

**Synthesis of graphene related materials by plasma chemical
vapour deposition method for device applications**

**(電子デバイス応用のためのプラズマ化学気相
成長法によるグラフェン関連材料の合成)**

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Abstract

Discovery of graphene is regarded as one of the major event in the field of material science which was seen as the possible solution for Moore's law and fabrication of futuristic devices. Hundreds of other similar two-dimensional (2D) structured materials, which could complement graphene's electronic properties, have been discovered in last two decades. The 2D materials cater a range of electronic properties from insulating (hexagonal boron nitride; h-BN), semiconducting (transition metal di-chalcogenides) to metallic (graphene). The synthesis of 2D materials has been mainly dependent on relatively high temperature chemical vapor deposition (CVD) growth for better quality and on plasma CVD process for the comparable material quality at low temperature growth.

My work was dedicated to synthesis and application of carbon nanowalls (CNWs) which are multilayer vertically stacked film of graphene films with curled structure. In the process, plasma chemical vapor deposition (PCVD) method was employed for the deposition of CNWs on the patterned substrate with line and space carvings. The field effect transistor (FET) was fabricated using CNW film grown by PCVD and its feasibility to be used as pH sensor was explored. In the later stage of work, hexagonal boron nitride was synthesized as a substrate for graphene film and CNWs by PCVD method.

In the experimental work of synthesis of CNWs, I explored the possibility of linear current voltage (I - V) characteristics for the a relatively low temperature synthesis at 500 °C as compared to previously reported CNW's growth at 600 °C. For doing so, a buffer layer of CNW was employed that was grown at 400 °C in same growth experiment of CNW's at 500°C. The CNW films synthesized both with and without its low temperature buffer layer underneath them, were compared using Raman spectroscopy and I - V characteristics and a relative enhancement in the linearity was observed for the film grown above its low temperature buffer (LTB) layer. Raman spectroscopic study revealed that LTB layer improved micro-crystallinity in the film and reduced the edges from the walls which are formed as result of spontaneous growth and stacking of smaller carbon nano flakes. I - V characteristic revealed that the effect of

geometrical patterns, that favour self-aligned growth of CNWs due to geometrical confinement and thereby furbishes defects in the film arose due to strain, was decreased. A linear I - V characteristic was observed for LTB-CNW as compared to conventional non-linear curve for as-grown CNWs and the result demonstrated the efficacy of LTB layer as a relaxation layer.

The as-grown CNWs were used as a channel in CNW-FET wherein oxygen and hydrogen plasmas were employed in reactive ion etching method to etch the CNWs grown outside the pattern and improve the contact between CNW and Ti/Au electrode respectively. The oxygen plasma treatment reduced the gate leakage current from 30 μ A to 25 pA while hydrogen plasma treatment enhanced the drain current from 4 μ A to 200 μ A.

The CNW-FET was further explored as a pH sensor and the obtained I - V characteristic showed a change in non-linearity in curve with changing values of pH. The noise properties demonstrated an increase with increasing values of pH. The results advocated for CNW-FET device application such as biosensor.

The possibility of synthesis of h-BN, as substrate for CNWs and graphene, at the same temperature of 500 °C was explored. The wafer-scale uniformly grown h-BN was obtained at 500 °C growth temperature. The transmission electron microscopic result confirmed the polycrystalline nature of the film and an interlayer spacing of 0.34 nm showed the hexagonal structure which was further supported by Fourier transform infrared spectroscopic data. The characterized film showed an excitonic optical absorption at 276 nm due to incorporation of oxygen and carbon impurities and might open the possibility to engineer the band gap in h-BN during synthesis with further improvement and change the course of future electronics.

Abbreviations

1, 2 and 3D	1, 2 and 3 Dimensions
CNW	Carbon Nanowall
CNT	Carbon Nanotube
h-BN	Hexagonal Boron Nitride
c-BN	Cubic Boron Nitride
DIW	De-Ionised Water
CVD	Chemical Vapour Deposition
MWPCVD	Microwave Plasma Chemical Vapour Deposition
MW-SW-PCVD	Microwave Surface Wave Plasma Chemical Vapor Deposition
SAW	Surface Acoustic Waves
UV-Vis	Ultra-Violet Visible
NIR	Near Infrared
FT-IR	Fourier Transform Infra-Red
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
XPS	X-ray Photoelectron Spectroscopy
OM	Optical Microscope
AFM	Atomic Force Microscope
FET	Field Effect Transistor
sccm	Standard Cubic Centimeter per Minute
PMMA	Poly Methyl Meth Acrylate
AB	Ammonia Borane
LTB	Low-Temperature Buffer
L-CNW	Carbon nanowall grown on its low temperature buffer layer
as-CNW	Carbon nanowall grown directly on non-catalytic substrate
LDH	Layered Double Hydroxide
MOF	Metal Organic Framework
PSD	Power Spectral Density
FFT	Fast Fourier Transform

BP	Black Phosphorous
V_G	Gate Voltage
I_{DS}	Drain Current
PD	Probability Density
RIE	Reactive Ion Etching
ISFET	Ion Sensitive Field Effect Transistor
MOSFET	Metal Oxide Semiconductor Field Effect Transistor
DUV	Deep Ultra-Violet
ECR	Electron Cyclotron Resonance

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Motivation and Outline

Motivation

The future of flexible electronics depends on thin materials complying with the properties of other conventional materials such as metals, semiconductors and insulators. Atomically thin layered materials, also known as two-dimensional (2D) materials, have been discovered in last two decades in more than hundred in number. These 2D materials are expected to be suitable for future-electronics covering the desired properties collectively.

Graphene (a zero-bandgap semiconductor), transition metal di-chalcogenides (TMDC; semiconductors), hexagonal boron nitride (h-BN, an insulator) are few examples of most researched layered materials in recent past. However, obtaining a high quality crystalline layered structure by conventional synthesis method such as chemical vapor deposition (CVD), is still a challenge where scientists are working at large scale. One of the major challenges is the synthesis of highly crystalline 2D materials at lower temperature for device application since high temperature growth increases the overall cost of a device. Moreover, good crystallinity and area-selective growth during synthesis is another hurdle. The low temperature growth does not favor the complete bond-dissociation for a desired precursor which can be altered by varying ambient growth conditions.

The issues related to crystallinity control can be tackled during the synthesis process wherein various parameters for catalytic and non-catalytic growth are being explored. Plasma (P) CVD growth process has been widely utilized in last three decades for low temperature synthesis of semiconducting materials with a compromise in crystallinity of the film. The reproducibility and uniformity are two major reasons behind the popularity is PCVD method which was widely used for synthesis of nano-carbons (CNTs, CNWs, fullerenes, CNFs etc.) cubic BN and many other categories of films.

In this thesis, the relatively low temperature synthesis of graphene based materials such as carbon nanowalls and h-BN using PCVD method is explored.

Outline

Chapter 1 contains a brief introduction to 2D materials. The range of applications of 2D materials utilizing their most significant properties and the hurdles in their synthesis methods are briefly introduced. In the further discussion, this chapter contains the detail about properties and synthesis methods of graphene related materials. In this thesis, the synthesis experiments carried out for both carbon nanowalls and hexagonal boron nitride will be examined. Electronic properties of these materials are briefly discussed in qualitative manner barring the derivations from quantum mechanics and condensed matter physics. The synthesis methods and their efficacy have been discussed with their potential applications based on the quality of 2D film they produce.

Chapter 2 contains the experimental method for the synthesis and characterization of both CNWs and h-BN. The transfer method of 2D film from one substrate to other remains the same for both graphene and h-BN which has been discussed in the chapter. The synthesis method of CNWs is concisely written understanding the ease of plasma enhanced CVD process. The synthesis method of h-BN by MW-SW-PCVD process is also discussed.

Chapter 3 contains the standard results of various characterization methods along with their basic concept behind those results. The results will be compared with those obtained in the synthesis of graphene based materials mentioned in later chapters in the thesis.

Chapter 4 contains the results obtained by the synthesis of CNW over its buffer layer grown at lower temperature. The results will be compared with CNW grown without buffer and will put emphasis on advantages of using LTB for CNW growth.

Chapter 5 contains the effects of etching process on CNW-FET. The effect of O₂ and H₂ plasma on enhancing the CNW property is discussed in the chapter and linearity of current voltage (I - V) curve will be examined.

Chapter 6 contains the discussion for application of CNW-FET in pH sensors. The fluctuation in current in FET system, under the influence of various pH liquid solutions, is examined and compared. The result is deduced after comparison with I - V data of CNW-FET measured under ambient conditions.

Chapter 7 contains the synthesis method and results of h-BN film grown by MW-SW-PCVD. TEM, FT-IR and XPS data show the growth of h-BN film that will be corroborated in the chapter with a discussion of incorporation of impurities which change the optical properties of the material.

Chapter 8 contains the summary of the thesis in very short and opens up about the future prospects of performed experiment

Chapter1.

Introduction

1.1 Overview

The isolation of graphene from a pencil in 2004 was a major event [1] that resulted into winning Nobel Prize in 2010. This “two-dimensional” (2D) material, made up of a single layer of sp^2 carbon atoms, continues to attract the attention of researchers [2,3]. Many new members have joined the 2D material family since then. In the 2010s, other 2D materials were isolated or synthesized. Their exceptional properties opened up an increasing number of applications.

2D materials are thinnest possible “layered-material” of any kind having thickness of just one atomic sheet. They offer a wide range of physical properties applicable in modern day technology as shown in figure 1-1. As the technology is growing with rapid rate, the demand for new materials which could provide enhanced performance with cost effectiveness and efficiency is increasing and 2D materials are sought as the capable solution for the demand. The saturation of Moore’s law can be taken as an example where silicon technology, which is essential for nearly every electronic device, is slowly reaching towards highest attainable narrowness.

1.1.1 History of graphene and other 2D materials

The history of 2D materials, which started with graphene, dates back to 1947 when P.R. Wallace calculated the band structure of graphite using a simple model [4]. He precisely identified graphite as a zero band-gap semiconductor and made the prediction of long mean free path for electrons in the material. 40 years later, Di Vincenzo and Mele found out that the charge carriers in graphene demonstrate zero effective mass that leads to linear dispersion of electrons in electronic band structure near K-point [5]. However, a material at atomic scale thickness was predicted thermodynamically unstable only to be negated by A.K. Geim and K.S. Novosolov in 2004 after the finding of

thermodynamically stable atomic layer of graphite and deduced the properties. Soon after the discovery, the gold rush of discovering new 2D materials, which could complement graphene, started. The phenomenal physical, electronic and optical properties of graphene led to the investigation of more similar layered materials such as hexagonal boron nitride (h-BN) [6], transition metal di-chalcogenides (TMDC; e.g., MoS₂, TiS₂, TaS₂, WS₂, MoSe₂, WSe₂, etc.) [7–10], graphitic carbon nitride (g-C₃N₄) [11] layered metal oxides [12] and layered double hydroxides (LDHs) [13]. Numerous new type of ultra 2D crystals such as metal organic frameworks (MOFs) [14,15], covalent organic frameworks (COFs) [16], polymers [17–19], metals [20–23], black phosphorus (BP) [24], silicene [25] and MXenes [26] have also been explored in recent years. The range of electronic applications with electronic structure for some important materials is given below. Emergence of 2D materials such as TMDC, graphene, phosphorene (also known as black phosphorous) etc. have paved the way for flexible electronics.

1.1.2 Properties of graphene and other 2D materials

Graphene, which revitalized the area of electronics and optoelectronics citing its phenomenal electronic properties such as high carrier mobility, tensile strength, chemical inertness etc., has been of paramount interest in last one decade [27]. Graphene is by far a well-known 2D material and also the first that was discovered [1,28,29]. Graphene has best electrical conductivity (theoretical room-temperature mobility 200,000 cm²/ (V.s)) [30] around 100 times larger than silicon, strongest material strength (130 GPa) [31,32], exceptional heat conductor (2000 W/(m.K)) [33–35], transparent with only 2.3% of absorbance [36] which conflicts with the properties of normal high mobility possessing materials [31,37], lightweight and highly flexible (can be stretched by 20%) [32,38]. The material is impermeable to gases [39] and can withstand very high density of electric current (10⁶ times higher than Cu) [40]. In addition, the electrons behave as a massless moving particle in graphene sheet that gives rise to such a high carrier mobility that sets apart graphene from all other known materials. Graphene can be chemically functionalized to support the necessary physical and biological applications [41–43]. These properties accredit graphene for replacement

of many existing materials. However, the lack of band gap renders graphene useless as a semiconductor that led to emanation of many other 2D materials to fulfill the band gap requirements for semiconductor based device applications.

While graphene has zero bandgap semiconducting properties, there are other counterparts such as TMDCs, phosphorene and h-BN that demonstrate a wide variety of electronic, optical, chemical and physical properties on atomic-layer scale. Their band gap may vary from 0.3 eV to 6 eV while the direct or indirect transition may depend upon number of layers in the film. Typically the 2D materials up to 2-3 layers show best properties for opto-electronic devices utilizing their layered structure.

