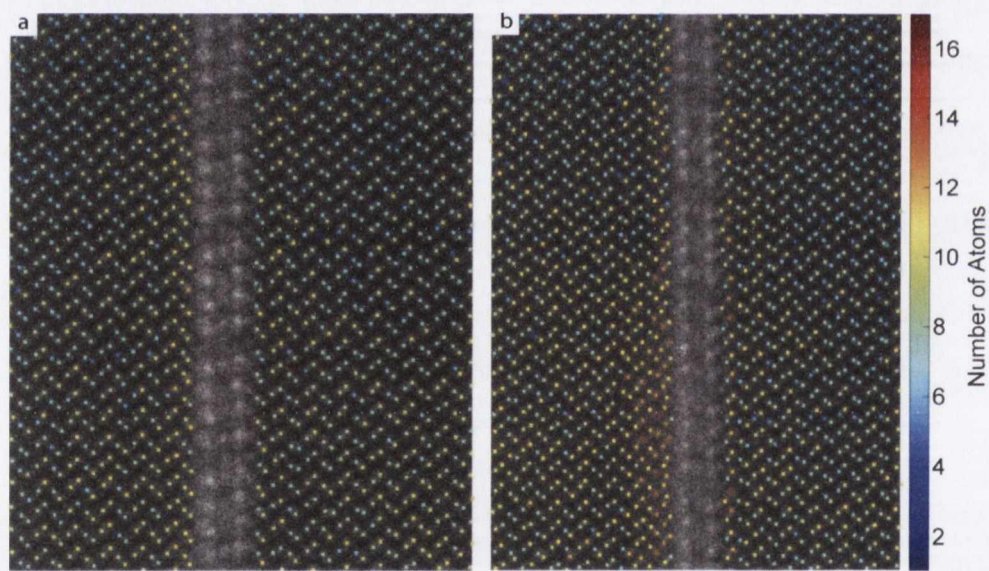


Figure 5.9 STEM quantification performed over a Cu//BP flake in its [101] direction.

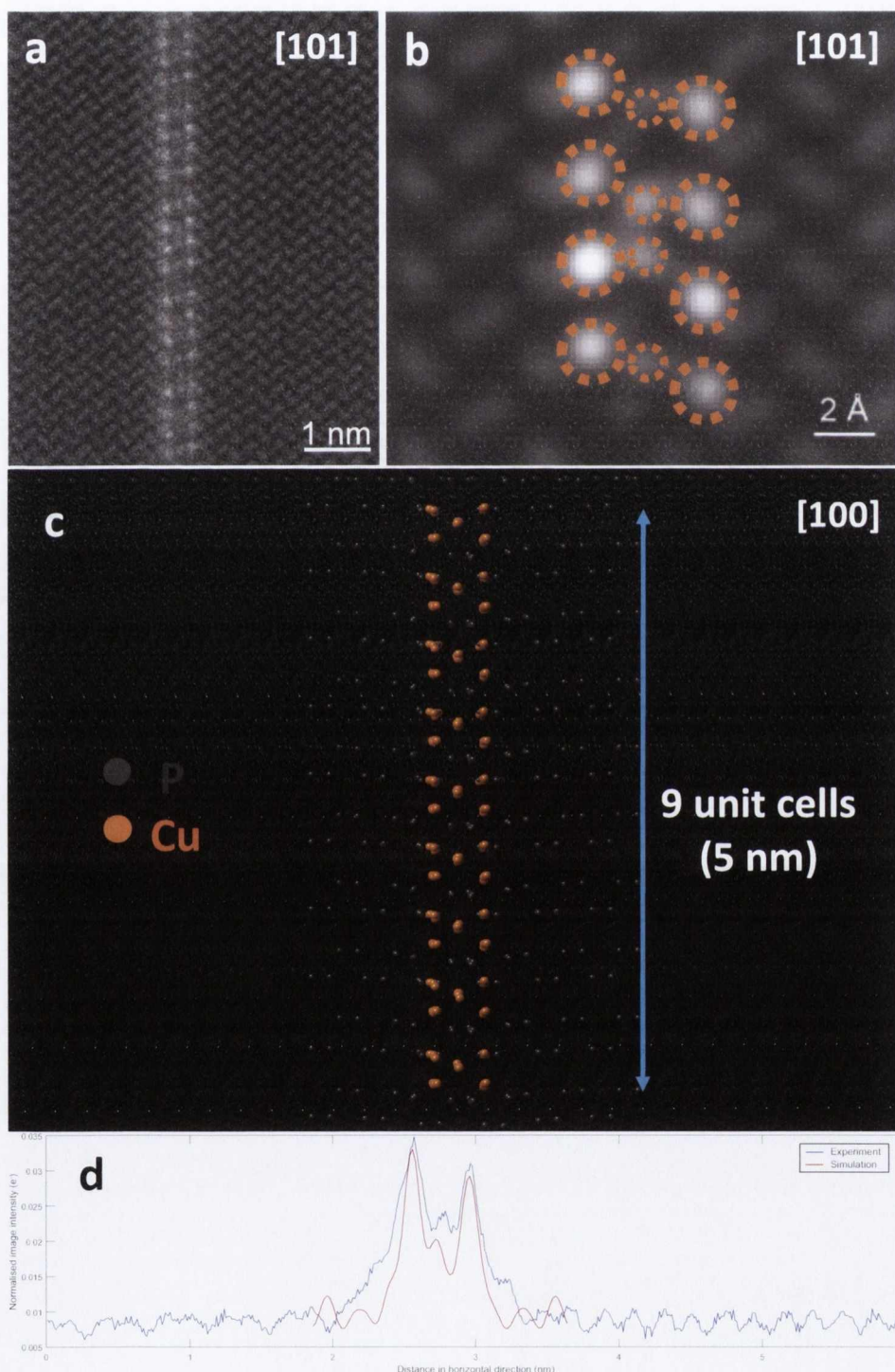


Figure 5.10 (a) represents the region over which experimental STEM quantification was performed in [101] projection. (b) is the simulated STEM image obtained via MULTTEM using the DFT calculated model. (c) represents the cross-section of the BP-Cu wires in [100] projection indicating wire penetrates through the structure of BP having ~ 5 nm thickness). The intensity profile shown in (d) showed a good match between experimental (blue plot) and simulated (red plot) images.

The uninterrupted wire structure at the flake step edges is only possible if the Cu is interstitially coordinated. This was the key information (with precise thickness measurement) in enabling us to perform quantitative image simulation. Also, the question whether the copper penetrates through the full thickness of the sheet or not was of significant importance. This demanded further quantified STEM simulations over the wires using MULTTEM[24]. Here, the mean image intensity of the experimental image, shown in figure 5.10 (a), has been directly compared to the mean intensity of the simulated image[24], shown in figure 5.10 (b), where the DFT model has been used as an input for the atom positions. In this simulation, 9 unit cells were stacked (figure 5.10 (c)). Comparing the experimental and simulated image intensities shown in figure 5.10 (d) indicates that the Cu wire penetrated through the whole P flake. The residual deviations arise from additional diffuse (Huang) scattering by static disorder due to the different atomic radii of Cu and P and the interstitial positions of Cu.

5.7 – Summary of the findings

In this chapter, the Cu 1D structure was investigated using a quantitative approach in the aberration-corrected STEM, and DFT calculations backed with image simulations. Here we can describe for the first time how chemical anisotropy in BP enabled the fabrication of atomically-thin (3.6 Å in width), highly-directional 1D Cu structures by a very simple and reproducible approach. The growth method is extremely simple and controllable as discussed in the next chapter.

With the help of spectroscopy (EELS and XPS), the Cu peak was not found to be associated with pure metal, and the oxidation state of Cu varied across the wire. By using atomically resolved HAADF imaging, EELS and image simulations it was demonstrated that the wire structure to be composed of copper phosphide. Copper Phosphide is a semiconductor and can be used as FET (field effect transistors) and also in batteries.[30], [31] The minimum distance between two parallel wires grown in BP was found to be 1 nm which is remarkable in designing semiconductor heterojunctions.

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Chapter 6

Exploring the Future of Integrated Circuits

“Moore’s law is really a thing about human activity, it’s about vision, it’s about what you’re allowed to believe. Because people are really limited by their beliefs, they limit themselves by what they allow themselves to believe about what is possible”.

... Carver Mead

6.1 – BP in Semiconducting Industry

In the previous chapter, black phosphorus and copper interactions were well characterized by the use of TEM; aberration corrected STEM and first principle calculations followed by simulations. The ultimate electrical properties of these novel systems are yet to be characterized. BP has already shown promising future in the semiconducting industry[1][2]. The application of Cu₃P wire grating over 2D BP system will be far more interesting. In this chapter, we discuss very preliminary in-situ SEM and TEM electrical measurements on these novel systems.

In past decade, the electronic device community has been attracted towards 2D materials. While graphene transistors are still on the agenda, work has been extended towards other materials such as MoS₂, boron nitrides, heterostructures etc.[3]–[5] The prospects of the 2D materials are controversially debated and thought to be for academic purposes rather than applying them into the real world. Defects, durability and contact resistance are major hurdles which need to be taken seriously in the semiconducting industry. However, we cannot just give away their remarkable applications in the field of flexible electronics, 2D transistors, digital logic gates that has been demonstrated by the two-dimensional nano-sheets.[6]–[10]

The work here discussed is very preliminary and substantial amount of work is still needed to understand the ultimate electrical properties conclusively. Interaction of BP-Cu as discussed in the previous chapter has predicted to have an ohmic contact[11], not to forget the reduced degradation effect seen in chapter 4. This will be perfect for the semiconductor world to explore nanoelectronic devices which are 2D. Unfortunately, the electrical analyses presented in this chapter is not conclusive. The shear feature size of the wire makes it close to impossible to characterize by conventional device fabrication procedure. Nonetheless, controlled growth of Cu based wires was proved successfully by using conventional lithography technique and selectively positioning of Cu-based wires by placing Cu nanoparticles using micromechanical manipulator. In future, the application of a single tri atomic Cu based wire should be explored.

6.2 – In-situ Electrical measurement using SEM

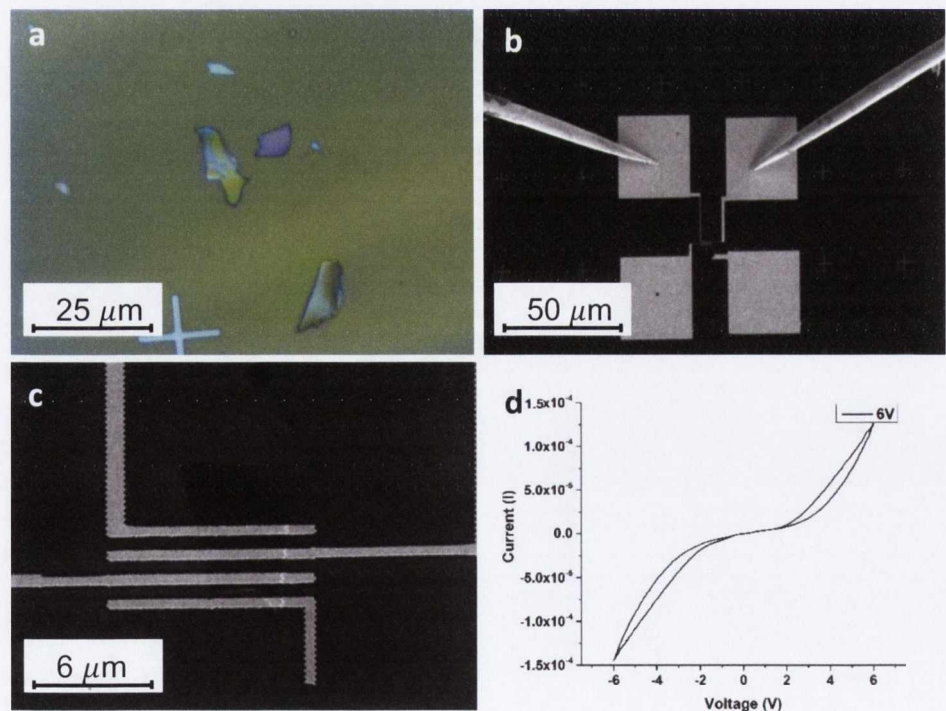


Figure 6.1 (a) shows the optical image of the selected BP nanosheets (purple colour). Figure (b) shows four contact pads (Ti/Au) with two probe needles inside SEM. The I/V curve measurement done over pristine BP in figure (c) is plotted in figure (d).