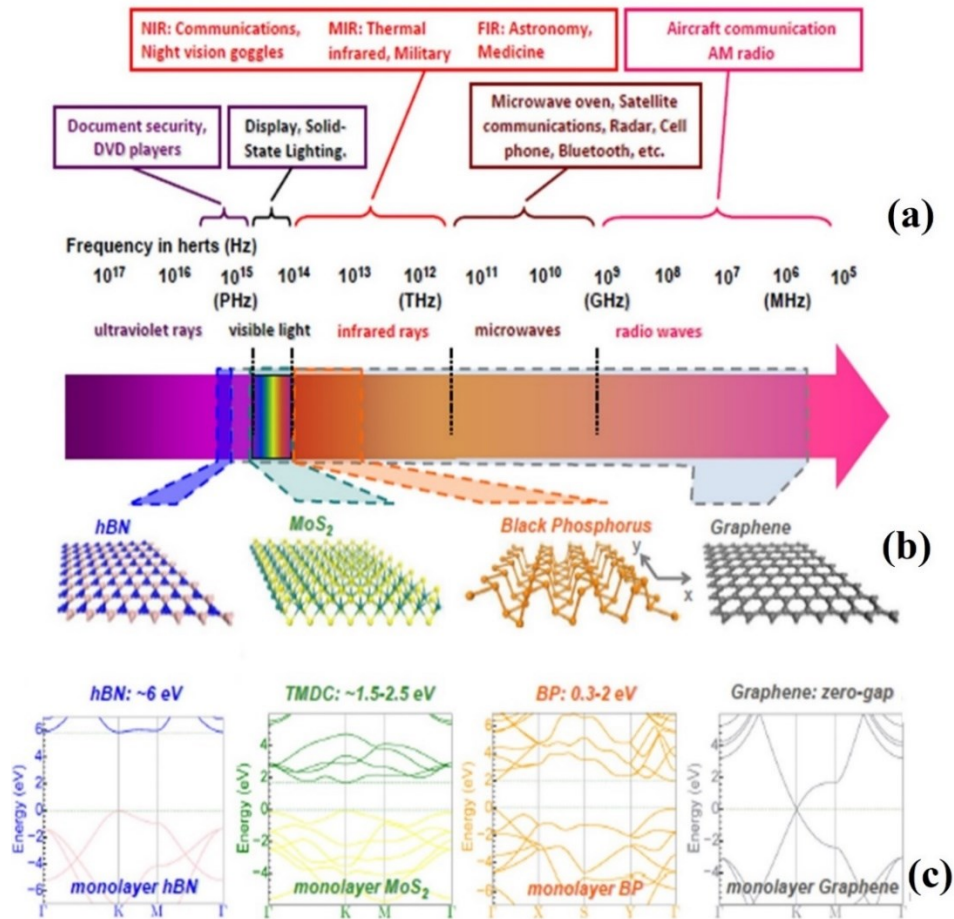


Figure 1-1(a) Energy spectrum of various 2D materials and their atomic crystal structures, (b) electronic band structures of h-BN, TMDC, black phosphorous, and graphene; and (c) energy level diagrams of the selected semiconducting TMDCs [44]. Reproduced with permission from reference [44] and [45].

The high mobility of graphene is seen as the tremendous advantage from material and a great deal of research has been carried out from its synthesis to application, to avail this property. Both the small domain size and dangling bonds present on the substrate's surface, such as on SiO₂ or glass, in graphene film lead to scattering of electrons thereby reduce the carrier mobility. Efforts have been made to enlarge the domain size using chemical vapor deposition (CVD) method. Numerous methods have been attempted to remove the dangling bonds and surface states from the substrate, particularly SiO₂ which inhibits the mobility in graphene. A dangling bond-free h-BN substrate is used to tackle the issue of surface states of SiO₂ substrates [30,46].

1.2 Hexagonal boron nitride (h-BN)

Boron nitride (BN), a III-V compound, is one of the most sought materials among scientific community after graphene and other 2D materials [47,48]. Boron and nitrogen atoms are alternatively linked in 1:1 stoichiometric ratio in BN compound. BN possesses three major crystalline varieties such as: (i) cubic BN (c-BN), (ii) wurtzite BN (w-BN) and (iii) hexagonal BN (h-BN). The crystalline structures for all three forms are different. For example, c-BN possesses the structure analogous to diamond, w-BN has lonsdaleite like structure while h-BN is sp² bonded layer of B and N atoms in AB stacking. It is notable that the rhombohedral BN (r-BN) in ABC stacking also has the same covalent bonding between atoms. BN can be found in zero-dimensional (0D) nanoparticles, 1D nanotubes and nanoribbons, 2D nanosheets and 3D nano-porous BN [49–55].

1.2.1 Properties of h-BN

The chirality of hexagonal sheet of h-BN is defined in similar fashion as that of CNT and graphene. The lattice orientation in single layered h-BN is also expressed in two unit vectors viz a_1 and a_2 while their chiral vector would be described as $C_h = na_1 + ma_2$, where both n and m are indices of nanotube as shown in figure 1-2 [56]. Hence the orientation can attain the values in (i) $C_h = (n, 0)$ for zigzag structure, (ii) $C_h = (n, n)$ for armchair structure and (iii) $C_h = (n, m)$ which lies between both zigzag and armchair

structures as shown in figure 1-2 (c) and 1-2 (d) [57,58]. Orientation plays an important role in tubular BN. On the other hand, the structural orientation determines the mechanical and thermal transport properties in h-BN sheet [59].

The bonding nature of h-BN is different from h-graphite because of the involvement of heteroatoms. The heteroatom induces partial ionic character in B-N bond due to difference in electronegativity of both B and N atoms. The electrons involved in B-N bond localize towards N in s-orbital while one electron from p-orbital of boron and 3 electrons from half-filled p-orbital of nitrogen are weakly delocalized. This bond-ionicity phenomena breaks the symmetry of electronic states and induces a wide band gap in h-BN sheet which results in furnishing insulating property to the material [55,60].

h-BN has drawn attention in scientific community having the effects of low-dimensional quantum confinement and surface, that result in a unique combination of electrically insulating and high thermal conductivity in the material. In addition, it shows low carrier density, a wide band gap (~ 6 eV), very high hardness and a chemically inert behavior. These unique properties have fascinated the researchers for application in heterostructures, advanced insulators, thermal management, optoelectronics such as deep ultraviolet (DUV) detectors and functional composites [61–65].

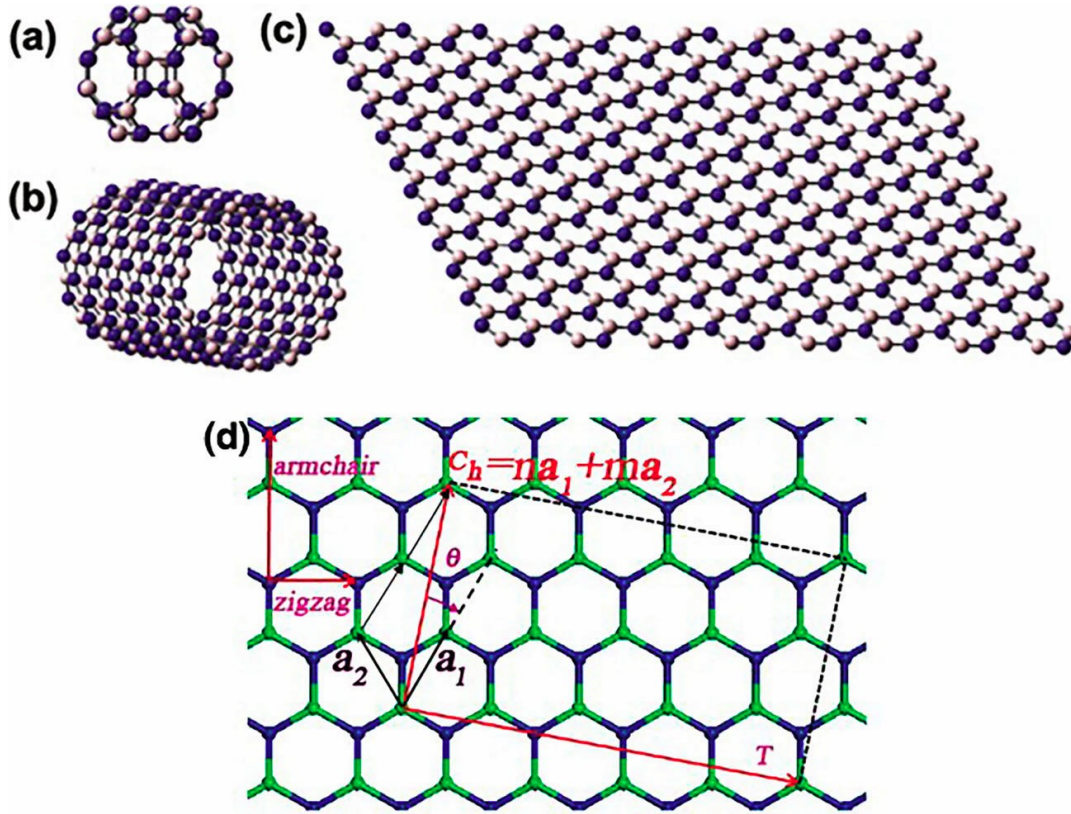


Figure 1-2 Schematic BN nanostructures: (a) fullerene (0D, $B_{24}N_{24}$), (b) 1D BN single-walled nanotube (1D), (c) mono-layer BN (2D) [74]. (d) Orientations in monolayer h-BN, where, a_1 and a_2 are the unit vectors of h-BN in real space and C_h is the chiral vector. Image adapted from [56] with reprinting permission.

1.2.2 Synthesis of layered structure of h-BN

The growth of layered structure has been limited up to nanoscale in thickness. Both top-down and bottom-up synthesis approaches have been tried in h-BN growth. The synthesis methods of h-BN match overall with graphene which will be discussed next.

1.2.2.1 Top-bottom approach

The interlayer van der Waals interaction of h-BN has been overcome by direct mechanical forces for peeling off BN nanosheets [66]. Ball milling is one of the renowned method for applying shear forces to separate thick BN layers into nanosheets. However, this method provides low yield and smaller flake size in microns [67].

Liquid exfoliation methods have also been used to synthesize BN layers similar to graphene wherein few layered BN flakes undergo ultrasonic vibrations and ultimately the van der Waals layers (atomic layers bounded together by van der Waals force such as 2D materials) break into nano-sheets due to surface tension of polar solvents [6,68–71]. However, BN nano-sheets are more difficult to be exfoliated using same route as graphene due to stronger interlayer interaction than graphite as BN also shows partial ionic bond character unlike graphite having 100% covalent bonding. BN nano-sheets have been also exfoliated using molten hydroxides and were created via layer by layer etching under electron beam irradiation [72–74]. The major disadvantage of chemical method is surface contamination of nano-sheets and non-uniformity in the thickness of flakes. Thus various other methods were introduced to remove these challenges.

1.2.2.2 Bottom up approach

This approach for BN nanosheet synthesis can be classified into substrate based and substrate free types. In substrate free type process, BN nanosheets were synthesized using boric acid and urea in a direct chemical reaction [75]. In a similar process, B_2O_3 is separately used with both melamine and graphite in different reactions to give BN nanosheets as the byproduct [76,77]. Many other chemical processes such as chemical blowing [78] and biomass targeted carbo-thermal route [79] have also been tried. However these techniques provide low yield with uneven sizes and thickness of BN as compared to thermal processes (substrate based type) that will be discussed next. The substrate based synthesis of BN nano-sheets includes CVD methods such as low pressure (LP) CVD, catalytic CVD, plasma enhanced (PE) CVD, sputtering, electron beam evaporation and ion beam deposition etc. The advantage of substrate based technique is the thickness controllability of h-BN film.

Here I will discuss about thermal CVD method for h-BN growth while plasma based synthesis experiments will be discussed in chapter 2 and 7.

Thermal CVD process for h-BN synthesis

CVD is the most popular method for 2D material synthesis due to its large area production fulfilling requirements of industrial applications. CVD growth process for h-BN involves four steps:

- (i) the adsorption of molecules from a gaseous precursor on the substrate's surface
- (ii) the dissociation of molecules of precursor into energetic radicals
- (iii) diffusion of the dissociated energetic radicals and
- (iv) nucleation and growth of the film by further incorporation [80].

The grown film covers the entire substrate thereby centimeter scale growth is possible using this technique. Single layered h-BN (white graphene) had been synthesized using this technique on surfaces of Ni, Pd and Pt in 1994 [81]. Later h-BN was grown on Cu, Ni, Co, Fe, Ru, Pt, graphite, Si [82–91] by CVD method using solid (ammonia borane), liquid (borazine) and gas (diborane and ammonia) [82,85,92,93] and Al_2O_3 , by CVD method [82–92].

1.3 Carbon nanowalls (CNWs)

Carbon nanowalls (CNWs), another class of 2D materials, are vertically stacked, self-assembled multilayer graphene sheets in maze or petal-like structure [94–96]. The CNW boasts high aspect ratio; theoretically twice compared to CNTs and fullerenes. They are also termed as graphene nanowalls, carbon nano-flakes (CNFs) and carbon nano sheets (CNSs). One CNW may contain 10-20 layers of graphene and has a thickness of few to ten of nanometers [95]. Many applications utilizing the curled and wavy structure of CNWs, as shown in figure 1-3, have been sought; such as field emission [97–99], templates for nano-structures [94], blackbody coating [100], gas sensors [101], biosensors, electrochemical capacitor [102] and fuel cells [103–105] where large surface area of the material is required. CNWs have high density of atomic-scale graphitic edges which are normal to the substrate's surface so their applications have been realized in field emission [95].

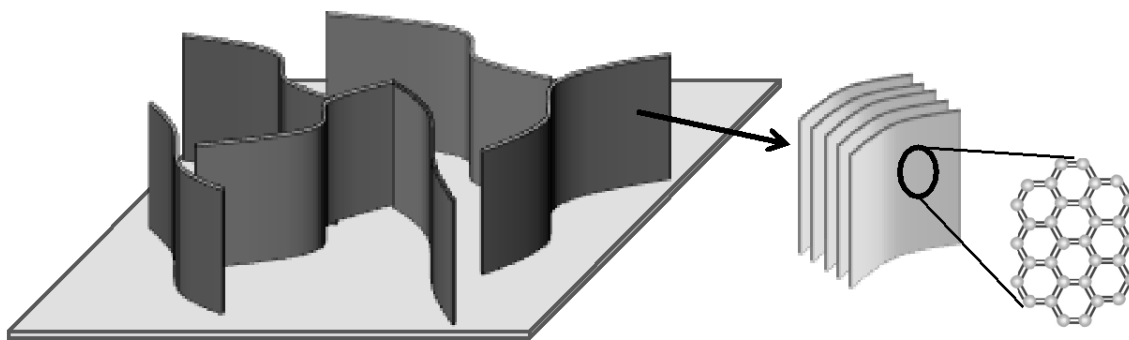


Figure 1-3 Schematic of vertically aligned CNWs. Image adapted from [94].

CNW can be synthesized both as a 2D and 3D material [106,107]. The 3D CNWs have made the realization of its application in electrochemical capacitors which reportedly has shown enhanced properties compared to its 2D counterpart [102,108,109]. The vertical alignment of graphene stacks also indicates that CNWs can be used as electrode if grown with controlled physical and electrical characteristics [94].

CNWs can be synthesized by both catalytic and non-catalytic method while its growth has been primarily dependent on PECVD technique. Many PECVD based synthesis methods such as microwave [94,106,110–112], radio frequency sputtering [98], capacitive coupled [95], inductive coupled [113,114], radical injection [115–118], electron beam excited plasma [119], helicon discharge [120], DC plasma [121] etc. while the main precursors used in the synthesis of CNWs are CH_4 [120], C_2F_6 , C_2F_4 , CHF_3 etc. since it was the first synthesis was reported by Wu et al. Wang et al [114] reported the synthesis of freestanding carbon nanosheets (CNS) on substrates, such as Si, W, Mo, Zr, Ti, Hf, Nb, Ta, Cr, 304 stainless steel, SiO_2 and Al_2O_3 without catalysts or special substrate treatment using radio frequency PECVD.

One of the main reasons behind using PECVD technique for the growth of CNWs is controllability of nucleation sites and surface morphology. The ease of growing the carbon nano structures at relatively lower temperature with reproducibility enables PECVD technique suitable for large scale production.

Researchers have investigated the doping of CNW with nitrogen, for the measurement of the change in electronic properties [97,118,122,123]. Undoped CNWs show p-type conductivity since major carrier conduction is through positive hole and mobile π electrons would be easily trapped by the defects. Shimoyama et al reported

that N atoms can substitute C atoms and act like a donor in graphitic crystal structure [124]. Cho et al reported that the electrical conductivity of walls increases for first 30 seconds by treatment of nitrogen plasma while it starts decreasing after the additional treatment time [122]. The n-type conductivity was observed by addition of nitrogen atoms in the crystal and the deposition temperature has been found to be dominant for increasing the sp^2 cluster size and crystallinity over Ar or N_2 gas concentration [117,122,125].

The properties of CNWs are determined by length, height and thickness of the walls [126]. Height of a CNW varies from 1.5-3 μm while its thickness may vary from 5-10 nm on an average as reported till date [95,126]. Both the uniformity and density are also very important deterministic properties of the CNWs as reported by Kurita *et al* [126] and Hiramatsu et al [95]. In addition, high carrier density and large surface area make CNW suitable for various applications.

One of the major challenges in the synthesis of CNW is its controlled growth. The control over height, length and thickness of the walls, film uniformity, defects in the film are still a major challenge due to spontaneous growth of CNWs. In the process of improvement of quality of the film, a change in electrical properties such as decrease in carrier density and increase in mobility have also been investigated [117,127].

The vertical growth of graphene paves the way for curled structure of the walls rather than the required straight structures. Usually the density of nucleation sites decides the height and thickness of the wall at ambient temperature. Furthermore, the catalytic growth is rapid and gives rise to uneven morphology comprising length, height and thickness of the wall. Controlling the nucleation sites with moderate growth should lead to the aligned structure.

1.4 Chemical vapor deposition (CVD) process

Chemical vapor deposition (CVD), as manifested from the name, is a chemical method for depositing thin films. In the CVD method, the substrate is exposed to one or few volatile precursors. The precursor molecules are decomposed into radicals after supplying a certain amount of energy by heating or other energy sources. These radicals are further dissociated and settled on the substrate's surface to produce desired deposit.

In the process, the precursor molecules are brought in the proximity of the substrate surface by carrier gases. The unwanted byproducts after the bond dissociation are removed outside the CVD system by these gases [128,129].

CVD technique has been largely used in semiconductor industry for growth of polycrystalline, amorphous and epitaxial Si, SiO₂, SiGe, Si₃N₄, TiN, nano-carbons and other 2D materials and even in the production of synthetic diamond

Some of the popular forms of CVD methods for thin film synthesis are thermal CVD; both advance pressure (AP) and low pressure (LP), atomic layer (AL) CVD, metal organic (MO) CVD, plasma enhanced (PE) CVD, microwave plasma assisted (MW)CVD, remote plasma enhanced (RPE) CVD, ultra-high vacuum (UHV) CVD etc.

1.4.1 Plasma Enhanced CVD process

Physics of plasma

Word “plasma” usually indicates a system of charged particles that can correspond collectively. Plasma is collection of free charged particles that move randomly thereby they are charge neutral. Some of the important features of plasma are:

- (1) They are electrically neutral
- (2) There should be charged particle collision with neutral gas molecules
- (3) Surface losses at boundaries are important
- (4) Electron and ions are not in thermal equilibrium state

Plasma is also considered fourth state of matter in which a gas is in ionized form [130]. It implies that at least one electron has been removed from the atom/molecule/group of molecules. Plasma strongly interacts with electromagnetic field due to presence of free charge particle. Plasma is closely related to gas phase as it does not have a definite volume. Plasma is widely considered to be more than a gas although the presence of gas is necessary for plasma generation. Even a partially ionized gaseous system, wherein as little as 1% of particles are ionized, can behave as plasma in the presence of magnetic field since it is highly conductive [131,132].

Usually the characteristics of plasma are determined by Debye screening length which is short as compared to physical size of plasma. This depends on the large number of particles within sphere with a radius of Debye length and mean time between the collisions is long when compared to the periodic plasma oscillations.

The degree of ionization is one the most important parameters for plasma generation. In the process, UV radiation, energetic particles or strong electric field can be used. However, the electrons are ionized by heating gaseous molecules in such a way that they are close to thermal equilibrium with electrons.

The plasma is termed as cold plasma if only a small fraction (1%) of gas molecules are ionized. The ionic temperature in cold plasma is near ambient temperature although the energy of electron is equivalent to several thousand degrees in such condition. These plasma are technologically used by often creating very high electric field to accelerate electrons in order to ionize gaseous atoms/molecules.

Hot plasma, on the other hand, are nearly fully ionized. These are found in Sun and actually called fourth state of matter. The temperature of electrons and ions is nearly same in hot plasmas.

Another most important parameter for plasma generation after temperature is plasma density that usually refers to free electron density in a cross section. The ion density is related to this by average charge state $\langle Z \rangle$ of the ions through $n_e = \langle Z \rangle n_i$; where n_e is density of electrons and n_i is the density of atoms at i -th state of ionization. The third important quantity is density of neutrals n_0 . The quantity n_0 is small in hot plasma but plays an important role in its physics. The degree of ionization is $(n_i / n_0 + n_i)$.

Electric potential plays an important role in plasma physics for plasma being good conductors. The potential (Φ) in a plasma is measured as the average space between two charged particles. It can also be called space potential. If an electrode is introduced, the plasma potential will generally lie considerably below to Debye sheath. Electric fields in the plasma are generally very small to carry out good electrical conductivity of plasma. The density of neutral plasma must be very low, otherwise it will be dissipated by the repulsive electrostatic force.

1.4.2 Microwave plasma

The limitations of capacitive driven RF discharges and their magnetically enhanced variants have led to the development of generation of low pressure high density plasma sources [133]. The high density MW plasma has many advantages over capacitively coupled RF plasmas [133,134]. A few advantages of MW plasma are:

- (a) No electrode is required which removes the source of contamination.
- (b) MW power can be directed to target area precisely which prevents from unwanted radiation loss to external source and allowing high density plasma generation.
- (c) Change in gas pressure does not change the plasma discharge.
- (d) The impedance can be matched using simple components as MWs are transmitted by a waveguide.

However, traditional PECVD processes are widely used in industries over MW plasma due to limited area growth of MW plasma, lack of uniformity and higher reflectance of MWs in the absence of external magnetic field when the plasma density is higher than cut-off density ($7.5 \times 10^{10} \text{ cm}^{-3}$ for 2.45 GHz) [135]. This creates difficulty to generate over-dense plasma. These problems are tackled using electron cyclotron resonance (ECR) and surface-wave excited plasma (SWP) which will be discussed next.

1.4.3 Surface wave plasma (SWP)

Microwave plasma sources were not considered suitable without magnetic field in the generation of high density plasma for a long time. Electromagnetic waves are reflected at the plasma surface due to the skin effect and turn into an evanescent wave. Since the penetration depth of evanescent wave is non-vanishing, it opens an alternative way to heat plasma by coupling the conducting plasma to propagate along the surface of plasma. In the process, the traversing of plasma is not required. The evanescent wave transfers the wave energy to the plasma in such a way that the energy enters perpendicular to the surface and decays exponentially with increasing skin depth. This energy transfer mechanism by evanescent waves permits the generation of over dense plasma having electron density exceeding the critical density. The plasmas excited by this method i.e. by the propagation of electromagnetic waves, are called surface waves (SW) [136,137]. Surface wave plasmas (SWP) are divided into two groups based on the generation of plasma by its own waveguide by ionization and non-ionization. The ionized plasma is called self-guided plasma. The SW mode generates uniform high-frequency plasma in large volumes whose side-wise dimensions stretches over several wavelengths of the electromagnetic wave, e.g. the wavelength adds to 12.2 cm

for microwaves of 2.45 GHz.

SWP can be operated in a large variety of recipient geometries. The pressure range accessible for SWPs depends on the process gas and the diameter of the recipient [138–140]. The larger chamber diameter and the lower and minimal pressure are necessary for SWP mode. Analogously, the maximal pressure where a stable SWP can be operated decreases with increasing diameter. The numerical modeling of SWP is quite involved plasma is created by the electromagnetic wave, but it also reflects and guides this same wave. Therefore, a truly self-consistent description is necessary.

Considering the aforementioned synthesis-challenges in the obtained film of graphene based materials i.e. CNW and h-BN, different methods for material's synthesis have been performed which will be discussed next.

Chapter2.

Experimental procedure

2.1 Carbon nanowall's synthesis

2.1.1 Substrate patterning

Silicon substrate having 500 nm SiO₂ layer was put under etching process for patterning. The substrate was carved in line and space patterns. In the process, it underwent electron beam lithography (EBL) using ZEP-520A etching mask. The resist was etched away by reactive ion etching (RIE) method using CF₄ etchant. 12 minutes of etching was performed under 100 W of plasma power while the depth of pattern was obtained to be 300 nm. The convex pattern was etched with a width of 400 nm while the concave width was 600 nm for FET structure.

2.1.2 Growth of CNW by microwave plasma CVD

CNW was grown at the temperatures of 400 °C and 500 °C by plasma enhanced CVD (PECVD) method. The deposition time was chosen for 30 minutes for each growth experiment.

In another set of CNW synthesis experiment, CNW was deposited on the patterned substrate at 400 °C. Half of the substrate was covered by a movable plate. Instead of taking out the sample from the chamber, another layer of CNW was deposited above the layer at 500 °C. Thus the layer grown at 400 °C at the bottom served as a buffer layer of CNW grown at lower temperature. In the process, the movable plate was slid back and the synthesis was let to occur on the entire substrate. We termed CNW film grown above its low-temperature buffer (LTB) layer as “L-CNW” while the CNW film grown directly above SiO₂ substrate will be termed as “as-CNW” which is abbreviation for “as-grown CNW”. The same terminology will be used in entire thesis.