BP devices have been well studied by conventional electrical measurement techniques[2], [12]. However, as mentioned previously, it is impossible to view the wire structure formation without the TEM and SEM (with some level of difficulty). Doing in-situ electrical measurement using e-beam is also not straightforward due to electron beam induced current which needs to be taken into consideration.[13]

In this experiment, initially a pristine BP (as a controlled device) was exfoliated over the Si wafer, and a device (for two probe measurement) was fabricated using the technique described in Chapter 2 (Section 2.6) including the measurements carried out inside SEM. Figure 6.1 (a) shows optical micrographs of the BP flake under investigation (purple colour). Figure (b) shows the micromanipulator used to do the measurements followed by the four contacts (c). The middle two contacts were used to supply the voltages depicted in figure (c). The I/V curves is shown in figure (d) which gave a typical semiconducting response for a sweep from -6V to +6V.

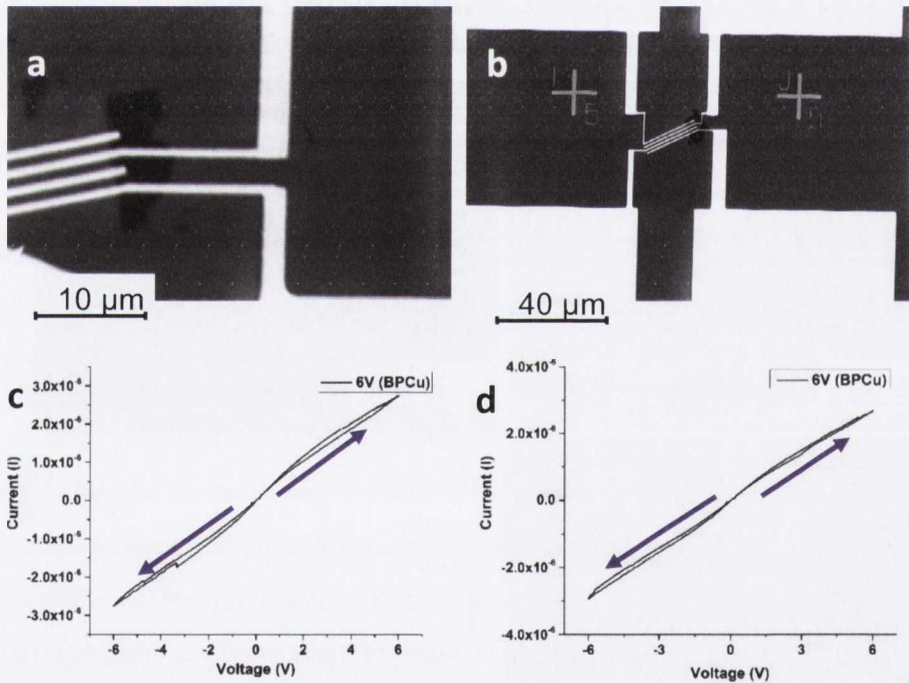


Figure 6.2 Cu treated BP sample electrical measurement over the nanosheet shown in (a) and (b) with their respective electrical measurements in (c) and (d).

The results were then compared with the Cu treated BP device by annealing (160 °C) the flakes with Cu nanoparticles for 5 min. Two devices were fabricated on the Si wafer as

shown in figure 6.2 (a) and (b). The respective results (c) and (d) showed improved performance as seen from the reduced hysteresis. However, the results are not conclusive as the measurements are not done on the same device. The carrier mobility of BP is highly dependent on the number of layers, channel length and due to mobility anisotropy.[14], [15]

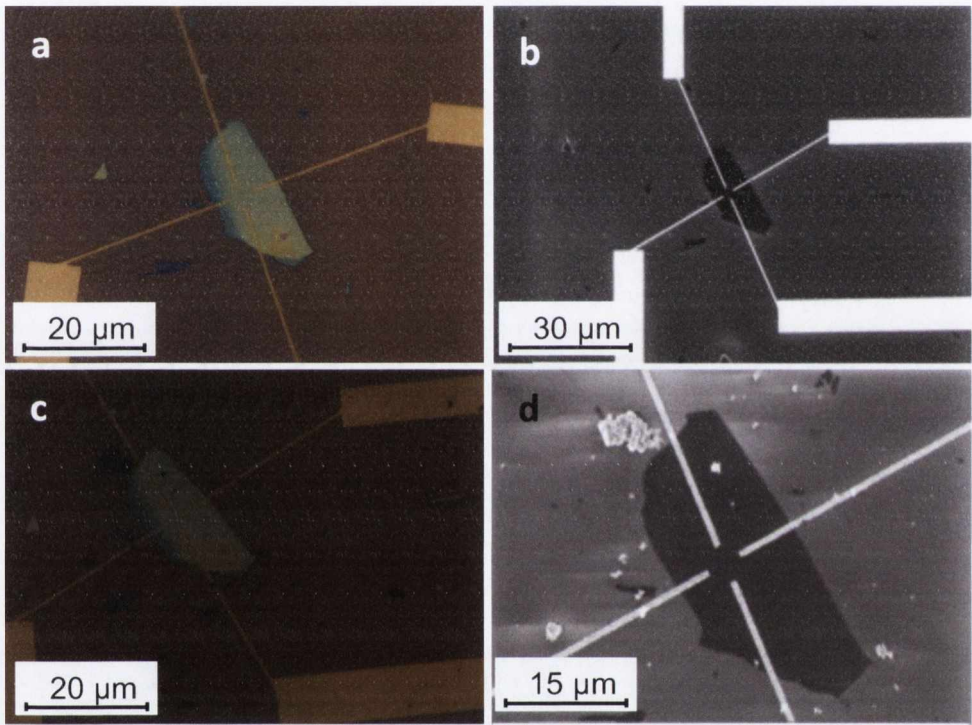


Figure 6.3 Optical and SEM micrographs of the BP nanosheet shown in (a) and (b) followed by Cu treatment by drop casting Cu nanoparticles and heating in (c) and (d) respectively. The electrical measurements on the pristine and Cu treated BP is illustrated in figure 6.4.

To investigate this further, device performance was characterized on the same device before and after the Cu treatment. Similar pristine BP device was fabricated with the procedure mentioned before. Figure 6.3 (a and b) are images taken by optical microscope and SEM of pristine BP respectively. Cu nanoparticles were then drop-cast over the flakes and heated at 160 °C for 5 min. (as seen in figure 6.3 (c) and (d)). The electrical measurements were done on different contact pads combinations as illustrated in figure 6.4 (g) with corresponding I/V curves shown from the figure (a) to (f). The Cu

treated BP did perform well delivering more current due to a reduction in hysteresis (blue curves).

To get a better idea of the conductance change in the sample (before and after Cu treatment), measurement of sheet resistance was necessary. For a two-probe measurement case we will first define resistivity (ρ) as given by the following equation;

$$\rho = \frac{R A}{l} \tag{6.1}$$

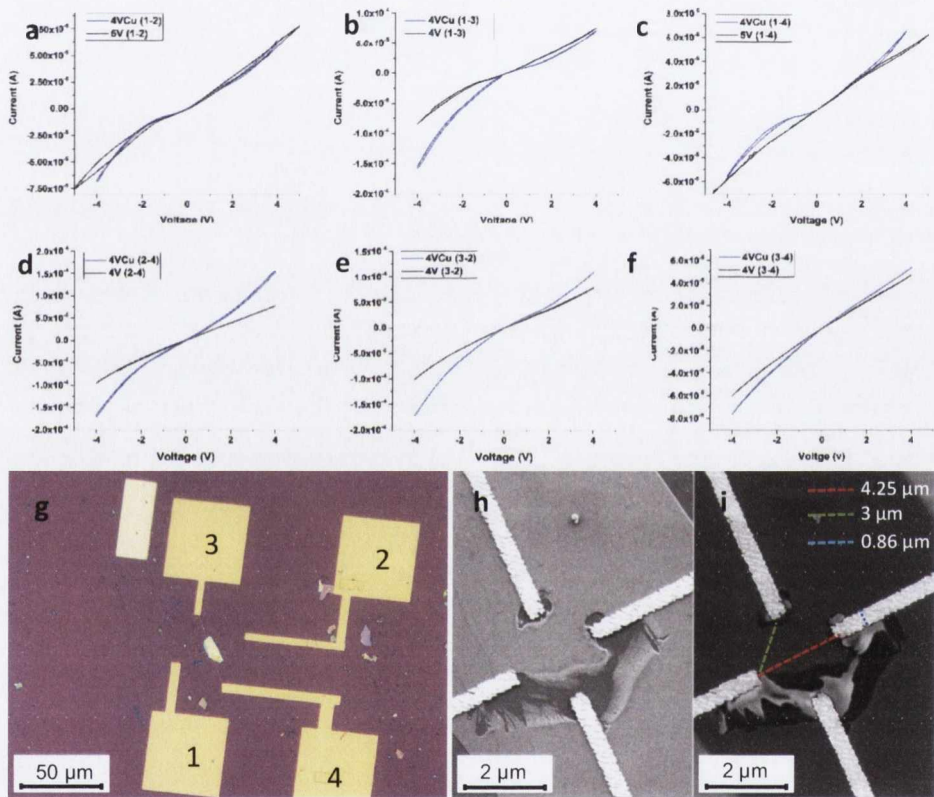


Figure 6.4 (a) to (f) represents the I/V curves taken over different contact pads marked in figure (g). Figure (h) and (i) illustrates damaged device seen via secondary electron and in-lens detector respectively. The red, green and blue dotted lines in figure (i) illustrates respective distances for the sheet resistance measurements.

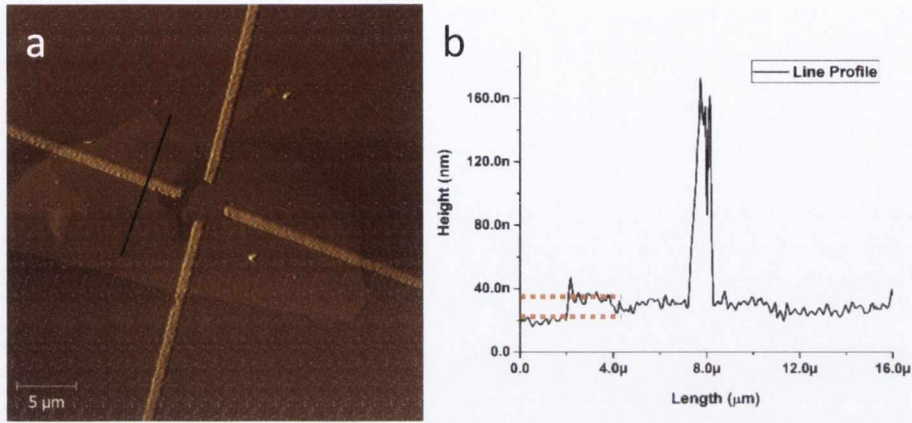


Figure 6.41 (a) AFM image with a line profile (b) taken from the black line denoted in (a). The dotted orange line in (b) is the profile average taken to calculate the flake thickness which is ~ 15 nm.

where, R = Resistance (V/I), A = Area and l = Channel Length.