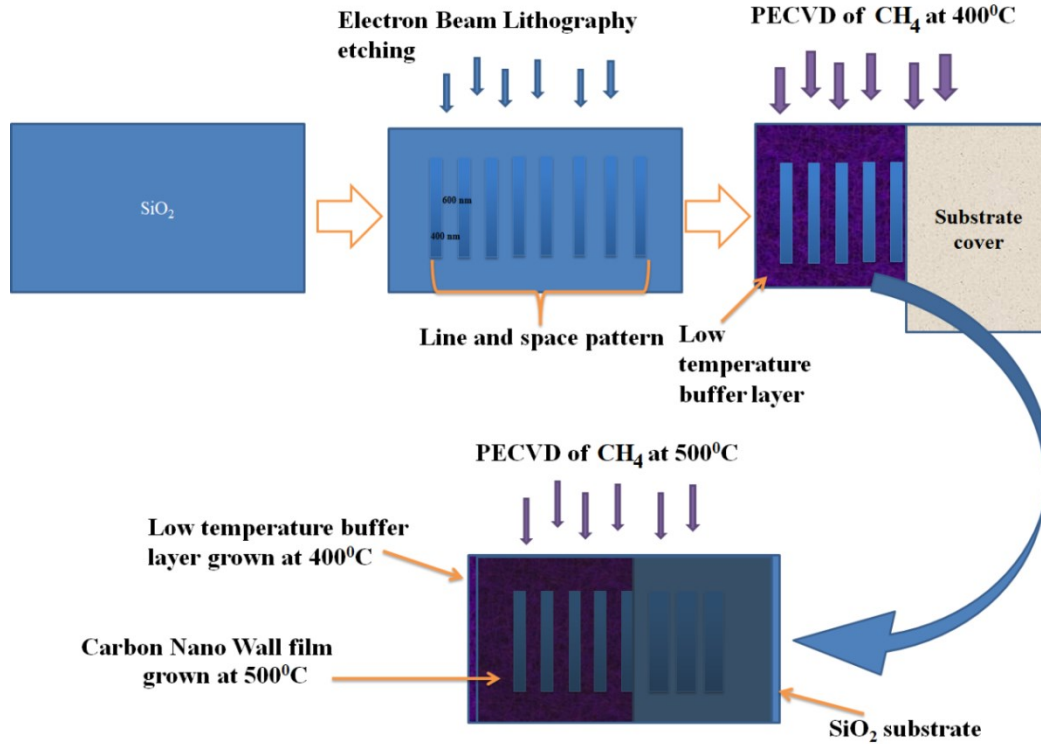


Figure 2-1 The schematic of CNW grown at its LTB layer. Line and space pattern was carved for CNW's application as a channel in FET structure.

2.1.3 Electrode preparation for CNW channel

Au electrode was prepared on Ti buffer layer by electron beam evaporation method as drain and source contact for the measurement of electrical characteristics. Ti layer was chosen for the better adhesion with CNW channel [141]. The film grown outside the patterned region was etched out using oxygen plasma for 3 minutes using 100 W plasma power in photolithography process. The effects of H_2 etching prior to electrode deposition using the inductively coupled plasma chamber were also examined.

2.1.4 Plasma treatment of CNW channel

The as-CNW sample was brought under plasma treatment for the electrode fabrication by RIE method. In the process, it was first treated by oxygen plasma at the power of 100 W by photolithography process in order to etch out the CNWs grown outside the channel region. The O_2 plasma etching was continued for 3 minutes and the CNW grown outside the channel region was cleanly removed. Thereafter, the sample was

further treated by H_2 plasma in order to improve the contact between the channel and electrodes.

2.2 Synthesis of h-BN by MW-SW-PCVD

2.2.1 h-BN synthesis under Ar and Hydrogen gas.

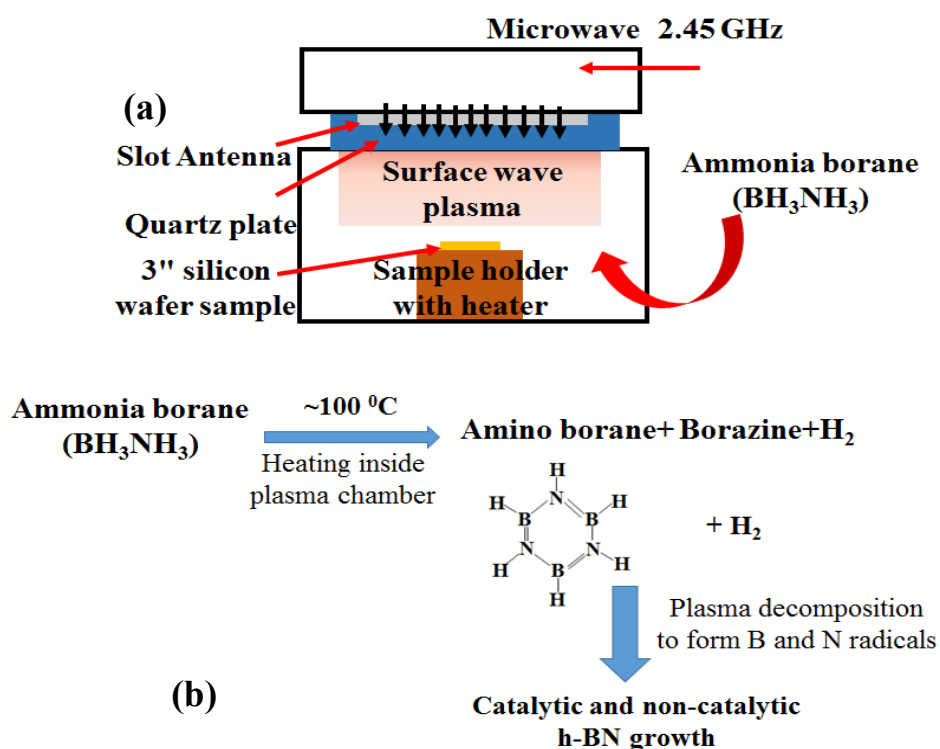


Figure 2-2 (a) The schematic of MW-SW-PCVD system. (b) The bond dissociation mechanism of ammonia borane.

Ammonia borane (AB, Sigma Aldrich, 20 mg) was used as precursor for the synthesis of h-BN film by the microwave assisted surface wave plasma CVD (MW-SW-PCVD) process. Silicon wafer of 3 inch diameter was chosen as non-catalytic substrate, while Cu was coated on another Si wafer by thermal evaporation technique and was taken for catalytic growth. Both the Si wafers were cleaned by acetone and ethanol to remove the surface impurities. The substrates were placed inside the MW-SW-PCVD chamber heating holder as shown in figure 2-2 (a). The sample holder is attached to the rod and its height can be adjusted digitally. The heating rod of the sample holder in

MW-SW-PCVD system is around 9 inches from the base of the CVD chamber as depicted in figure 2-2 (a). The precursor is kept at the bottom of the sample holder and it is stuck with the rod by inclining the precursor-boat using an alumina plate at its (boat) base. The chamber is slowly closed so that the boat should not slide from the alumina plate to maintain the connection between the rod and boat. In this way, heat is transferred to AB powder by convection method.

The PCVD chamber has perforated quartz plate which is used for plasma generation. The perforated quartz plate helps in producing plasma without any density fluctuation and generates two times higher plasma density as that of flat quartz plate [142]. Following the advantage, high density surface wave plasma can be generated in meter-scale and large scale deposition can be achieved comparatively faster than other plasma CVD methods. The CVD chamber was evacuated to a base pressure of 4.1×10^{-4} Pa and substrate temperature was set at 500 °C for deposition. The precursor was kept below the stage in a boat clung to it so that it could be sublimed by heat of the substrate holder. Since the distance between substrate holder and quartz plate was kept fixed, the gap between precursor's boat and the substrate holder also remained fixed (10 cm). The substrate holder starts heating first. The heat reaches to the bottom of the holder and transferred to the precursor.

The deposition was carried out diluting evaporated AB by Ar and H₂ of 100 sccm and 5 sccm flow rates, respectively. The growth duration was 3 minutes with a fixed microwave power of 1000 W.

2.2.2 Heating test of h-BN film

The deposited sample was taken to heat test where it was put on hot plate at 150 °C for 15 minutes as shown in figure 2-3. An elaborated explanation of heating test is mentioned in chapter 7 section 7.3.1.1. The sample deposited on Cu substrate was transferred on SiO₂ by wet etching method that will be discussed next.

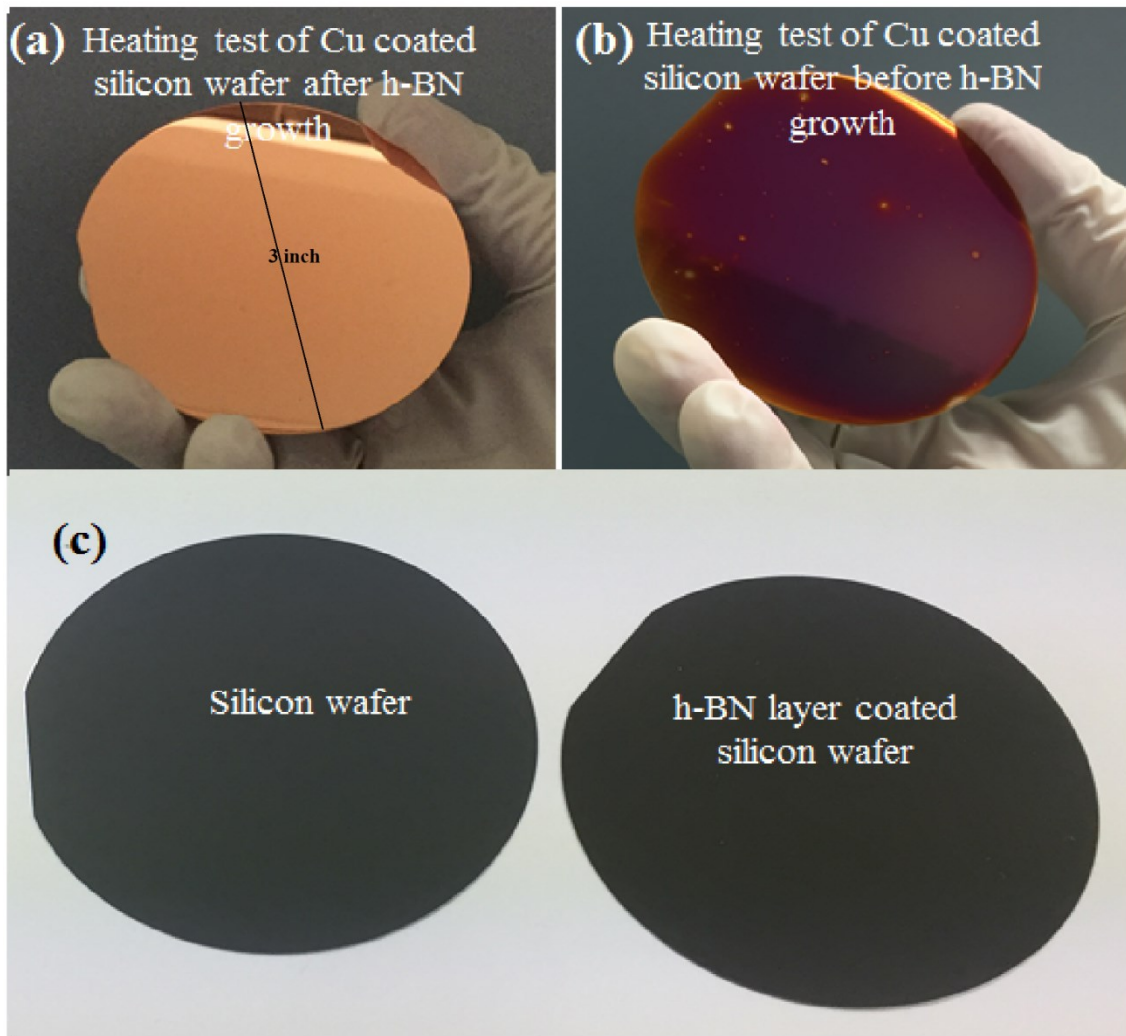


Figure 2-3 The heating test of AB. (a) the wafer is covered by AB layer so Cu could not get oxidised. (b) The bare Si/Cu substrate after heating test. (c) Si wafer pre and post deposition of h-BN layer.