So, area 'A' will be the width of the contacts in this case 860 nm (figure 6.4 (i) blue dotted line) and the thickness of the sample (t). However, since sheet resistance is given by $R_s = \rho/t$, the final equation is;

$$R_s = \frac{RW}{l} \quad 6.2$$

Here the channel length depends on which contacts we want to measure. It will be either $4.25 \mu\text{m}$ (for contacts 1-2 and 3-4) or $3 \mu\text{m}$ (for contacts 1-3, 3-2, 2,4 and 4-1). The width will be fixed to 860 nm for all calculations. Taking the average V (Voltage) and I (Current) values in each graph, sheet resistance was obtained as following;

- Figure 6.4 (a);

Untreated - For 5V sweep between contacts (1-2): $80.66 \text{ k } \Omega$

Treated - For 4V sweep between contacts (1-2): $58.73 \text{ k } \Omega$

- Figure 6.4 (b);

Untreated - For 4V sweep between contacts (1-3): $63.15 \text{ k } \Omega$

Treated - For 4V sweep between contacts (1-3): $37.12 \text{ k } \Omega$

- Figure 6.4 (c);

Untreated - For 5V sweep between contacts (1-4): 76.03 k Ω

Treated - For 4V sweep between contacts (1-4): 80.79 k Ω

- Figure 6.4 (d);

Untreated - For 4V sweep between contacts (2-4): 49.66 k Ω

Treated - For 4V sweep between contacts (2-4): 21.45 k Ω

- Figure 6.4 (e);

Untreated - For 4V sweep between contacts (3-2): 50.79 k Ω

Treated - For 4V sweep between contacts (3-2): 36.75 k Ω

- Figure 6.4 (f);

Untreated - For 4V sweep between contacts (3-4): 77.4 k Ω

Treated - For 4V sweep between contacts (3-4): 64.48 k Ω

As seen from the sheet resistance measurement, the resistance decreases after Cu treatment (termed as Treated above). Except for the figure 6.4 (c) where there is a slight increase. This can be due to different sweep voltages used. Nonetheless, this is not conclusive as even though the measurements are done on the same device the annealing effect over the nanosheets cannot be ignored. Also, the Cu wire formation was not observed as in the case of figure 6.5 (b). This does not rule out the Cu presence as the Cu diffusion in SEM is visible only when it is in excess. Knowing the nanosheet orientation (seeing the Cu wire growth) is also important to interpret the results due to anisotropy in carrier charge mobility in BP.

The measurements inside the SEM also have issues of sample discharge which led to flake damage across the Ti/Au contacts figure 6.4 (h) and (i) using the secondary electron detector (SED) and in-lens detector respectively. Fortunately, this occurred after the measurements were taken. The thickness of the BP nanosheet was found to be ~ 15 nm which is around 25 unit cells.[16] The AFM carried out over the device is shown in figure 6.41 (a) with its corresponding line profile in (b).

6.2.1 Control Seeding by EBL and Discharge Issue

To control the seeding of the Cu on BP nanosheets, rather than randomly drop casting the Cu nanoparticles, two-step e-beam lithography was performed. In the first step, Ti/Au contacts were deposited by e-beam evaporator followed by four Cu squares using the sputter coater. The Cu pads (Figure 6.5 (a)) further enhanced electron discharge (Figure 6.5 (b)) followed by deterioration of the device. This included contacts being vaporized as seen in figure 6.5 (d). To tackle the discharge problem, electron transmission technique was taken into account. This approach would possibly nullify the electron charging issues faced in the scanning technique.

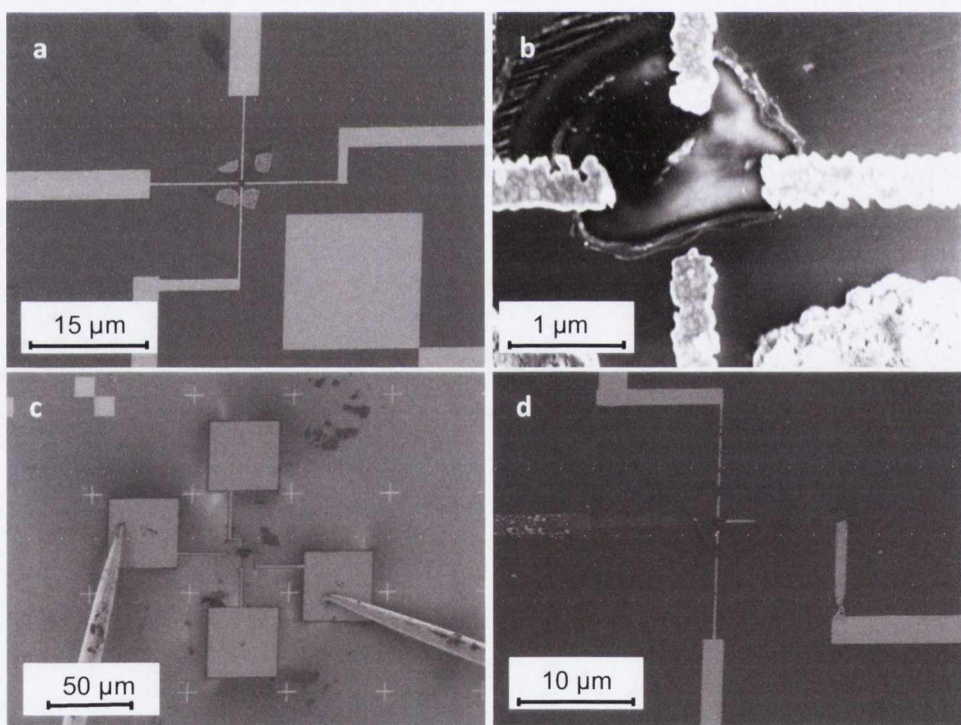


Figure 6.5 (a) shows nanosheet over which controlled Cu has been deposited using e-beam lithography. The discharging problem is seen in (b). Figure (c) illustrates another pristine BP showing similar discharging problem under the electron beam.

6.3 – In-situ electrical measurement using TEM

To avoid the discharge issues in SEM, in-situ electrical measurements were performed inside TEM using the MEMS heating chip provided by DENS solutions. Since the chip and holder (DENS Wildfire) is for heating experiments only, the MEMS chip was modified to carry out the electrical measurements. This is mentioned in the section 2.6.2 in Chapter 2. The MEMS chip was first tested inside SEM as illustrated in figure 6.6 for proper functioning contacts. The device performance was not as good as the previous once due to FIB-deposited Pt. contact and increased channel length.

The MEMS chip was then inserted into TEM using the DENS Wildfire holder. As can be seen from the figure 6.7 (b), the I/V curve over the MEMS chip showing better performance due to high vacuum inside the TEM column. Before and after the electrical measurements the contacts were intact (Figure 6.7 (a) and (c)). However, after the chip was heated to 160 °C (ex-situ over the hot plate for 5 min) the contacts were broken.

6.3.1 Testing with Pt deposition

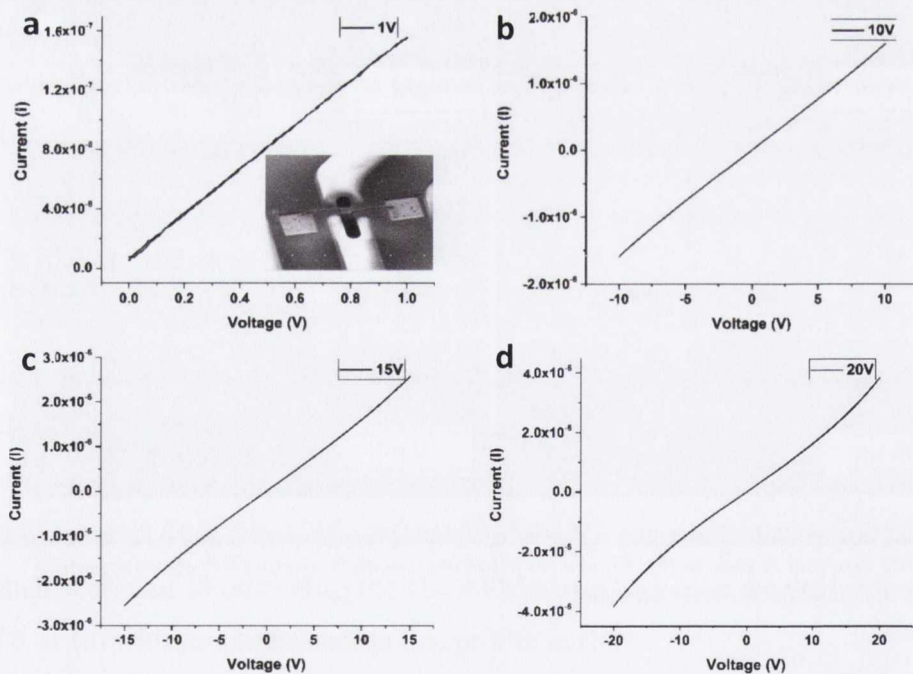


Figure 6.6 I/V curves taken in SEM over the device shown in the inset (a) for different voltages from 1V to 20 V (a to d) respectively.

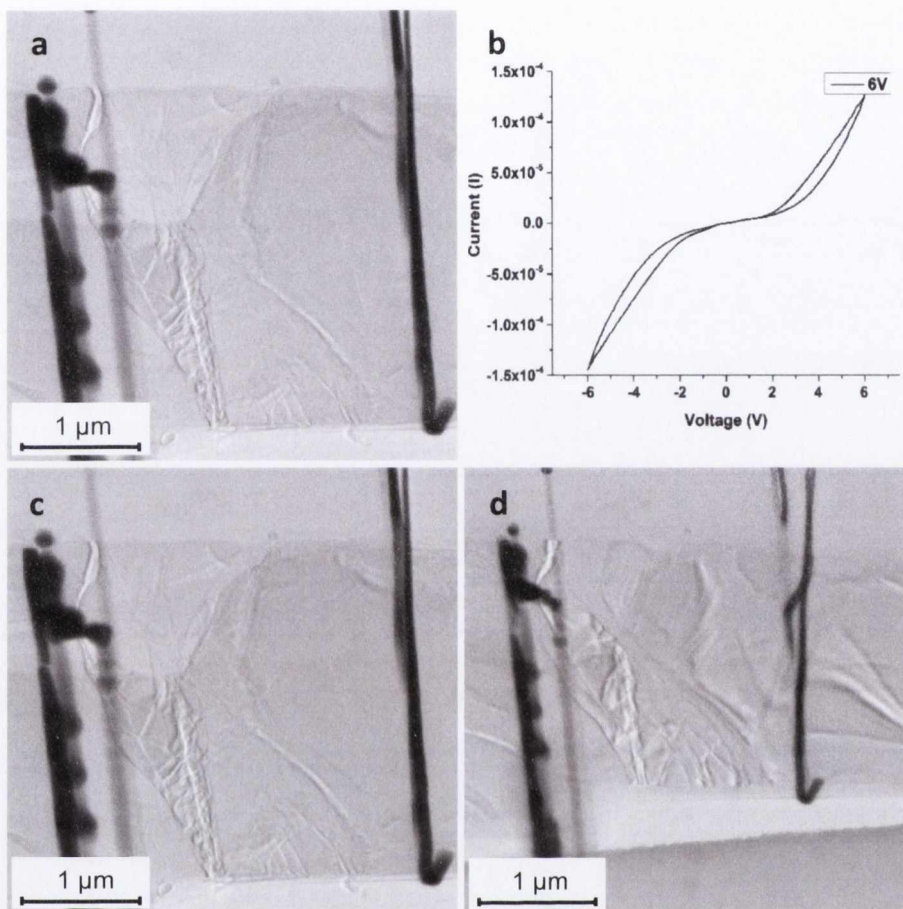


Figure 6.7 (a) showing TEM image of a nanosheet with two Pt contacts by e beam deposition before any electrical measurements. (b) shows a typical I/V curve for the 6V voltage applied. (c) shows TEM image after electrical measurement with no damage done. Figure (d) shows broken contact (right) after 160 $^{\circ}\text{C}$ annealing over a hot plate.

6.3.2 In-situ Probing of Chemical Nature

Besides the fabrication technique, the essence of the material behaviour during switching or conducting is still a research focus. Many mechanisms are playing a role in the interface barrier change,[17][18][19] redox reaction,[20] Joule heat effect,[21] surface plasmons,[22] polaron ordering and melting model.[23] As a result, there are also intrinsic physical changes occurring due to the external electric field. The element

species also changes from one state to another, and the recovery of the state is possible by applying proper external field.

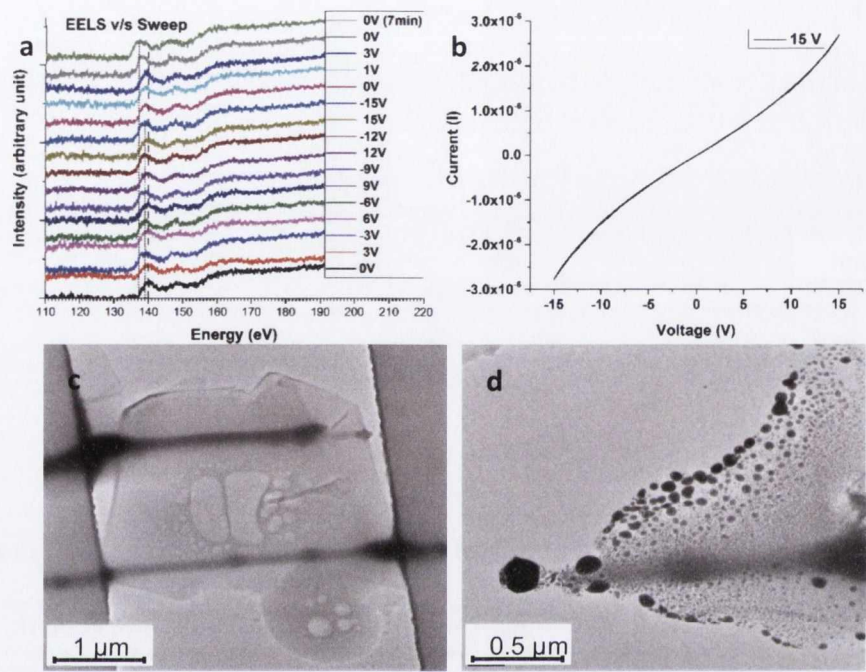


Figure 6.8 (a) EELS plot with respective sweep from -15V – 0 – -15V shown in (b). Device degradation is seen in figure (c) and further applying the voltage the device degrades completely with Pt particle formation.

To investigate this in-situ EELS analyses were performed over the electric sweep from +/- 15V (Figure 6.8 (b)). The core loss analyses were carried over 'P' L-edge with simultaneous sweep in succession with an interval of 3V (Figure 6.8 (a)). It is observed that the 'P' L edge shifts to higher energy during positive voltage and vice versa for negative values indicating that it goes under reduction for positive voltage. It will be also helpful to simultaneously probe the O K edge in the future.

The contacts were made by depositing Pt-C by FIB and the device did not survive for long causing it to disintegrate (Figure 6.8 (c)). As more current was passed via the BP the contacts got melted forming into small Pt nanoparticles.

6.3.3 Testing with Sputtering and e-beam evaporation

Since the contacts deposited by FIB Pt deposition does not yield proper adhesion, this method is not ideal for heating and electrical measurements

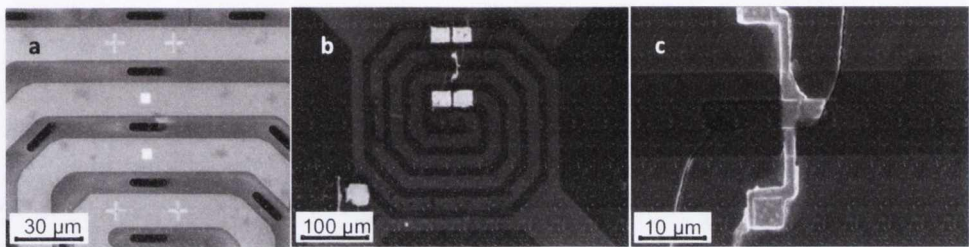


Figure 6.9 SEM image of the heating MEMS chip with four cross markers for lithography reference (a). (b) shows Cu metal deposited by sputter coating. (c) shows over deposition of Cu due to which the film was broken.

Following similar lithography procedure, the contacts (using Pd/Au target) were deposited over MEMS chip by sputtering. This method failed due to the poor accuracy of the sputter coater layer deposition. The deposited metal was also contained big grain boundaries and poor adhesion. The sputtering of metal over MEMS chip usually lead to window damage (Figure 6.9 (c)).

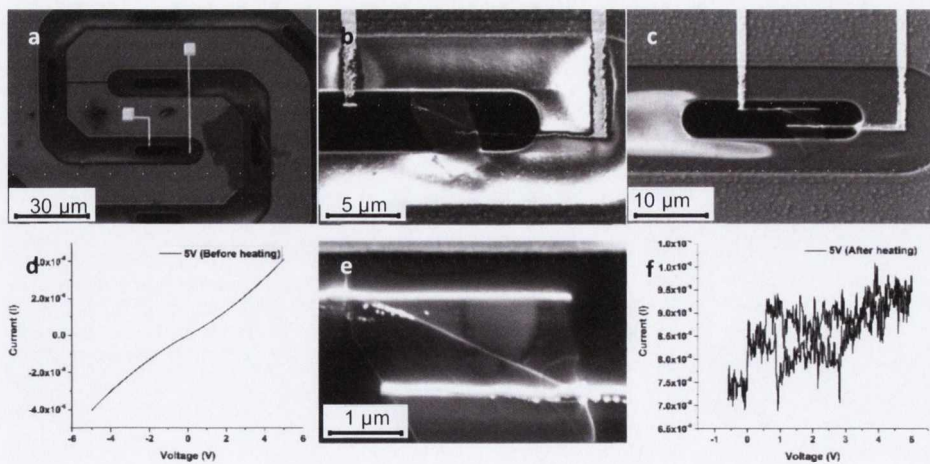


Figure 6.10 Equivalent Cu deposition by e-beam evaporation (a). (b) shows inconsistent deposition of Cu metal over SiN layer window. Pt deposited via electron beam in FIB system as shown in (c) with respective electrical measurement shown in (d) in SEM. (e) shows degradation of the device with respective dead signal illustrated in (f).

Finally, e-beam evaporation was implemented which precisely deposits desired metal thickness (Figure 6.10 (a)). However, due to poor backscattering of electrons at the transparent windows, the region was underexposed leading to less metal deposition (Figure 6.10 (b) and (c)). Pt was then deposited using FIB technique over the windows region only. The technique developed did work for TEM analyses (Figure 6.10 (d)) but due to many fabrication steps and prolonged exposure to the ambient environment, the device quickly degraded as seen in the figure 6.10 (e) and (f).

To make the electrical contacts one-step process, different dose tests were applied over the MEMS chip to verify the appropriate electron dose for EBL over the MEMS chip. Different magnification dose regions are shown in the figure 6.11 (a) to (c). It was found that any dose between 150 to 1000 $\mu\text{C}/\text{cm}^2$ works perfectly. Any dose less than 100 $\mu\text{C}/\text{cm}^2$ leads to the SiN region being underexposed and improper metal adhesion (Figure 6.11 (d)). To standardize the procedure, it needs further experimental work.

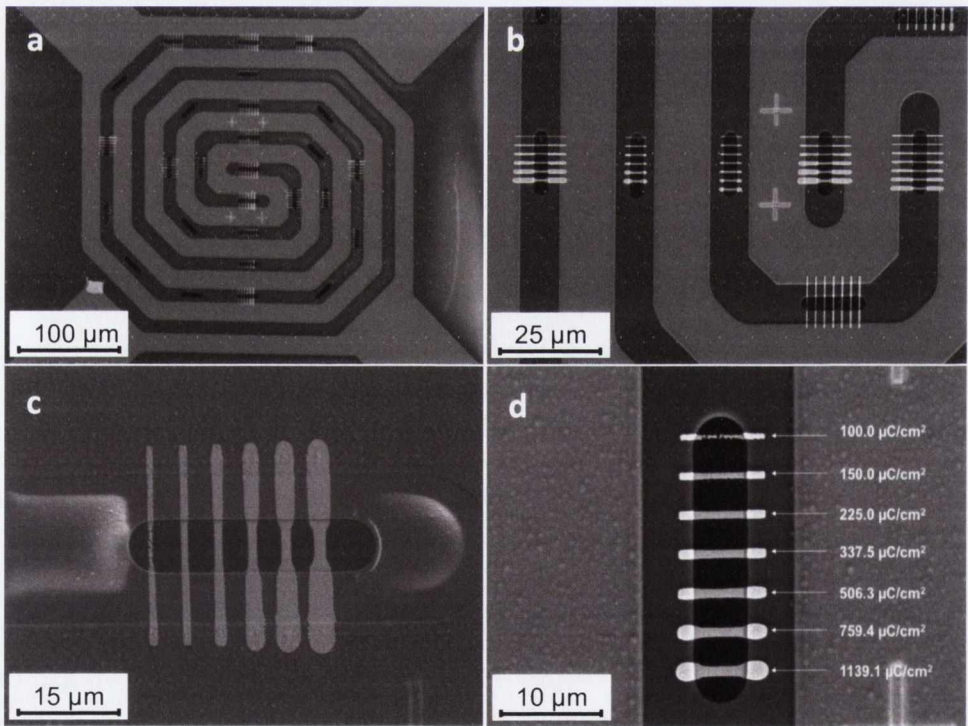


Figure 6.11 Dose test performed for the MEMS chip SiN window (a). Different electron dose deposition shown in (b) with a zoomed in area (c). (d) figure with the electron dose values.

6.4 – Controlled Templated growth of Wires

6.4.1 Microprobe Manipulator

Finally, we worked towards demonstrating that the self-assembly can indeed be controllably grown from certain BP areas. Controlled seeding of Cu was achieved by undertaking two different, nonetheless equally successful, approaches. In the first approach, Cu nanoparticles were drop-cast on a SEM stub and then lifted by Coulomb interaction using a fine needle in our focused ion beam (FIB) system. In this way, we can easily transfer these particles over exfoliated BP flakes deposited on a Silicon wafer. Cu atoms can then be diffused by simply heating the system as discussed above (Figure 6.12). Using a micromechanical manipulator controlled by Kleindiek system, a fine needle (by Picoprobe) was used (as seen in figure 6.12 (a)). This was performed in a Carl Zeiss Auriga FIB system operated at 5 kV. The Cu nanoparticles drop cast over Si-wafer were lifted by Coulomb interaction between the particles and the needle (Figure 6.12(b)). This was then transferred onto another Si-wafer with the mechanically exfoliated BP (Figure 6.12(c)). The Si wafer was then heated at 300 °C for 5 minutes on a hot plate. The Copper interaction with BP can be noted in the figure 6.14 (d).

The second methodology proved to be even more straightforward. This involved first exfoliating the BP nanosheets and transferring them onto a Silicon wafer, followed by lithography and deposition of copper by e-beam metal evaporation and thermal heating (Figure 6.13).