2.2.3 h-BN transfer on target substrate

The schematic of transfer process is shown in figure 2-4. After putting the sample for heating test, the film was transferred to desired substrate by wet-etching method which is also used for graphene transfer from Cu to another substrate. 0.1 M poly methyl meth acrylate (PMMA) dissolved in acetone solvent was spread over the sample by spin coater (3000 rpm) for 1 minute and then sample was put inside hot air oven for 10 minutes in order to dry out the PMMA film on h-BN sample. The drying ensures a robust adhesion between both PMMA and h-BN films. The rear side of PMMA coated

sample was partly scrubbed by the sand paper of softer quality in order to remove any backside synthesis of h-BN film. The sample was put in 0.5 M $\text{Fe}(\text{NO}_3)_3$ solution in water solvent and left for slow etching for three hours. The floating h-BN/PMMA film was rinsed in de-ionized water (DIW) four times before transferring on SiO_2 substrate. The purpose of multiple rinsing is to remove the remains of cohesive $\text{Fe}(\text{NO}_3)_3$ solution from the bottom of floating h-BN/PMMA film. The number of rinsing might increase in case of any yellow stains which are imparted from $\text{Fe}(\text{NO}_3)_3$ solute, do not disappear from floating h-BN/PMMA film. Another way to remove these stains is by dipping the h-BN/PMMA film into dilute HNO_3 (Nitric acid) solution since it reacts rapidly with $\text{Fe}(\text{NO}_3)_3$ solution. However, HNO_3 -rinsing process is usually avoided because it affects the properties of the film [143].

The adhesion between film and substrate is made sure to be airtight by removing all the water between SiO_2 /h-BN/PMMA junction. Even a tiny water or air droplet inside the junction might give rise to wrinkles and break the film once it gets dried. The sample was once again put inside hot-air oven for 15 minutes for airtight adhesion of h-BN/PMMA film on SiO_2 film. The PMMA layer was then removed using hot-acetone at 90 °C by multiple rinsing.

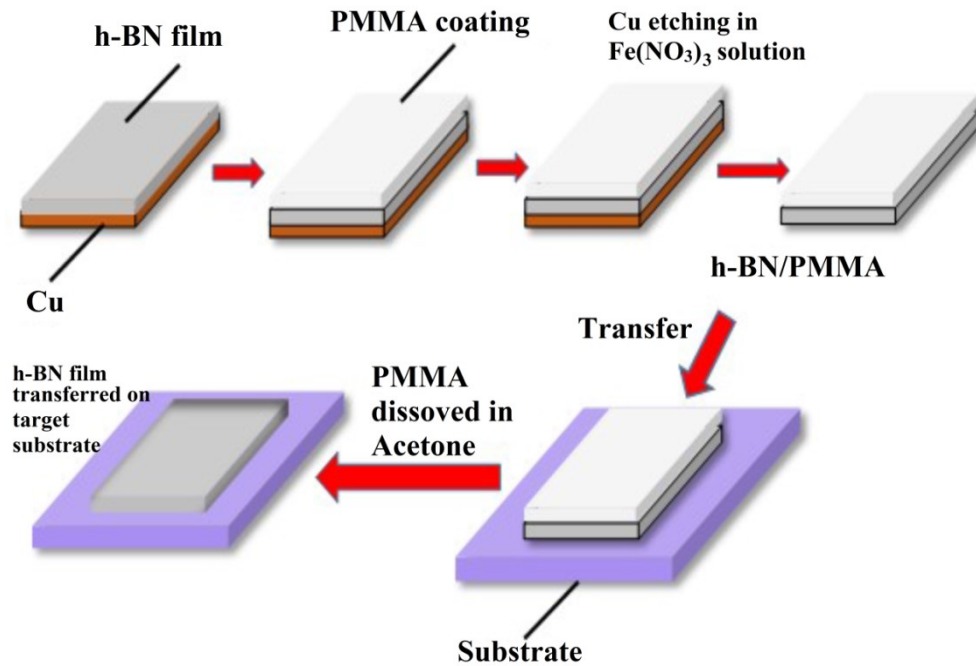


Figure 2-4 The schematic of wet etching transfer process of h-BN from Cu to target substrate.

2.2.4 h-BN film characterization

The sample was characterized by fourier transform infrared spectroscopy (FT-IR) technique using JASCO IRT-500 FT-IR microscope, followed by X-ray photo spectrometer (versa probe, monochromated Al K α excitation source of 1486.6 eV). The uniformity of h-BN film was observed by digital microscope (VHX-500, Eyence) with a Moticam 2000 2.0 mega pixel camera. It was further analyzed by field emission scanning electron microscope (FE-SEM, JEOL, JSM-7800F) keeping the accelerating voltage at 5 kV. The ultraviolet visible (UV-Vis) spectroscopy for absorption measurement was performed using JASCO-V670 UV-VIS-NIR double beam spectrophotometer which features the monochromator with dual grating. Tauc plot technique was used to determine the optical band gap of sample. The sample was also investigated by transmission electron microscope (TEM) using JEM-2100F with accelerating voltage of 200 kV.

Chapter3.

Characterization techniques

3.1 Ultraviolet-Visible (UV-Vis) Spectroscopy

This nondestructive characterization method is widely used for transparent solid and liquid molecules containing π bonds or non-bonding electrons since they undergo the transition in UV region. The transition from ground state to excited state is measured after the molecule absorbs the incident photon. The references are chosen as solvent in case of liquid and base substrate for solids. Both transmittance and absorbance of light from UV-Visible range can be measured. The chemical bonding in material determines the interaction of light with the sample.

In case of h-BN, the absorption peak is found near 215-217 nm [144,145] which lies in far ultra-violet region and enables the material for application as UV detectors [146,147].

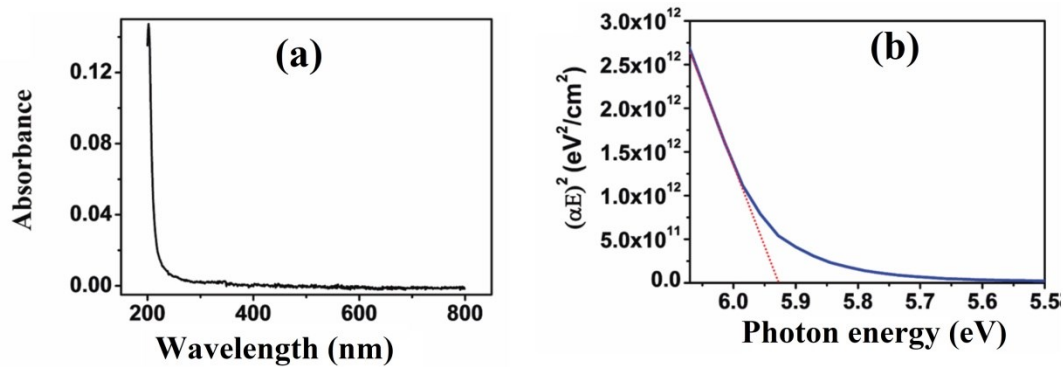


Figure 3-1 UV-visible absorption spectra and optical band gap analysis: (a) optical absorption spectrum of h-BN thin film transferred onto a quartz substrate; (b) optical band gap analysis from (a). Image adapted from [148].

UV-Vis is also used for determination of optical band gap in a material using Tauc plot as shown in figure 3-1 (b) which is mentioned in results and discussion section in chapter 7.

3.2 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR is an absorption spectroscopy in which the absorption of light at every wavelength is measured by shining the beam of light containing multiple frequencies and the absorbed proportion of beam is measured. The process is repeated with combination of multiple frequencies and the data is evaluated.

Both in-plane and out of plane vibrations are taken into account which gives rise to different peaks. Any impurity inside the crystal lattice disrupts the vibrations and therefore the vibrionic tone changes. A base substrate is needed to measure the background first. The absorption spectrum of film is measured in infrared region. In figure 3-2, the absorption peak near 1350 cm^{-1} is attributed to E_{1u} in-plane sp^2 B-N stretching vibrations and the peak at 817 cm^{-1} was corresponded to A_{1u} out of plane B-N-B bonding vibrations in h-BN [149].

In the earlier days of FT-IR measurements, transmittance measurement was a common method which was later adopted by the automatic conversion into absorbance after the arrival of microprocessors. Absorbance is a logarithmic scale measurement which enables the detection of weak signal adjacent to a strong signal. One of the major advantages of using absorbance scale instead of transmittance scale is that the absorbance scale allows the measurement of more intensive bands. A similar band in transmittance scale have distorted maxima.

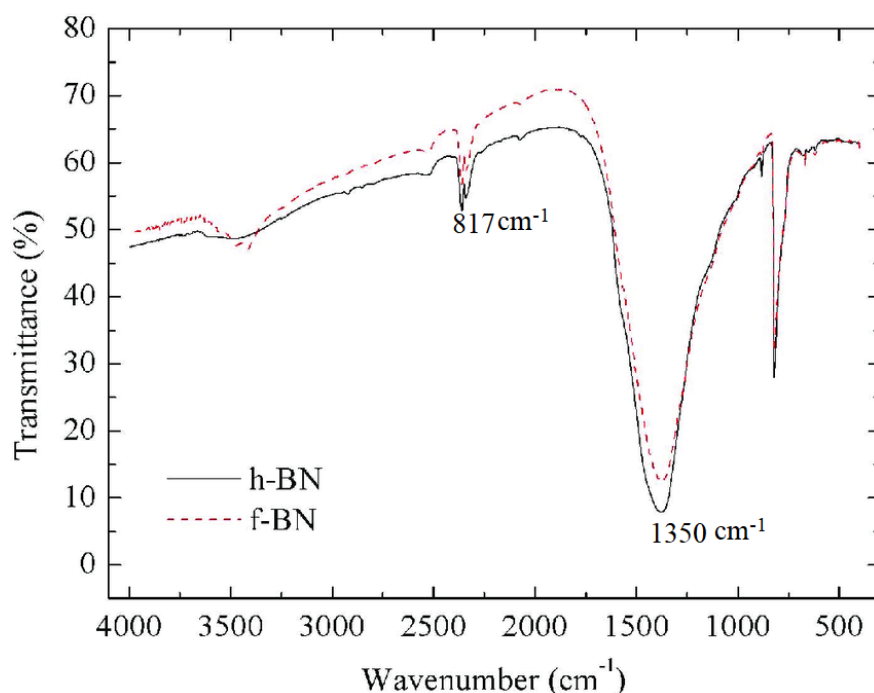


Figure 3-2 FT-IR spectra of h-BN vs polydopamine-funtionalized h-BN [150].

3.3 Raman Spectroscopy

Raman spectroscopy is the most widely used tool for investigation of the crystallinity of any material. The molecular vibrations due to incident energy by laser, are taken into account wherein inelastic scattering of monochromatic light are measured and spectra is taken by knowing the energy shift of scattered light relative to incident light. This technique measures vibrational, rotation and other low frequency modes in a molecular system. Vibrational mode describes long and short range crystallinity of materials. In addition, the nature of surface contaminants, grain size and crystal orientation can also be figured out by seeing the Raman spectra of a sample.

When a monochromatic light scatters in-elastically due to interaction with phonons, Raman scattering occurs. In other words, Raman scattering is the result of collision between photon and phonon wherein photon gets excited into higher (blue-shifted) and lower energies (red-shifted) while phonon returns to its original state in the crystal. In the process, higher energy possessing scattered-photon undergoes scattering known as anti-stokes scattering while the lower energy carrying photons undergoes stokes

scattering. Raman scattering is a very weak phenomena and occurs around 1 in a millions of incident photons.

Raman spectra of CNW is loosely based on the spectra of graphene. Single layer graphene is associated with longitudinal optical (LO) phonon mode that is found at 1580 cm^{-1} and is called the G band [151,152]. The second order dispersive Raman feature is called 2D band (or G' band) whose frequency depends upon laser's excitation energy and appears at 2700 cm^{-1} . A disorder-induced peak in graphene is obtained around 1350 cm^{-1} while other two phonon defect assisted processes such as D', D+G and 2D' are obtained near 1620 , 2900 and 3250 cm^{-1} respectively [153] as shown in figure 3-3. Both D and D' bands originate from inter and intra-valley double resonance.

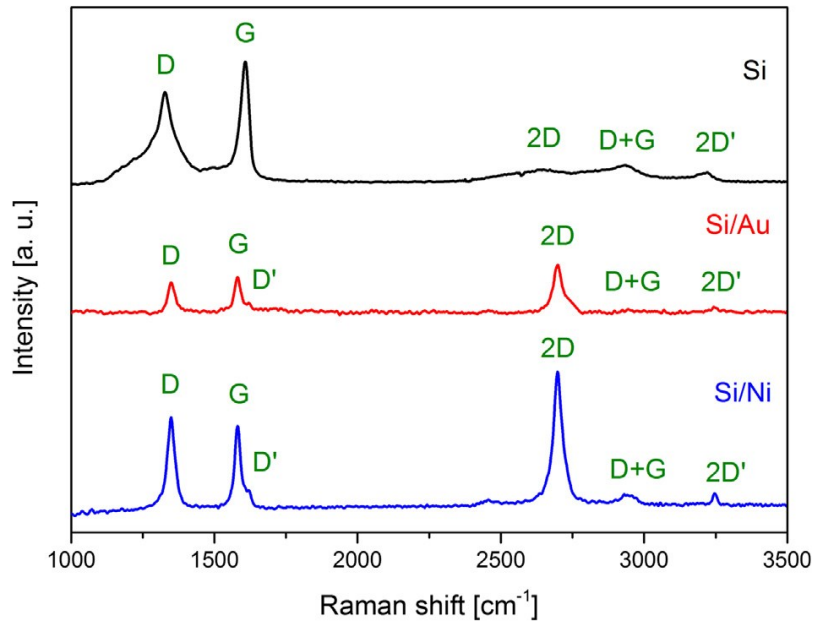


Figure 3-3 Raman spectra of carbon nanowalls grown on different substrates: Si, Si/Au, Si/Ni. [154].