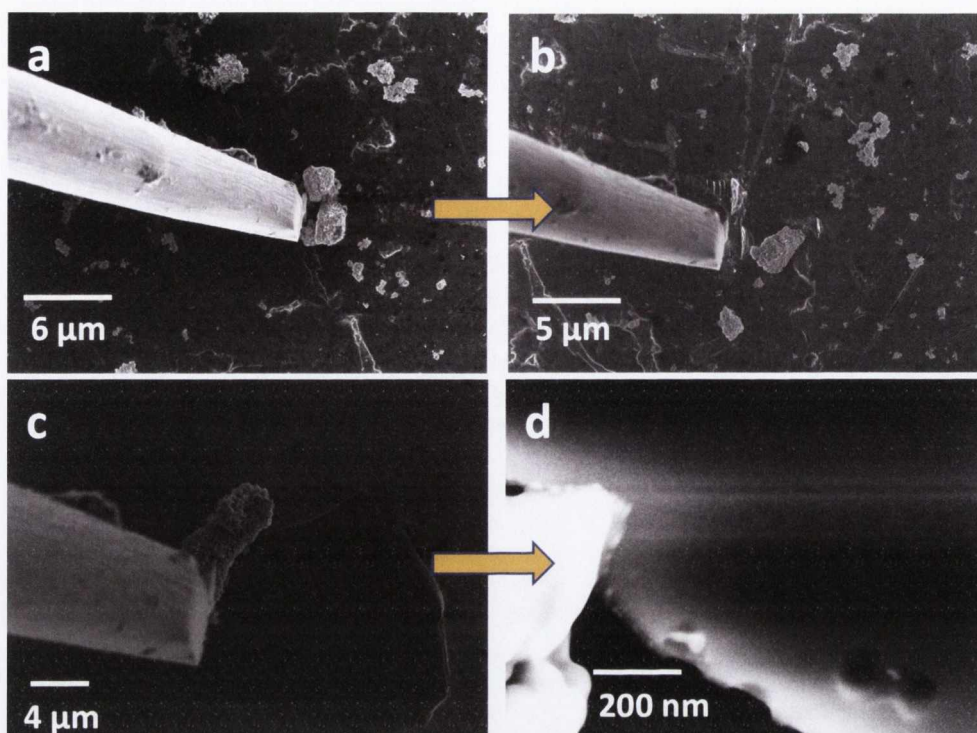


Figure 6.12 Selective placement of Cu nanoparticles onto a BP flakes using a needle. (a) and (b) show the copper nanoparticles drop-casted onto a SEM Al stub; these are successively lifted using a needle and dropped onto an exfoliated BP flake deposited on Si wafer (c). The agglomerated particles over the BP in (c) were then moved by the needle so that only a tiny part becomes attached to the nanosheet edge (d).

6.4.2 E-Beam Lithography

To demonstrate the feasibility of growing wires controllably on certain BP areas only, we used e-beam lithography to deposit Cu islands on the nanosheets selectively. This method consisted of exfoliating the BP nanosheets and transferring them onto a silicon wafer, followed by lithography, copper deposition by e-beam metal evaporation and thermal heating.

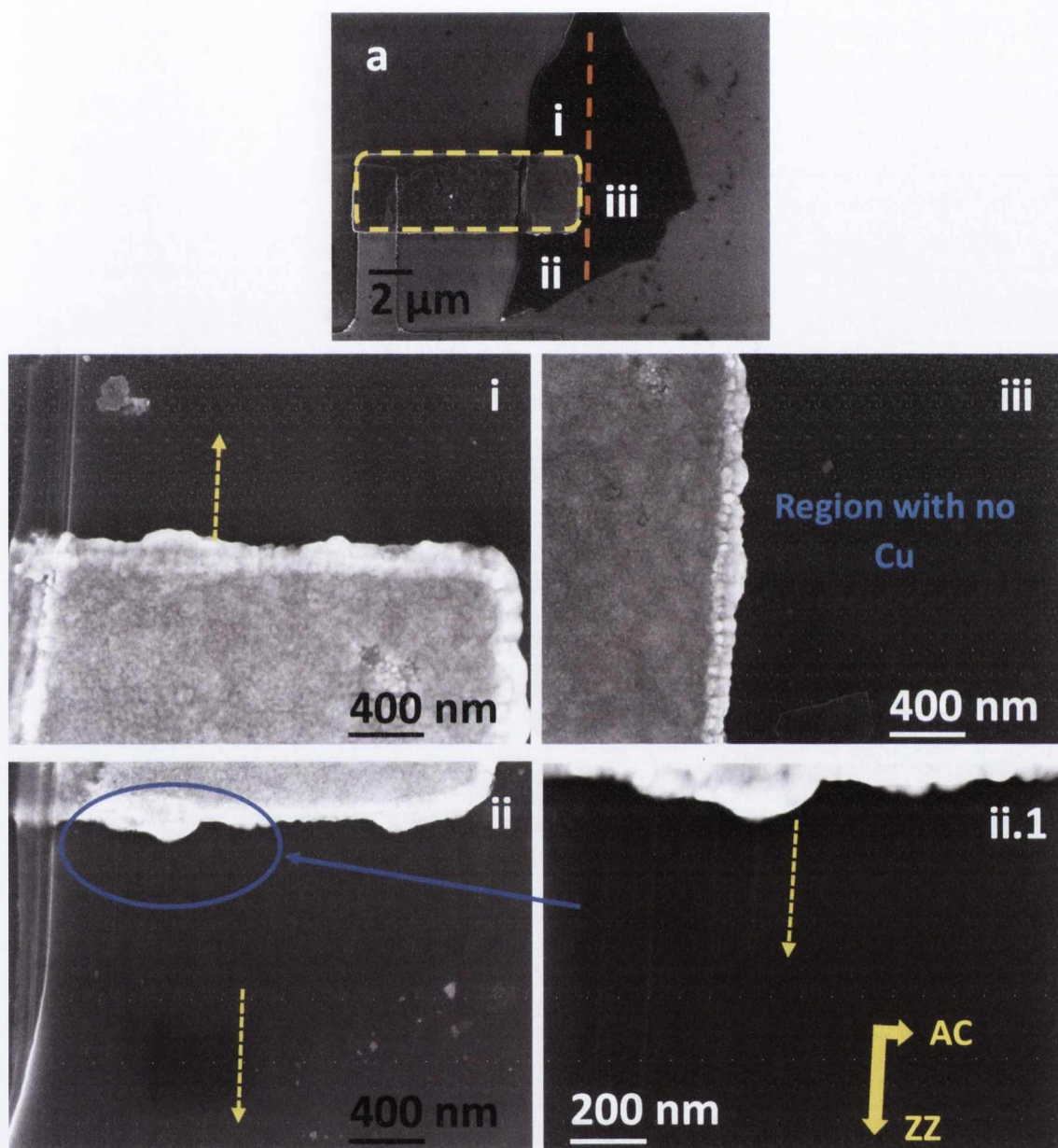


Figure 6.13 SEM images (in-lens detector) of electron beam lithography (EBL) carried out on a BP flake (a). Only the (i) and (ii) regions show Cu wires, whereas (iii) has no Cu wire formation. The region marked in the yellow dotted rectangle is the 60 nm copper deposited in Figure (a). The orange dotted line separates out the regions containing copper and pristine BP – (i/iii) and (ii) respectively. Figure (iii.1) is the magnified region marked in blue circle in (ii).

As can be seen from figure 6.13, the wires formed only at the region where the copper was deposited. The wafer was heated on a hot plate to 300 °C for 3 min and was imaged by Scanning Electron Microscopy. The yellow marked rectangle in figure 6.13 (a) shows

60 nm Cu deposited (by Temescal) using EBL (e-beam lithography) over a multilayer BP. SEM confirms the growth of Cu wires only in selected regions (i) and (ii) whereas no Cu wire presence in (iii). Being aware of the fact that the wire growth happens in channels along (010) direction, understanding the growth mechanism has enabled us to identify the orientation of the BP flake. By simply looking at the wire growth direction using SEM, marked as AC (Armchair) and ZZ (Zigzag) direction as shown in figure 6.13 (ii.1) (also refer figure 6.15 (c)). Figure (ii.1) shows the magnified view of the region marked in the blue circle. In figure 6.13 region (i) and (ii) shows Cu wire presence marked in yellow arrows. Whereas region (iii) does not show any Cu presence. This is also further proved by performing EDX (Figure 6.14). There was no Cu presence in the region (iii). The interaction between BP-Cu can also be viewed just under an optical microscope as shown in figure 6.15 (a) and (b). Using EBL, when copper is deposited over BP by the metal evaporator, the BP-Cu interface turns darker after heating the Si wafer chip at $\sim 300^{\circ}\text{C}$ for 3min. This implies that it is not only the Cu which diffuses into phosphorene layers but even the phosphorus can have diffused into Cu metal. Further investigation is needed into this exchange interaction.

In both methods, we have achieved controlled growth solely from the BP nanosheet areas where the copper had been deposited. The proved controllable growth of these Cu atoms in BP flakes is of crucial importance, enabling the development of some real applications.

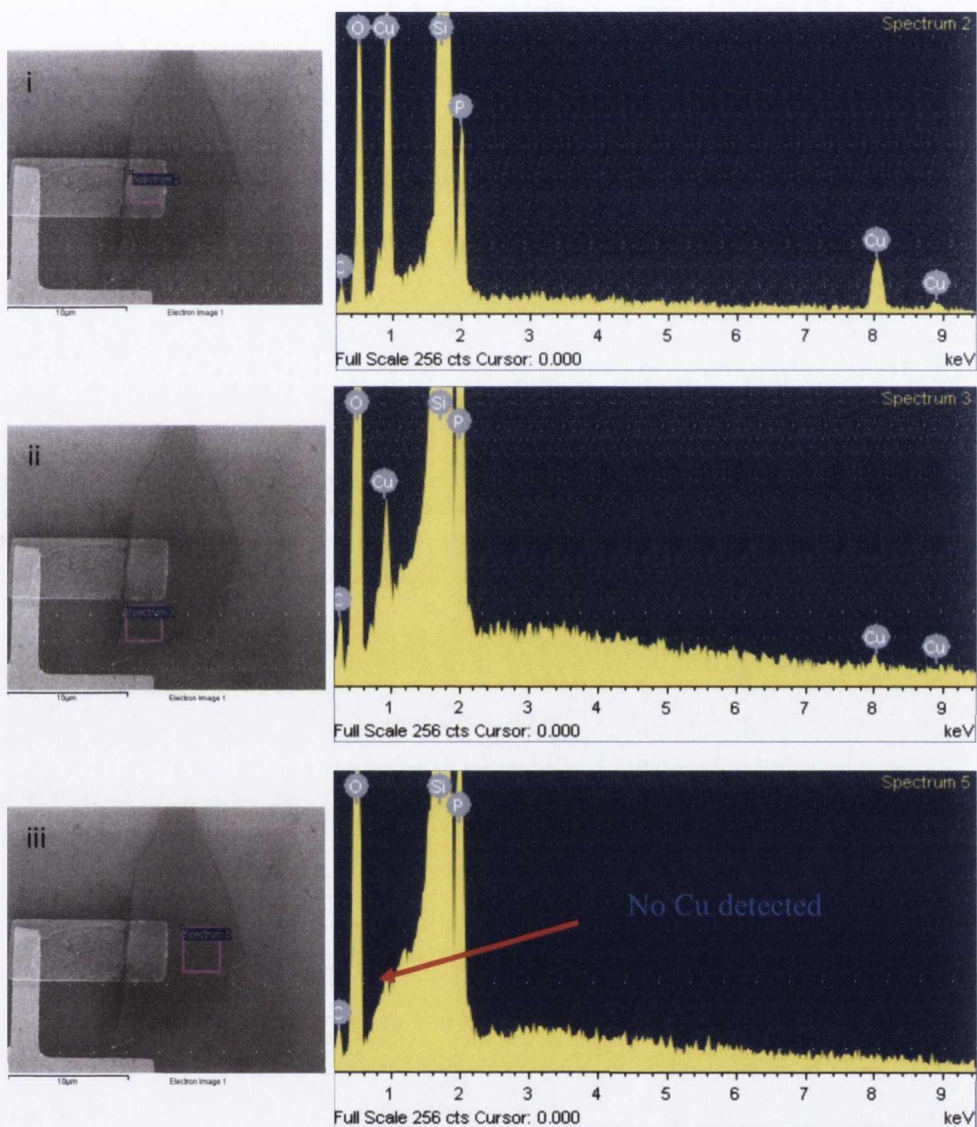


Figure 6.14 EDX acquired over the regions shown in figure 6.13, showing no presence of Cu in the region (iii) indicated by red arrow. All the right plots represent EDX taken from the respective left regions marked with rectangle.