Both intensity and width for G and 2D band change with change in number of layers [155] as shown in figure 3-3. An equal intensity of G and 2D band signifies a bilayer graphene while a 2D band double than G band represents single layer graphene. Furthermore, graphene with finite size has different kinds of edges with special shapes, stacking disorder between two layers and atomic defects with the layers which gives rise to D band around 1350 cm^{-1} . Thus seeing the width and intensity of D-band the impurity in crystallinity of a sample can be detected. 2D band broadens out with

increasing number of layers.

In case of CNWs, the disorder can not only be caused by the aforesaid reasons but also due to deformation in the shape of the wall which induces scattering of carriers. An elaborated explanation of Raman spectra for CNW film is given chapter 4 in section 4.3.2.

3.4 Scanning Electron Microscope (SEM)

This characterization method involves the scanning of h-BN film (or any other material) using high energy beam of electrons across the surface. The resolution of SEM features up to few nano-meters which makes it impossible to obtain the atomic resolution. However, this method provides useful information about 2D materials and other thin films grown by CVD process. [46,156].

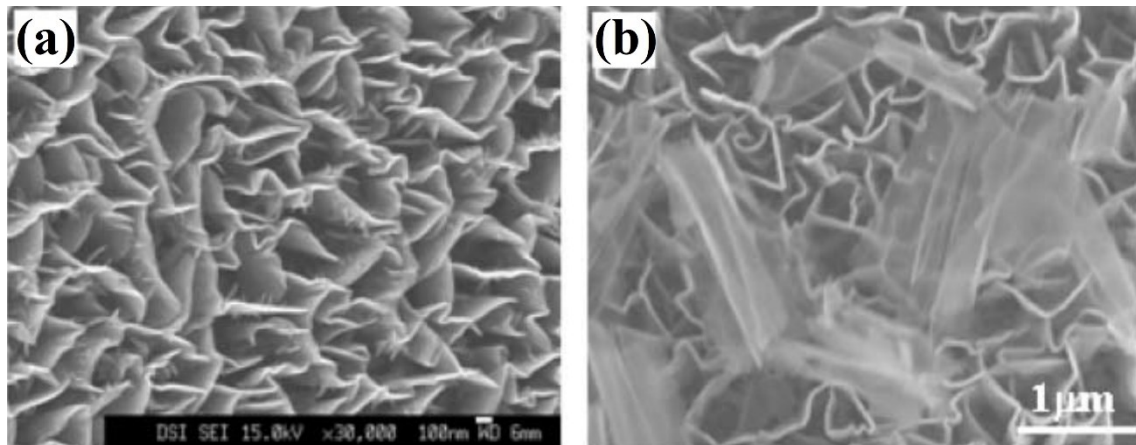


Figure 3-4 SEM image of CNWs. Scale bar (a) 100 nm (b) 1 μm. Image adapted from [157].

3.5 Transmission Electron Microscope (TEM)

The resolution of TEM goes down to atomic scale that makes it very useful tool for 2D films characterization. TEM is the electronic analog of optical microscopy; electrons go through the sample and the interaction between thin film and electrons is collected by detector. Since the de Broglie wavelength of electrons is much smaller as compared to visible light, much smaller features can be resolved. TEM provides the best images of

the structure of single and bi-layer h-BN films.

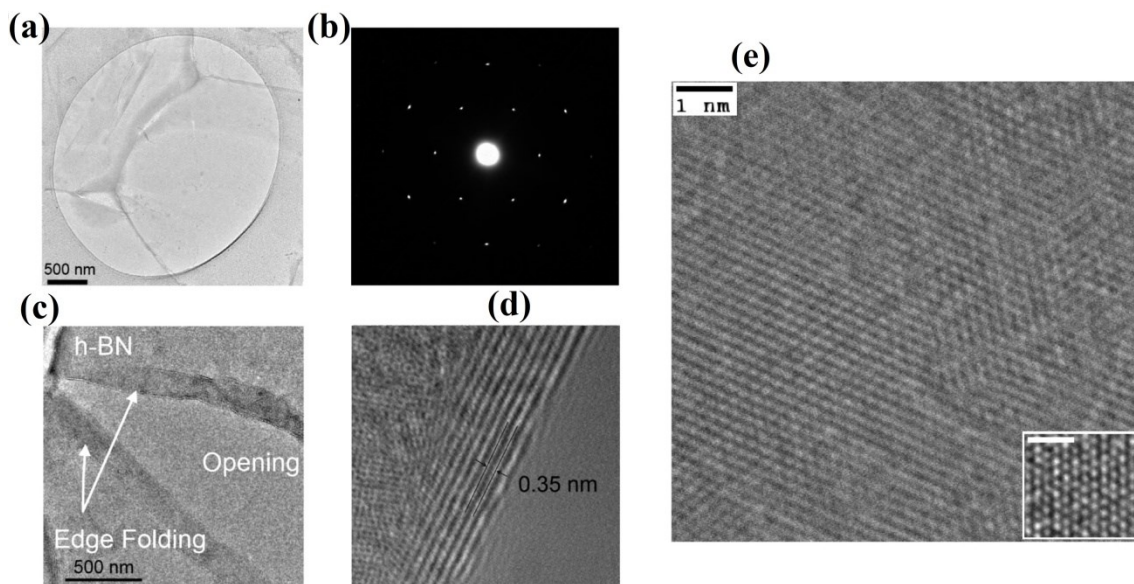


Figure 3-5 TEM images of a h-BN thin film: (a) low-magnification TEM image showing a CVD-grown h-BN thin film on a Quantifoil holey carbon grid; (b) electron diffraction pattern of the h-BN thin film taken from a freely suspended region; (c-e) TEM images of the h-BN thin film under different magnifications. (c) TEM image showing a broken part of the h-BN thin film and the edge folding. High-magnification TEM image showing the edges (d) and the surface region (e) of the film, with the inset of figure (e) showing a close-up high resolution TEM image on the h-BN surface, and the scale bar is 1 nm. Image adapted from [148].

3.6 X-ray Photoelectron Spectroscopy (XPS)

This surface sensitive characterization technique enables the determination of bonding nature of atoms in a material (film or powder). XPS provides information about both chemical and electronic state that are useful to determine the crystallinity in compound semiconductor films [158–161]. XPS spectra is obtained by irradiating x-rays on a film and simultaneously measuring the number of electron escaped in a range of 0 to 10 nm of material along with their kinetic energy. Each element possesses a unique characteristic peak for a specific bond in a compound. These peaks correspond to the electronic configuration of electrons within an atom. This characterization is very useful for the determination of crystallinity of h-BN. Usually BN can attain many other forms

of bonds in crystal lattice, based on the deposition conditions.

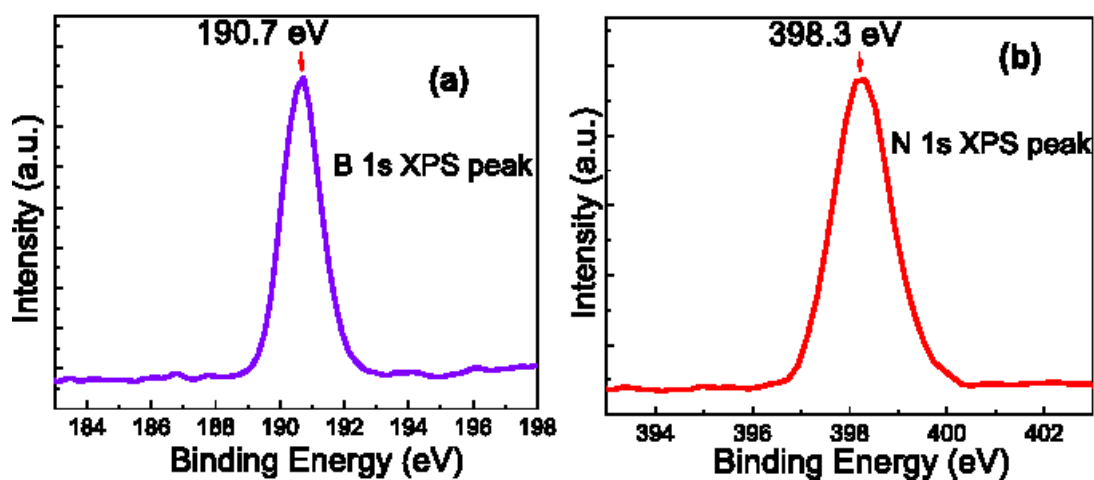


Figure 3-6 XPS image of h-BN showing (a) B 1s and (b) N 1s peaks. Figure adapted from [146].

The XPS data is calibrated corresponding to carbon peaks obtained in the multiple samples prior to curve plotting. The XPS data for carbon is plotted first for all the samples and the obtained values of binding energy are compared. The difference from the minimum value obtained sets out the adjustment in peaks for other atoms. Thus both B 1s and N 1s peaks for different samples are adjusted based on the values obtained for their carbon's binding energy and the difference from the lowest binding energy of carbon among them.

Chapter4.

Effects of low-temperature buffer on the growth of carbon nanowalls

4.1 Introduction

The synthesis of CNWs has primarily been dependent on PECVD method where various methods such as DC plasma, RF plasma, microwave plasma, capacitive coupled plasma etc. have been used for its synthesis on both catalytic and non-catalytic substrates within a temperature synthesis range of 450-700°C [94,97,104,105,116,157,162,163]. The synthesized film has demonstrated semiconducting properties as reported by various research groups [164,165]. The semiconducting property in CNW pertains to several reasons such as amorphous carbon layer at the bottom of the substrate during its initial period of growth, the graphitic edges during formation of the walls and poor crystallinity of materials. These properties hinder the migration of carriers in the structure. Both semiconducting behavior and position control during growth delimits the application of CNW as an electrode. Thus I aimed for synthesizing the defect free CNW film non-catalytically at relatively lower temperature.

Kawahara et al reported non-catalytic growth of CNWs by PECVD method at 400-600°C where the film demonstrated metallic properties even after self-alignment process that gives rise to strain in the structure [166]. The graphitization was reported to dominate over the strain of material at high temperature growth. Under similar growth conditions at lower temperature of 400 °C and 500 °C, CNW showed non-linear characteristics. Following the same process, a layer of CNW was grown at 500 °C while its buffer layer was grown below the same film at 400 °C. The buffer layers such as metal oxides and molecular layers, have been previously used in atomic layer deposition process in semiconductor growth [167–169]. The motivation behind using these layers was to establish a different layer for the nucleation of precursor radicals.

In this chapter the characterization results of CNW grown above its low-temperature buffer (LTB) layer, with the CNW film grown directly on the non-catalytic Si/SiO₂ substrate (as-CNW) will be compared.

4.2 Materials and methods

The synthesis method of L-CNW has been mentioned in chapter 2 section 2.1. The electrode preparation for CNW channel is mentioned in section 2.1.3.

The heavily doped n-type Si substrate (As-one, (100)-plane, 0.02 Ω .cm) acted as back gate contact and a suitable FET structure was fabricated. The current-voltage (I - V) characteristics were measured by the semiconductor device analyser B1500 from Agilent technology. A step interval of 1V was kept for the gate voltage (V_G) measurement between -5 V to 5 V. Drain-current (I_{DS}) along with constant drain-voltage (V_{DS}) was also measured under the dependence of V_G .

4.3 Results and discussion

4.3.1 SEM observation

The morphology of the CNW film was studied using SEM characterization technique. Figure 4-1(a) shows the CNWs grown spontaneously outside the pattern on SiO₂ substrate. The randomly oriented structure can be seen from figure 4-1 (a). This image shows the natural structure of CNWs synthesized under non-catalytic growth method. In figure 4-1(b), the natural curled structure can be seen marginally elongated along the geometrical patterns. The top and angular views of SEM have been shown in figure 4-2.

Kawahara et al reported that diminishing a substrate area favours the alignment in structure of the walls [166]. This phenomenon occurs due to higher probability density (PD) of precursor molecules at the crests (line pattern) of the substrate whereas the PD at the troughs (space pattern) decreases drastically. In figure 4-1, the self-alignment of CNWs is caused by the geometrical patterns carved on the substrate. The lined pattern is in convex form and thus it causes high PD of molecules as compared to the space pattern which has concave surface. The high PD leads to agglomeration of molecules at

the top surface of convex pattern. As a result, the precursor molecules present in the middle of convex pattern might give rise to the curl structure if there is adequate space available for both nucleation and agglomeration [94,104,114,165]. However, such a growth possibility was ruled out due to the narrow width (400 nm) of pattern. Subsequently, the walls were aligned along the edges of the structure while a minor growth of CNWs was observed in the space pattern.

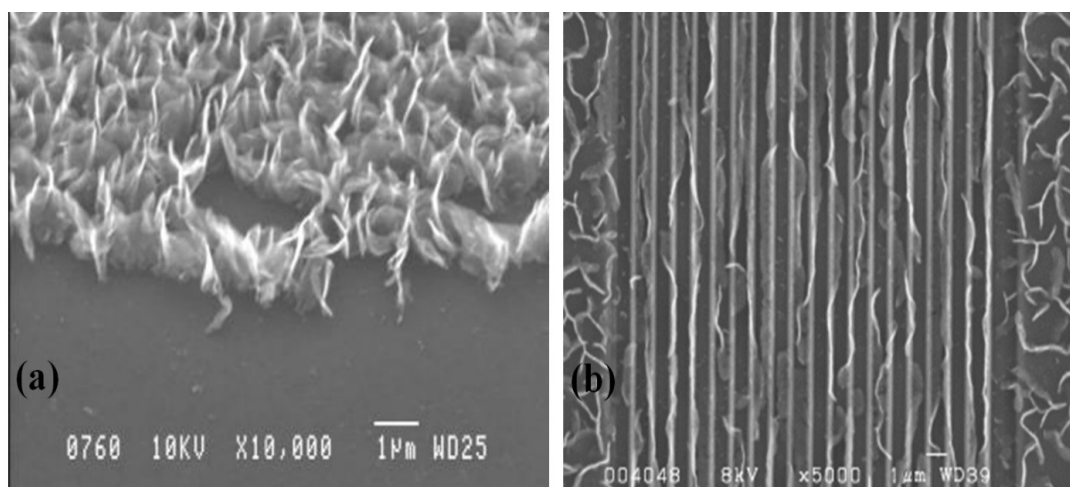


Figure 4-1 SEM image of (a) CNWs grown outside the pattern region and (b) self-alignment of CNWs in the pattern region.

Thereby it was deduced that the line and space pattern acts as geometrical catalyst that favours directional growth of CNWs by inhibiting the required surface area for the nucleation [170]. It was reported that the growth of flakes on the edge of the processed pattern at 400°C was minor and randomly oriented while a growth on 600 °C showed comparatively straight structure on the patterns [166]. In the experiment, the flakes of comparable size were obtained at 500 °C for above LTB layer. In addition, LTB showed similar self-aligned structure at 500 °C which was previously obtained at 600 °C. This result advocates for the catalytic effect of LTB layer.

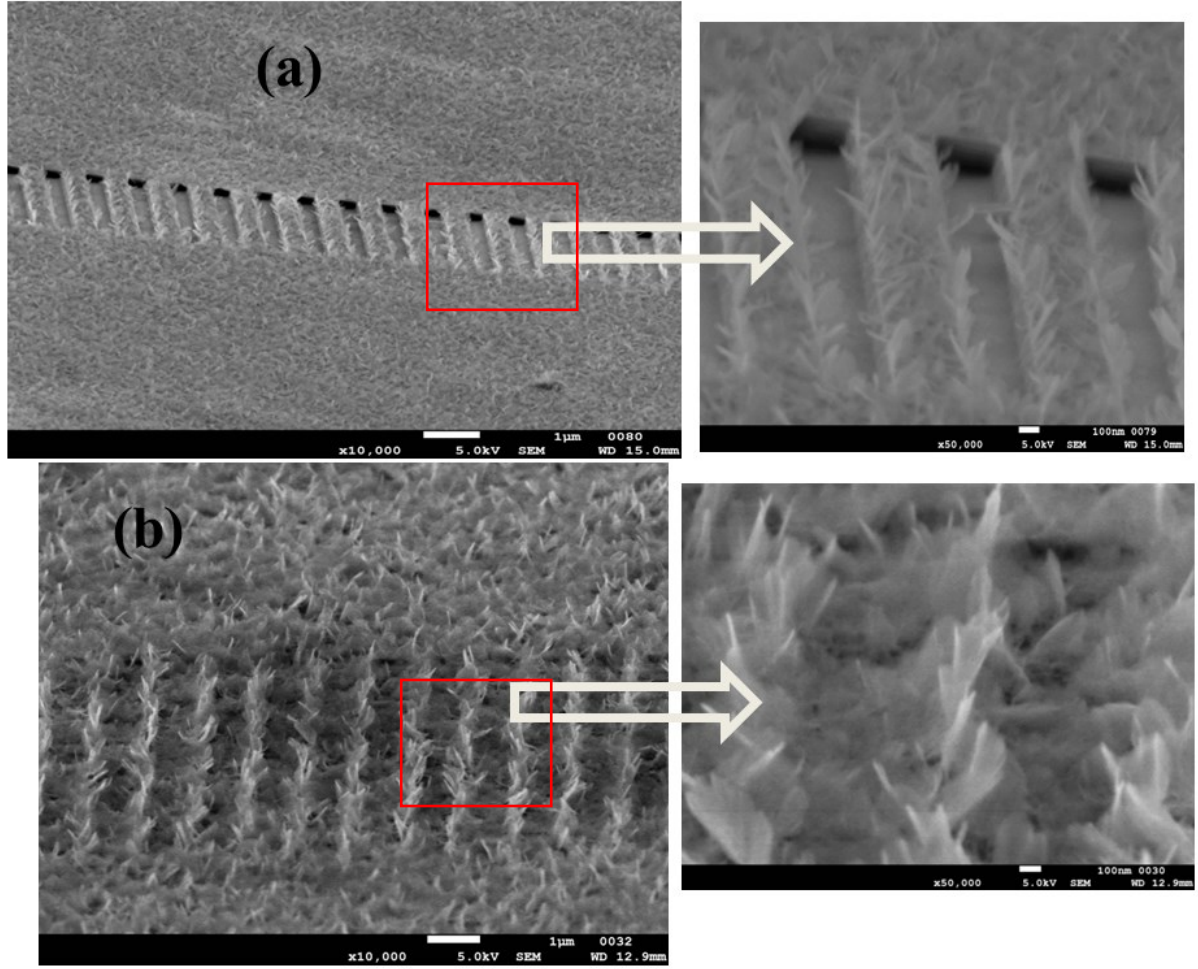


Figure 4-2 SEM image of self-aligned CNW grown at 500 °C on the patterned substrate. The scale bar in corresponding enlarged images represents 100 nm. (a) Angular view of as-CNW on SiO₂ substrate with its enlarged view and (b) Top view of L-CNW on SiO₂ substrate with enlarged view. Larger flakes can be seen in L-CNW.

4.3.2 Raman spectroscopy

The crystallinity of the L-CNW was analysed by Raman spectroscopy. The corresponding raman spectra for both as-CNW and L-CNW is shown in figure 4-3(a). This is an average spectrum of CNW film that was measured at five different points on the sample; at the midpoint of four sides and centre. In CNWs, D band arises at 1350 cm⁻¹, G band at 1580 cm⁻¹ and D' band at 1620 cm⁻¹. Similar to graphene, G-band represents the degree of graphitization (100% sp² carbon atoms) in the film, D-band represents the disordered structure that arises in CNW due to ring structure and

graphitic edges in the flake. D'-band speaks for the micro-crystallinity in the film as confirmed by Hiramatsu et al [95,126,171]. The G band was obtained for both L-CNW and as-CNW at 1578 cm^{-1} and 1575 cm^{-1} while D' band was obtained at 1619 cm^{-1} and 1614 cm^{-1} respectively. These results demonstrate that LTB has improved the crystallinity in the film. D band was obtained at 1343 cm^{-1} for both the samples while 2D band was obtained at 2688 cm^{-1} and 2683 cm^{-1} . A relatively smaller increment in G/D ratio, from 0.62 to 0.68, was found for L-CNW as compared to as-CNW which is shown in figure 4-3 (a). This result shows that L-CNW has improved the crystallinity of CNW film by a small degree. The spectra for both as-CNW and L-CNW broadly appear the same except G/D ratio.

The spectra was further investigated to compare the decisive D' band in CNW which provides the information about the micro-crystallinity in CNW film [95]. In the process, separate error bars were plotted to observe the relative deviation in the peaks for the measurement at five places. A smaller deviation in G-peak for L-CNW in figure 4.3(c) and 4-3 (d) showed that the uniformity was improved seeing the deviation of L-CNW. We further emphasized on the statistical analysis of D' peak to differentiate between L-CNW and as-CNW since other peaks such as G, D and 2D; did not show any significant difference.

The statistical analysis showed that D' band was present in both as-CNW and L-CNW. However, L-CNW showed an apparent and acute D' peak. This result confirms that LTB layer enhanced the micro-crystallinity in the film which might refer to the reduction in edges in CNW structure [166]. A reduction in edges occurs due to controlled growth of CNWs wherein molecules have enough energy to nucleate and agglomerate together [95]. The result advocates for the catalytic behaviour of LTB that assisted in lowering the nucleation energy and favoured more spontaneous growth [168,172,173]. The two possible reasons for such a favour in nucleation by LTB layers can be cited as the higher kinetic energy of molecules at the substrate's surface and its increased roughness which sometimes creates nucleation sites. However, this property varies according to chosen precursor and ease of atoms or radicals to nucleate.

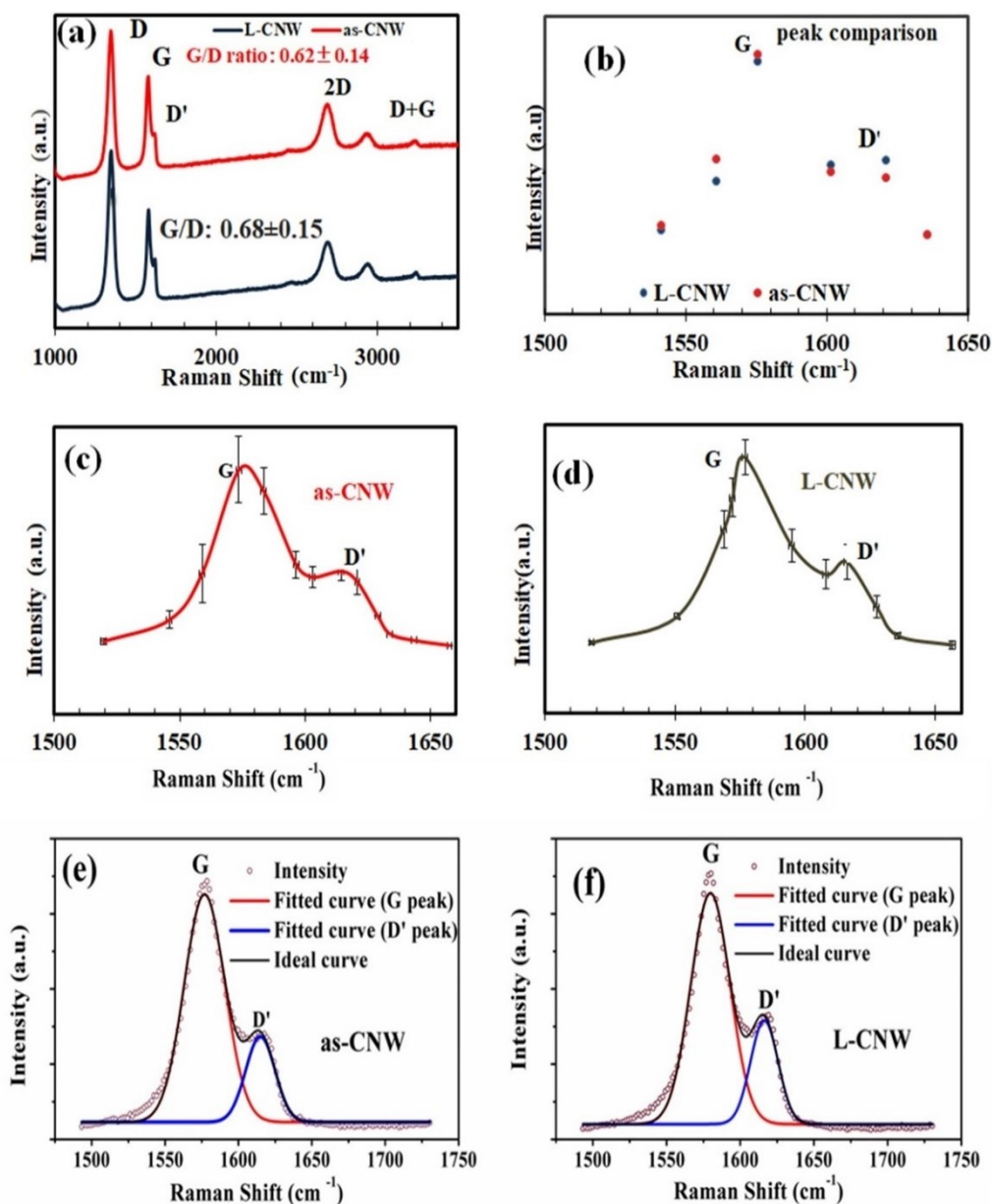


Figure 4-3 Comparative average Raman spectral image of both L-CNW and as-CNW films grown at 500 °C for 30 minutes. (a) Raman spectra and G/D ratio of as-CNW and L-CNW. Only the graphitic peak was taken into consideration in last three images. (b) Graphitic G and D' peaks of both as-CNW and L-CNW. The difference in D' peak is prominent. (c) and (d) represent the deviation from mean for both as-CNW and L-CNW films respectively. (e) and (f) show the de-convoluted G and D' peaks of corresponding as-CNW and L-CNW films respectively as Lorentzian. The intensity in figure (e) and (f) represents the actual curve.