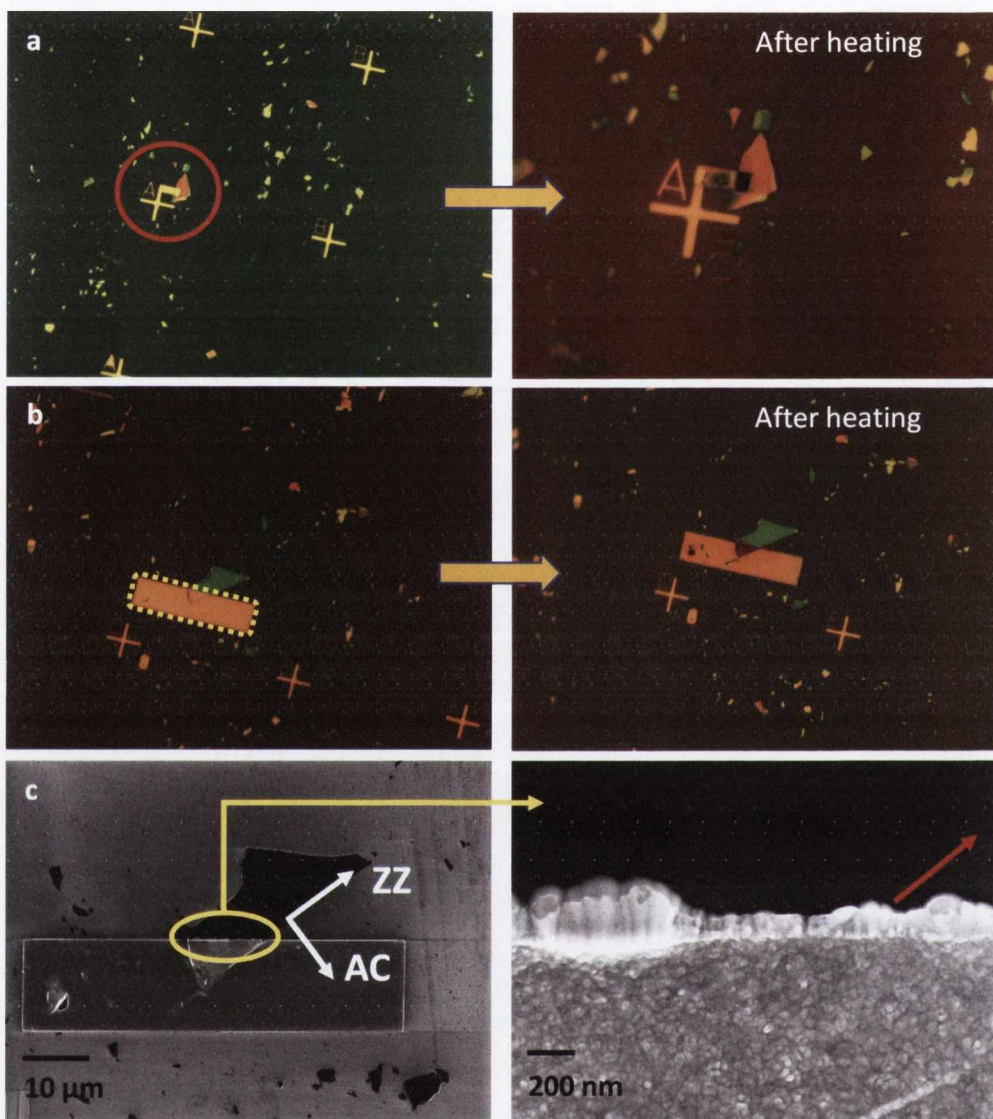


Figure 6.15 Optical image (a) of the EBL performed shown in figure 6.13 and 6.14. (b) an optical image and (c) its SEM image taken with an in-lens detector, representing the orientation of the flake, directions marked as ZZ (Zigzag) and AC (Armchair). In (a) and (b) the images on the right shows the interface turning dark when the Si wafer was heated at 300°C for three minutes. The yellow dotted rectangle in (b) represents the Cu metal deposited.

6.5 – Summary of the findings

Demonstrating a real application is of uttermost importance in the world of semiconductors. In this chapter, we saw the very first preliminary device measurement done on the Cu 1D structure in BP. Due to the atomic feature size (0.36 nm width) of the wires, it is difficult to apply conventional fabrication methods. The presence of the self-assembled Cu atoms could only be seen using electron microscopes, especially inside TEM. The device after Cu treatment did show lower resistance. It is also highly possible that this could be because of the sample annealing. A similar comparison was not achieved in TEM. The chemical nature of Phosphorus during the positive and negative sweep of the device was also explored by investigating its core loss spectra (P, L-edge). It was found that the 'P' undergoes reduction when a positive voltage is applied which is well known for other devices as well. However due to oxidation of BP similar work was not done over Cu treated BP. It will be very interesting to perform dual EELS over the O K-edge and the Cu L-edge in the future. Oxygen K-edge being very sensitive to EELS, it gives better indications in the ELNES (Electron energy Loss Near Edge Structure) providing vital information about the oxidation states.[24]

The inclusion of more than one fabrication steps in making a device over the MEMS chip (Etching SiN layer + Au/Ti deposited Contacts + Cu deposition) makes the BP nanosheets vulnerable for contamination and damage. A simultaneous heating and electrical holder (like the DENS lightning holder[25]) would solve the issue. This would require only one step fabrication of depositing Cu metal either by drop casting or by e-beam lithography.

Nonetheless, control growth of Cu atoms was successfully demonstrated by transferring the Cu nanoparticles by the micromechanical manipulator. Moreover, controlled seeding of copper 1D structures in BP was achievable by e-beam lithography, a standard technique used in the semiconducting industry. Importantly, controlled growth by using EBL and the resistance to degradation of Cu treated BP (as described in Chapter 4) can enable the use of existing technology and hardware to fabricate and design future BP based electronic devices.

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Chapter 7

Conclusion

“If your experiment needs statistics then you should design a better experiment.”

... Ernest Rutherford

In understanding the fundamentals of the 2D materials, the work presented in this thesis is a modest contribution to the collective effort of the research community. A novel method has been unravelled in fabricating 1D Cu structures (atomic wires) in 2D black phosphorus. In this case, the Cu interaction with BP is found to be easily reproducible by thermal interrogation ($100^{\circ}\text{C} < T < 300^{\circ}\text{C}$) of BP nanosheets with metallic Cu. The source of heat (oven or hot plate) and Cu metal (TEM Cu grid, nanoparticles, Cu foil or e-beam evaporation) was found to be indifferent to the formation of these triatomic wires.

The major structural and spectroscopic analysis was done using transmission electron microscopy. All the preliminary studies were done using TITAN 80-300 kV non-aberration corrected machine. By performing EDX and EELS analyses, the 1D structure was found to be comprised of Cu element. Growth kinetics were studied by in-situ heating in the TEM, and ballistic self-assembly was found to occur at 300°C at a speed of ~ 100 nm/sec along the [010] direction. HRTEM and diffraction studies were incapable of solving the structure and found to have a damaging effect at 300 kV.

High-angle annular dark field (HAADF) imaging was undertaken using aberration-corrected STEM (AC-STEM) to study the 1D Cu in BP structure at the atomic scale. The Z-contrast STEM images revealed that the formation of the 1D structure is highly localized (width of $3.6 \text{ \AA}$) and does not affect the entire BP substrate. The wire growth

was only interrupted at the edges plausibly due to BP oxidation. The self-assembled structure exhibits a long-range translational ordering.

A combined X-ray photoelectron spectroscopy (XPS) and electron energy-loss near-edge structure (ELNES) study were performed to gain insights into the nature of the bonding occurring between Cu and P atoms and reveal the valences of the copper in the structure. In case of the XPS, the Cu treated BP sample was compared with pristine BP and reference copper phosphide sample. The 2p phosphorus component was sharp indicative of pristine BP, demonstrating that the thermal treatment does not have any detrimental effect on the underlying BP flakes. The Cu treated BP spectrum showed peaks related to a phosphate group and copper component which were also present in the reference sample (copper phosphide). To gain further insight into the nature of the Cu-P bonding, fine structure analysis of the Cu L_{2,3} spectrum (acquired with high spatial resolution) was performed across the wire structures. It was also observed that the Cu located at the structure's edge showed different oxidation states (Cu²⁺) when compared to the Cu located at the centre (Cu²⁺ and Cu¹⁺). The results obtained from the XPS and comparing the Cu L_{2,3} (from EELS) with standard EEL data for metallic Cu and CuO; it was concluded that the wire structure is not pure metallic and must be either oxidized Cu or BP-Cu composite.

Ultimately, to solve the structure first principle calculations were performed using density functional theory (DFT). The calculations suggested that the formation of a Cu wire is kinetically viable, revealing that the diffusion of a Cu atom on a BP surface occurs interstitially or substitutional, along a zigzag pathway between centres of adjacent BP hexagonal chairs. The ultimate structure featured hexagonal Cu₃P-like motifs. In addition to forming interstitially, different metastable Cu 1D structures were also found to be possibly adsorbed on the BP surface. Simulating the HAADF images using QSTEM software, the model was found to be matching qualitatively with the experimental results. Going one step further, the results were confirmed by rigorous dynamical simulations (using MULTTEM software) and by undertaking quantitative approach towards STEM (Q-ADF) imaging. This demonstrates that the tri-atomically

wide 1D structures are indeed made of copper phosphide interstitial units extending across the BP layers.

Being the most stable allotrope of phosphorus, the Cu diffusion is found to have a profound impact on BP degradation which is the major roadblock in BP device fabrication. This may also have profound implications tuning the band gap, rather than being confined to the number of layers and stacking differences. This needs to be investigated in the near future as Cu is also predicted to have a good ohmic contact compared to Ti/Au in BP which will reduce the cost of manufacturing transistors drastically. Using this method, it is possible to grow arrays of parallel Cu₃P lines spaced by as little as 1 nm. This controlled growth is shown to be achievable using conventional electron beam lithography (EBL) and site-specific placement of Cu nanoparticles. As both Cu₃P and BP are semiconducting, this method paves the way to fabricate local, nanoscale semiconductor-semiconductor heterojunctions or even quantum well arrays. Extending this growth process to other metals or 2D substrates may yield a versatile fabrication methodology to produce long-range self-assembled structures with short-range patterning capability. It is still to be investigated whether such property exists or can be triggered in other 2D or bulk materials.

Chapter 8

Future Work

“Physics is like sex: sure, it may give some practical results, but that's not why we do it.”

... Richard Feynman

8.1 – Band Gap

Using a monochromatic source, **low-loss EELS** can be performed to measure the band gap of a variety of semiconductors and insulators. The method can be extended to 1D Cu structure in BP to investigate any change in the band gap depending on the number of layers and wires. Even though it is expected that the electrical properties of the wire would be different than that of the BP, it will be very interesting to probe the properties using scanning transmission electron microscopy (STEM). Further investigation at low temperatures will be ideal.

Recent development in energy resolution of electron energy loss spectroscopy down to 10 meV in the STEM,[1] including the ‘aloof’ beam spectroscopy (beam positioned just outside the sample avoiding radiation damage) has allowed **vibrational spectroscopy** using high spatial resolution. This a powerful tool which can analyze bonding arrangements and identify chemical compounds giving similar information to IR and Raman spectroscopy at the atomic scale.

Scanning Tunneling Microscopy/Spectroscopy (**STM/S**) is another technique that can be undertaken to investigate the electrical properties of the wire formation. This will be not trivial as the diffusion is found to be interstitial and also the surface contamination plays a critical role in getting STM work.

8.2 – In-situ experiments with spatial resolution

Studying **kinetics at high spatial resolution** will be the key to understand Cu diffusion into BP. Investigating in-situ growth of Cu atoms at atomic scale while heating the sample will be a classic experiment to prove the DFT prediction of zigzag pathway growth direction of Cu_3P motifs formation. Also, probing the Cu-BP (metal-semiconductor) interface while the Cu atoms initially migrate into phosphorene lattice will be interesting. Using optical imaging, it was found that the Cu metal colour changes during Cu diffusion implying 'P' migration into Cu. Reducing action of phosphorus in Cu metal is well known. Designing a junction of a thin film Cu with BP nanosheet will be a perfect experiment to investigate inside TEM. Getting a **cross-sectional image** of wire is very difficult. The FIB (Focused Ion Beam) does not work due to heavy damage. For now, it can be plausible if the Cu treated nanosheet is attached to a special high tilt tomography holder to get the necessary tilt. In fact, high spatial resolution **STEM tomography** reconstruction with EELS will be a perfect technique in order to build the Cu 1D structure in 3D.

As stated in chapter 6, the in-situ electrical measurements were very preliminary studies and did not yield any conclusive evidence. However, testing the Cu treated BP sample using simultaneous **electrical and heating holder** (DENS Lightning Holder) will be a much better approach. Fabricating a field effect transistor by applying back/top gate will be ideal however is not straightforward in transmission microscopy.

8.3 – Classical/ Quantum Applications

- **Simple macroscale p-n junction:**

First principle studies exploring metal contact for black phosphorus predict that Cu is the best candidate to form an ohmic contact.[2], [3] The results obtained by observing optical micrographs (Chapter 5, figure 6.15) and the well-known phosphor reducing

action in Cu metal.[4], [5] suggest that there is an exchange interaction between Cu and P on either side. Forming a simple heterojunction (either p-n or ambipolar) at the interface of BP nanosheet and an equivalent thin film of Cu is highly plausible. The transistor properties can then be characterized using different metal contacts. To avoid the complexities of atomically thin wires, this will be a very simple design to undertake for investigating any novel properties. However, care has to be taken not to overheat the sample to avoid excess Cu diffusion and damage over 300 °C.

- **Stand-alone wire**

Various techniques have been used to fabricate atomically thin 1D structures, including; encapsulating the atoms inside carbon nanotubes,[6] using molecular structure directing agents,[7] angstrom-sized electron probe in the STEM,[8] and by scanning tunnelling microscopy (STM).[9] However, such techniques are not scalable or easily implementable for large-scale production. Displaying a robust, reproducible design of self-assembly at long range is the way forward but lacks required application proofs. To etch out the wire from the BP substrate also seems to be a herculean task. The e-beam etching done in Nion UltraSTEM (in Appendix (A.1)) will not allow the long wire to be etched without damaging it. One of the ideas can be to use thermal activation and nano-indentation to trigger self-tearing and peeling of the wires using AFM (Atomic Force Microscopy).[10]

Taking another step forward will be in the fascinating field of **Racetrack Memory** (Atomic Structures in 3D).[11], [12] Recently, in fact, in past three years, distinct physical phenomena have been discovered related to spin-orbit coupling. This enables us to manipulate the domain walls. The key finding is the magnetic moment being perpendicular to each other in chiral fashion rather than being parallel (as in Ferromagnet) or antiparallel (as in Antiferromagnet). In magnetism like in the electrical case of Cu interconnects, if you shrink a metal to the nanoscale you would lose the magnetism eventually. The magnetic moment becomes thermally unstable. You need a material which is magnetic and isotropic so that the magnetism is fixed along one direction at long timescale. The self-assembled wire in BP can be tested for exhibiting this domain walls due to the isolation from one another by the phosphor atoms (in

conventional materials thinning down materials like Ag, Al, Au etc. disorder wins resulting in becoming an insulator). This experiment will be only possible near Kelvin temperatures.

- **2D Electron Gas (2DEG) – Heterojunctions and Quantum Wells**

Everything around us is three-dimensional. In quantum mechanics, if the Fermi energy is in between two quantized potentials you can say that the z-degree of freedom is frozen. This brings us to something termed as a two-dimensional electron gas. This occurs at low cryogenic temperatures and usually at interfaces (Semiconductor-Oxide, both insulators etc.). The recent emergence of 2D layered structures has broadened the zoo of materials exhibiting 2DEGs. BP having high carrier mobility plays a crucial role in observing the quantum Hall effect and high-speed device applications.[13] One dimensional transport and quantization of the ballistic conductance (carrier transport without scattering) are some of the interesting properties which have been demonstrated by the 2DEG especially in semiconductor heterojunctions.

The work discussed in this thesis demonstrates an elegant way to build up **complex heterostructures** based on 2D materials by using self-assembly, an approach which is currently unattainable. The parallel heterojunctions formed in this work may create a quantized channelling effect in the carrier transport properties. Demonstrating the self-assembly of 1-dimensional Cu_3P nanostructures on a black phosphorus (BP) nanosheet is a major step forward in that direction. Various self-assembly combinations should be tried using Nb or heterostructures with NbSe. Getting atomic self-assembly in insulators like boron nitride will enhance our understanding in designing the next **topological insulators**.

Designing a simple quantum potential which can **trap electrons** will revolutionize the way we perform computing. In ‘electron chip’ or ‘nuclear chip’, you do not need a flow of electrons to measure 0 or 1 bit (or the superposition), but photon to detect the spin of an electron or the nucleus. This would solve the heating issues. A **single atom transistor** can be designed using STM.[9] Doping an atom in between the wires or inside wire will be fascinating to analyze. Though, the technical challenges in analyzing such designs are enormous.

To realize all these outcomes, it will be extremely important to initially characterize the properties of an individual Cu-atoms self-assembly at a different temperature, pressure and explore possibilities of self-assembly in other systems. Another technical challenge would be to find a process to control the placement of the Cu seeds (or any other desired element) 1-2 nanometer apart. This will give us the flexibility to fabricate wires where we desire. For the academic purpose, Scanning Tunneling Microscopy is the perfect tool to manipulate the atoms for now.

We have been scaling our drives for the past 40 years of the research namely magnetic disk and silicon-based flash drives. We have come to an end of scaling such IC's in two dimensions. 3D MOSFET would also hit its limitation due to quantum effects. So how do we go beyond this paradigm?

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Appendix

“You wouldn’t let your schooling interfere with your education.”

... Grant Allen

A.1 – Etching by a fine probe

The first attempt in fabricating stand-alone three atoms wide copper phosphide wire from the BP substrate is undertaken using a fine probe in UltraSTEM microscope. The experiment is initially approached by using e-beam at 200 kV to speed up the etching process. However, due to high-energy electrons at 200 kV, even imaging results in knock-on damage to the BP (Black Phosphorus) as seen in figure A1 – A3. While etching the desired area (marked in white or red dotted rectangle) 1 nm away from the wire (Figure A1 and A2) destroys the region totally. Getting the scanning area using descans 3 nm away does reduce the damage but still results in disintegration of the wire structures (Figure A3 (c)).

Even though working at lower kV’s increases the amount of time of etching we can still use different aperture sizes to increase the current at the same accelerating voltage (Section A.3). So, while for imaging purpose the standard aperture is used, the desired aperture can be replaced for etching. This method is much quicker and reliable rather than switching between high tension.

Figure A4 reveals that the Phosphor layers can be etched out not less than 1 nm away from the copper phosphide wires. This can be due to thermal diffuse scattering (TDS) by electron beam irradiation. This is more relevant in this case as the layers are not thin (i.e. more than 5 nm or 9 unit cells). Also, due to constant switching between the currents and realigning the beam aberrations with the aperture leads to e-beam overdose (Figure A4 (c)). As the current is decreased (Figure A4 (d)) the process time increases leading to

reduce control of the stage movement. Thinning down the layers at 16i aperture with reference 4 of the standard current is found to be ideal (Figure A4 (b)). Applying this beam conditions for larger thinning areas is found not to be feasible (Figure A5 (a) and (b)) as stage drift plays a major role in controlling the region of interest. Finding a bi or tri-layer system will be highly beneficial to undertake quick etching thereby reducing the beam damage due to prolonged exposure.

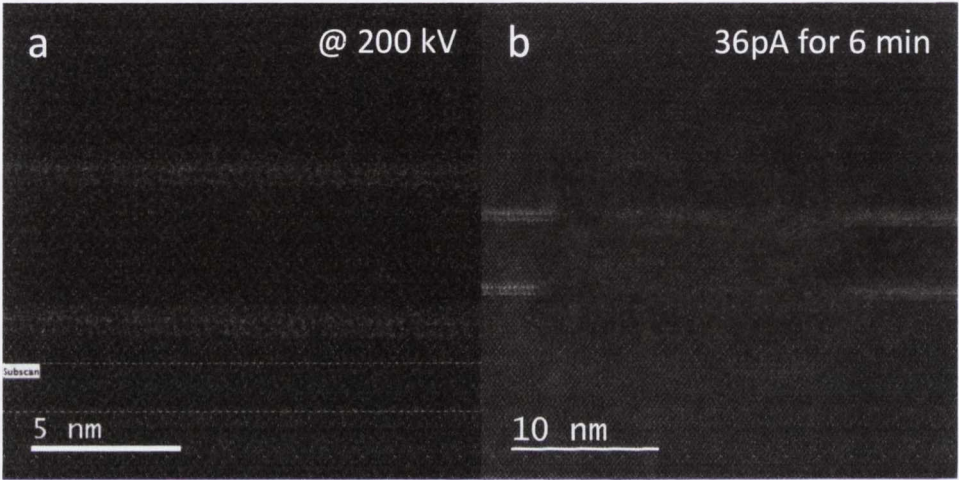


Figure A1 (a) Fast scan HAADF image at 200 kV to avoid beam damage. (b) Etching carried out using descans - 1 nm away from the wire (region marked with white dotted rectangle in (a)) resulting in total beam damage to the wires.

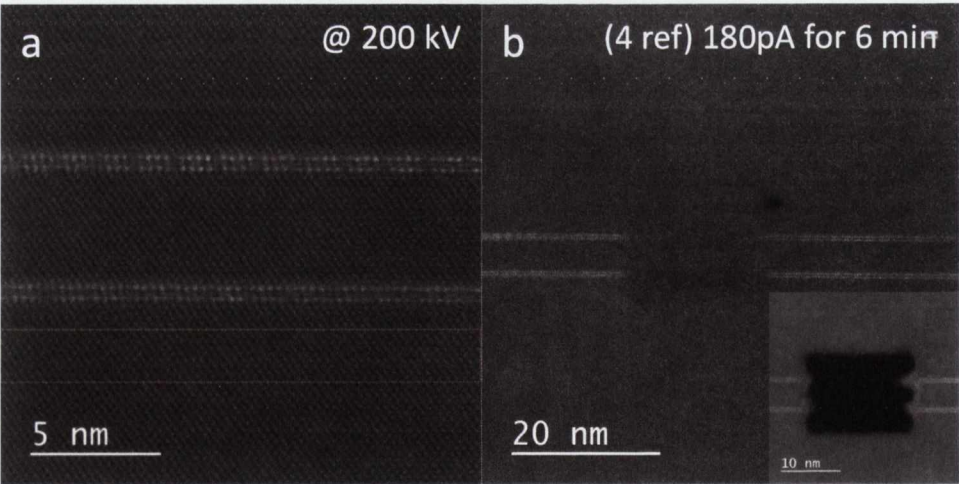


Figure A2 The probe current was increased to 180 pA using 4 times the standard reference current. Increasing the current just increase the chances of beam damage.

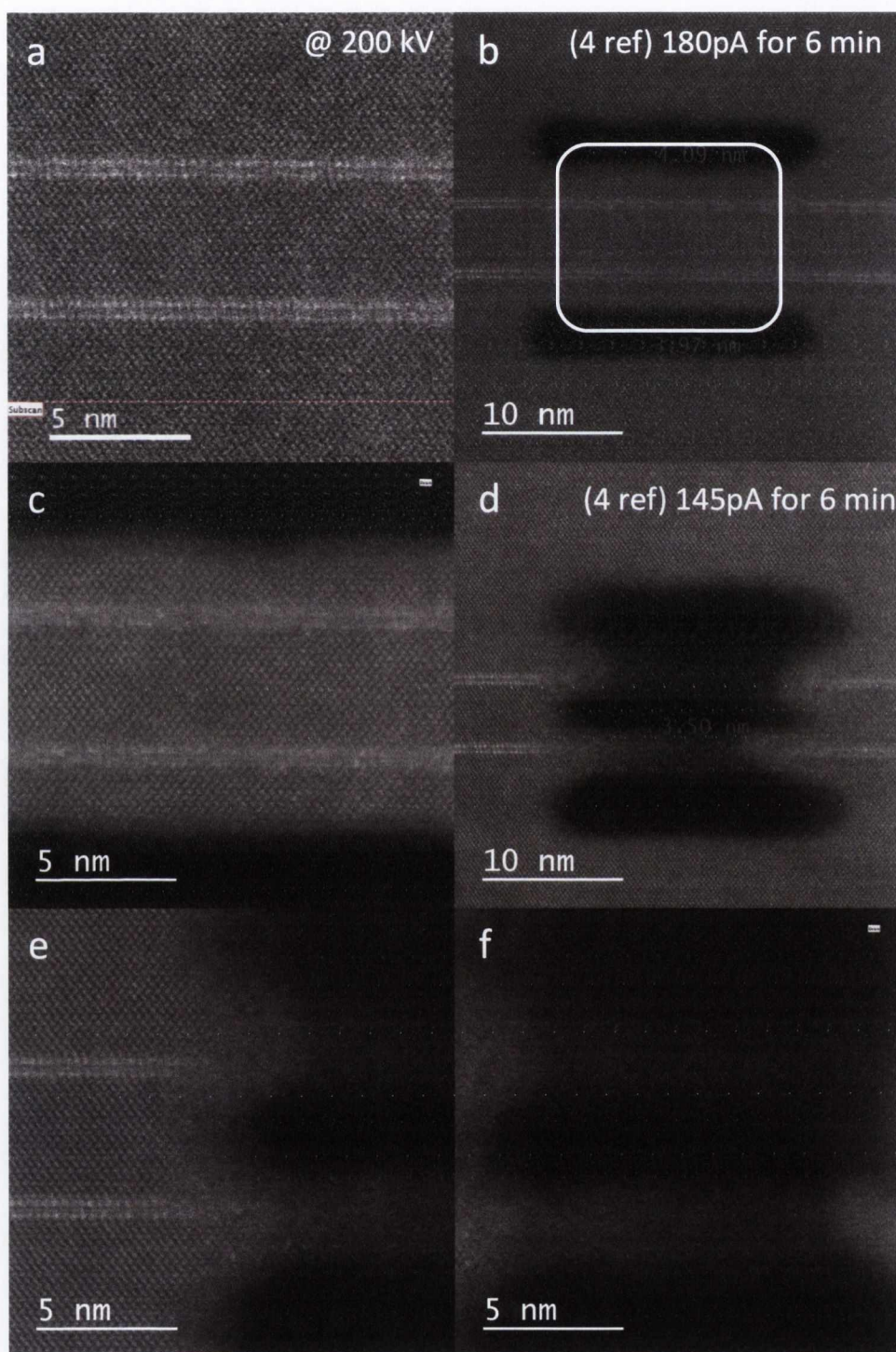


Figure A3 With the same probe current conditions as in figure A2, the beam was positioned 3 nm away from the region of interest (as seen in figure (a) marked with red dotted rectangle). This still resulted in beam damage as seen in figure (b), (c), (d), (e) and (f).

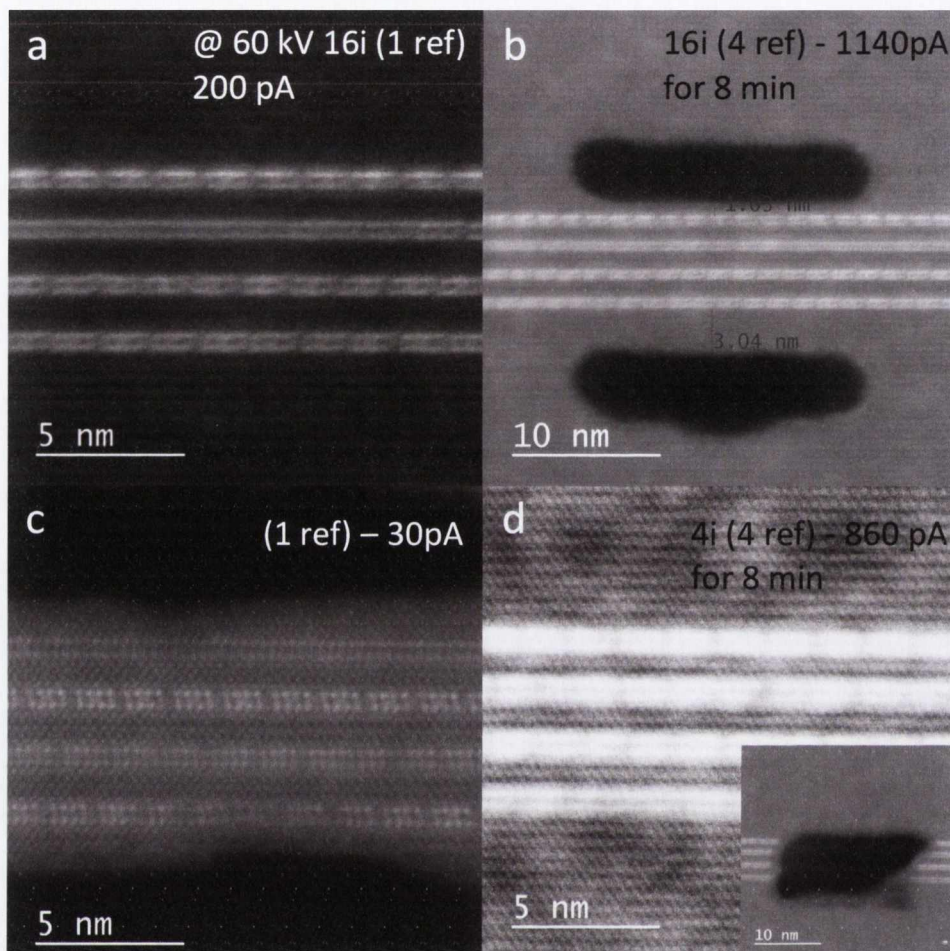


Figure A4 Keeping the beam scan 3 nm away from the region of interest @ 60 kV (figure (a) marked in red dotted rectangle). Figure (b) demonstrates that the closest Phosphor layer that can be etched should not be closer than 1 nm from the region of interest. However repeated scanning of the region to adjust the position do lead to damage of wires (figure (c)). Reducing the current further increases the time of etching hence more knock-on damage (figure (d)).

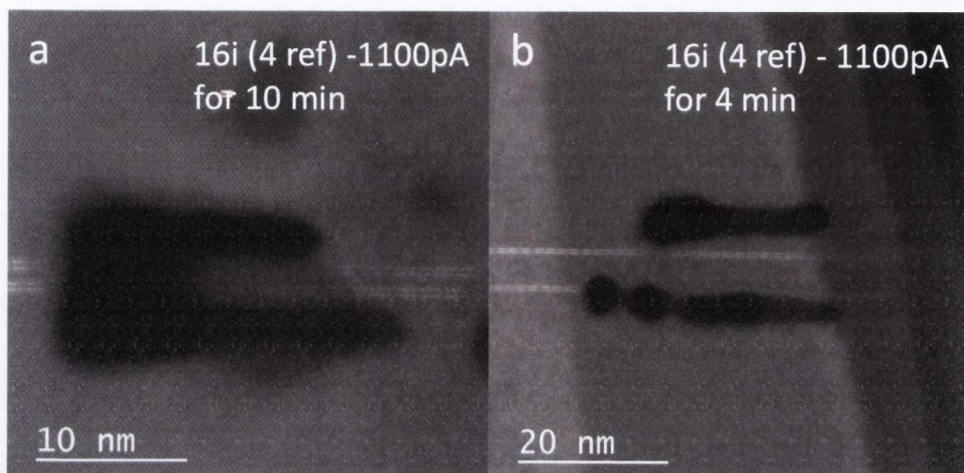


Figure A5 Applying the beam conditions undertaken in figure A4 (b) to etch larger areas did not work (as seen in figure (a) and (b)) as planned due to stage drift and change in current with time.

A.2 – Aberration Notation ^[1]

Aberration Coefficient	Krivanek notation	Order in K	Azimuthal symmetry
Image shift	$C_{0,1}$	1	1
Two fold astigmatism	$C_{1,2}$	2	2
Defocus (over focus positive)	$C_{1,0}$	2	inf
Three fold astigmatism	$C_{2,3}$	3	3
Axial coma	$C_{2,1}$	3	1
Four fold astigmatism	$C_{3,4}$	4	4
Axial star aberration	$C_{3,2}$	4	2
Spherical aberration	$C_{3,0}$	4	inf
Five fold astigmatism	$C_{4,5}$	5	5
Fourth order axial coma	$C_{4,1}$	5	1
Three lobe aberration	$C_{4,3}$	5	3
Six fold astigmatism	$C_{5,6}$	6	6
Fifth order rosette aberration	$C_{5,4}$	6	4
Fifth order axial star aberration	$C_{5,2}$	6	2
Fifth order spherical aberration	$C_{5,0}$	6	inf
Seven fold astigmatism	$C_{6,7}$	7	7
Sixth order axial coma	$C_{6,1}$	7	1
Sixth order three lobe aberration	$C_{6,3}$	7	3
Sixth order pentacle aberration	$C_{6,5}$	7	5
Eight fold astigmatism	$C_{7,8}$	8	8
Seventh order hexagon aberration	$C_{7,6}$	8	6
Seventh order rosette aberration	$C_{7,4}$	8	4
Seventh order star aberration	$C_{7,2}$	8	2
Seventh order spherical aberration	$C_{7,0}$	8	inf

[1] *Aberration-Corrected Analytical Transmission Electron Microscopy* - Rik Brydson.

A.3 – Nion UltraSTEM – Aperture Parameters

200 kV Set up:		
<u>Illumination (Condenser Modes)</u>		
Name	$\alpha/2$ (VOA) mrad	I_CAM (pA)
reference	27	70
QuarterIStdAp	27.5	15
2i_stdAp	26.5	162
4i_stdAp	27	360
4i_HighAngles	55	200
10i_stdAp	27.5	1100
20i_stdAp	27.5	1700
50i_stdAP	25.5	4300

60 kV Set up:		
<u>Illumination (Condenser Modes)</u>		
name	$\alpha/2$ (VOA) mrad	I_CAM (pA)
reference	35	44
QuarterIStdAp	36	19
2i_stdAp	35.5	81
4i_stdAp	35.5	268
4i_HighAngles	65	257
16i_stdAp	37	360
32i_stdAp	32	2000

“The scientist only imposes two things, namely truth and sincerity, imposes them upon himself and upon other scientists.”

...Erwin Schrodinger

(The Paradox of Origin)

“... Who knows from whence this great creation sprang? What was there at the beginning? We do not know, maybe the Gods know, but even they were created. Do the Sages Know? Perhaps they know not. Surely the creator knows, He from whom all this great creation came. Whether his will created or was mute, He knows it or perchance even He knows not...”

"not the non-existent existed, nor did the existent exist then"

... Nasadiya Sukta – Rig Veda – 10:129

“Plausibly infinite and a new beginning is just another transition...”[1][2][3]

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