In addition, the structures of walls were found to be self-aligned at the edges of line and space pattern as mentioned earlier. Kawahara et al reported that self-alignment process induces strain in the film against the natural curl structure [166]. The strain in the wall gives rise to defects in the structure as it reduces the carrier path length due to scattering caused by grain boundaries. Nano-edges at the boundary of pattern might induce the randomly oriented flakes. These small flakes coalesce together to form a large CNW and impart defect in CNW structure. This drawback was previously removed by self-aligned growth at 600 °C, since high energy of the precursor molecules will inhibit the growth of randomly oriented small flakes. L-CNW, on the other hand showed the reduction in defects as shown in figure 4-3 (d). This suggests that LTB suppresses the geometrical catalytic effect. LTB seems to have dominated over the edge effect. The SEM images in figure 4-2 (b) showed that the density of larger flakes dominated over the randomly oriented small flakes in the presence of L-CNW layer that again advocates for the catalytic effect of LTB layer.

4.3.3 Current-Voltage characteristics

Defect-free graphene shows linear I - V characteristics and behaves like a metal as a single layer. CNWs, on the other hand, generally demonstrate non-linear I - V characteristics owing to amorphous carbon (a:C) layer grown at its base during growth. Another reason for non-linear I - V characteristics is the incomplete graphitization during the growth process which induces defects in CNW film as reported by Hiramatsu et al [95,174]. In addition, the incomplete graphitization also leads to deposition sp^3 carbon between the walls which act as carrier scattering centers. However a:C was not observed in Raman analysis for both as-CNW and L-CNW.

The nano-flakes grown at edge also serve as scattering centers and disrupt micron level uniformity which ultimately reduces the conducting property of CNWs. Figure 4-4 (a) and 4-4 (b) show the change in I - V characteristics of CNWs when grown under low temperature buffer condition. The I - V measurement of as-CNW and L-CNW showed bipolar nature for as-CNW channel as shown in Figure 4-4 (a). An enhanced drain current (I_{DS}) was observed for positive drain voltage (V_{DS}) while keeping the gate

voltage (V_G) negative. Thus as-CNW channel demonstrates p-type character for negative

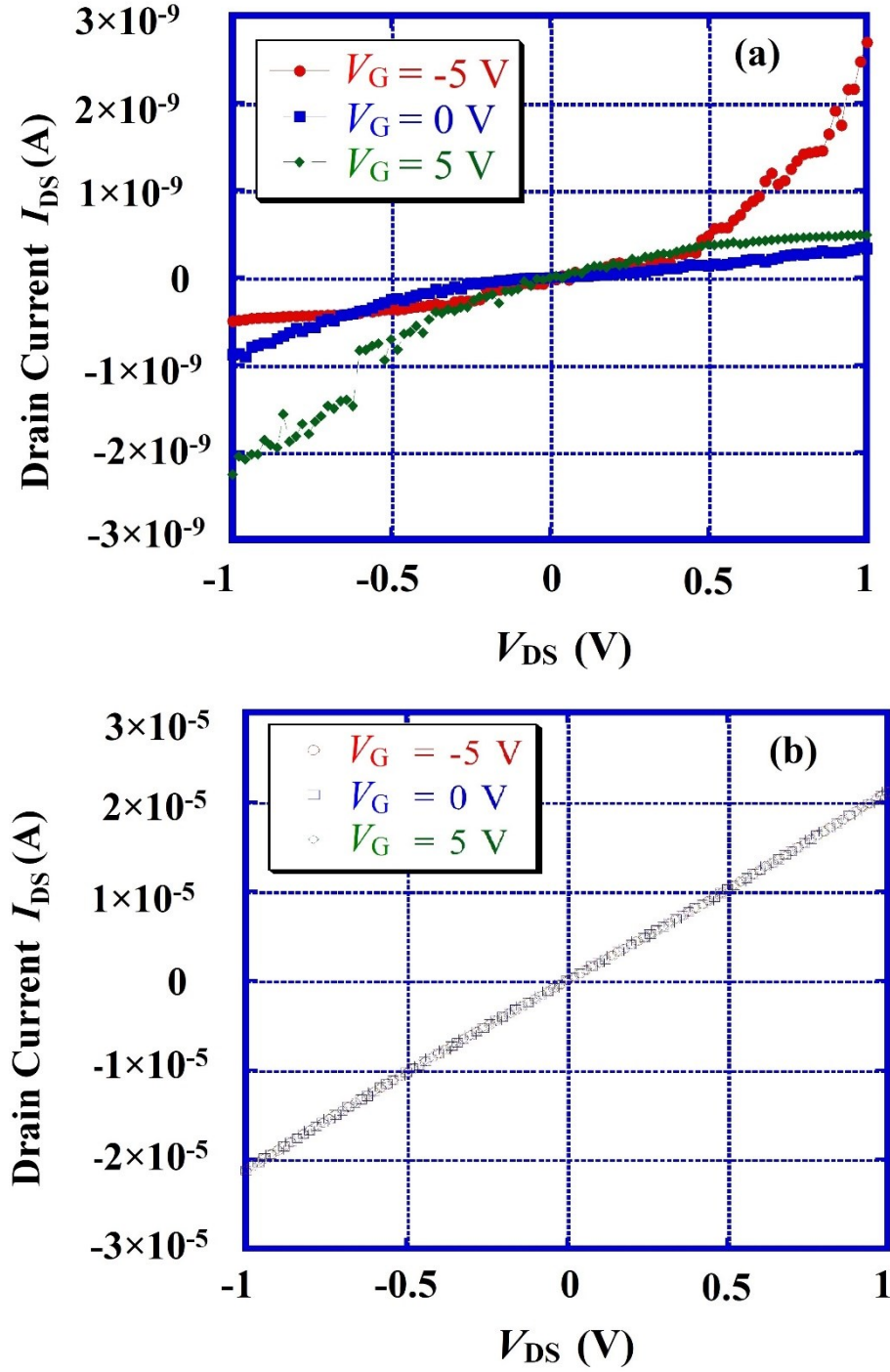


Figure 4-4 (a) as-CNW grown at 500 °C shows semiconducting property. (b) L-CNW at 500 °C shows metallic property.

V_G while an enhancement in drain current was observed at negative V_{DS} for positive V_G that again demonstrates the n-type character of self-aligned as-CNW channel. The asymmetrical contacts between electrodes and film along with strain in the flakes might cause such a non-linear characteristics in CNW film. In addition, a smaller sized graphite flake or grain modifies the band gap of material due to size effect of quantum confinement. Thus smaller flakes, strain in the structure, weak contact with electrodes and sp^3 carbon cumulatively seem to have caused the non-linear characteristics in as-CNW.

There was no V_G dependence obtained for L-CNW and the curve remained linear irrespective of the change in polarity as shown in Figure 4-4 (b). This showed that the crystallinity of the film was improved under the presence of LTB and metallicity was enhanced in the film. Furthermore, the contact between electrode and CNWs seems to have improved for L-CNW due to its larger flake size. The contact geometry between L-CNW and electrode seems to have changed as compared to as-CNW. Therefore it implies that LTB reduces defects from CNWs by suppressing both strain and edges from CNW structure. Earlier, it was found that L-CNW has enhanced D' peak as shown in Figure 4-1(b), which shows that the micro-crystallinity is improved for CNWs under the influence of its LTB layer. Thus from Figure 4-1(b) it could be stated that LTB reduces the defects from CNW structure by favoring the sharp edges without any residual a:C below the walls. Thereby it can be further stated that the catalytic effect of LTB seems to have reduced the strain from walls and the emanation of carbon nano flakes at the edges can be suppressed under its influence. The line and space pattern can be used as electrodes in transducers and various other optoelectronic devices.

4.4 Conclusion

Carbon nanowalls were grown over its LTB layer and characteristics of the film were compared with as grown carbon nanowalls on SiO_2 substrate, under the similar conditions. Raman spectral analysis and $I-V$ curve indicated that LTB enhanced the film quality by reducing defects in CNW's structure and suppressing the edge effect. The obtained L-CNW showed enhanced uniformity in crystallinity of the film. LTB layer acted as a catalyst to lower the activation energy under the given growth conditions.

This resulted in the growth of larger CNW flakes with steeper edges and reduced the strain from the walls. The reduced strain in the structure led to metallic behavior in the film. The self-aligned growth of CNW, which is caused by geometrical patterns on the substrate, was obtained at relatively low temperature on lined pattern. The patterned structure can be used as electrode in various transducers and other electronic devices owing to its position and growth control on the substrate.

Chapter5.

Effects of hydrogen and oxygen plasma processes on self-aligned carbon nanowall field effect transistor

5.1 Introduction

A great deal of effort have been put for controlling the crystallinity of CNWs by treatment by both N₂ and H₂ plasmas [97,122,191]. Position control of this self-supported sp²-carbon structure is another hurdle which inhibits the application in transistors. This important aspect has been addressed by us using self-aligned growth process as mentioned in chapter 4. The self-alignment method assists not only in straightening the natural curled structure of CNWs but also the position of the film can be controlled using the graphoepitaxy process [162,166,192].

Given that CNWs also possess a large surface area, their noise properties in relation to device applications should also be evaluated [193]. The advantages and disadvantages of self-aligned growth are discussed in chapter 4 and the suppression of defects occurred due to self-alignment in CNWs using low-temperature buffer. It was concluded that LTB restores the metallic character in CNWs at 500 °C in contrast to 600 °C growth.

Going forward, the FET structure was fabricated from self-aligned CNWs grown by PCVD synthesis process. The first of its kind, CNW-FETs showed the characteristics comparable to other FETs that will be discussed ahead in this chapter.

5.2 Materials and methods

The growth conditions for CNW synthesis have been mentioned in chapter 2 section 2.1.2 while substrate patterning process is mentioned in section 2.1.1. The electrode fabrication process is provided in section 2.1.3 along with plasma processing method. The electrical characterization method is mentioned in chapter 4 section 4.2. It is

noteworthy that as-CNW grown at 500 °C has been used for FET fabrication. Noise power spectral density was calculated by subjecting the time-dependent drain current data into Fourier transform analysis.

Figure 5-1 shows both schematic and optical microscopic image for the processed channels. The dark area in the aligned patterns in figure 5-1 (b) is for the remaining CNWs. The electrodes can cover the CNW channel. The dimensions of line and space pattern are also represented the schematic.

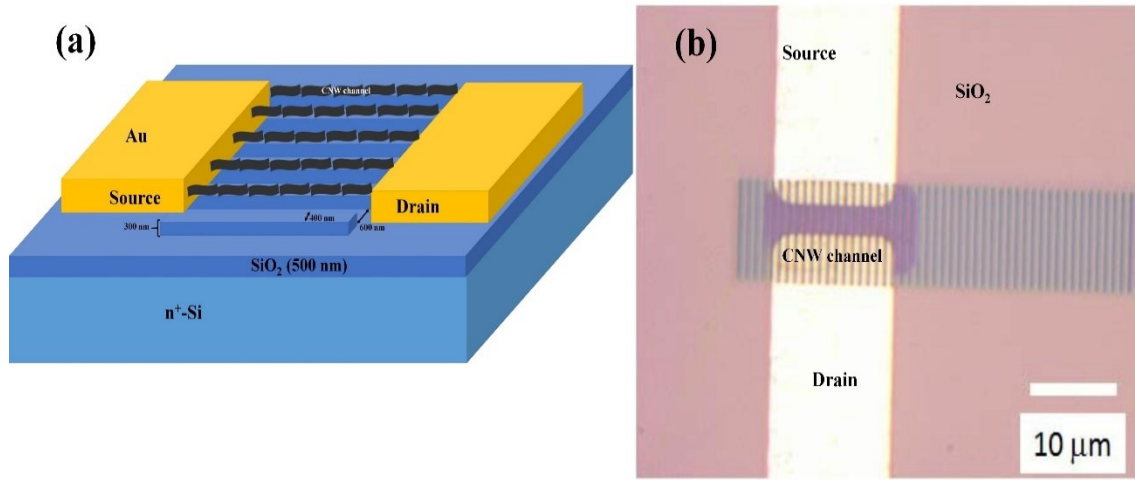


Figure 5-1 Representative CNW channel for the O_2 plasma etching process. (a) Schematic of CNW-FET device, and (b) optical microscopic image of CNW-FET after etching by O_2 plasma.

5.3 Results and discussion

5.3.1 Oxygen plasma treatment

Figure 5-1 (a) shows the schematic of CNW-FET device. The space-patterns shown in the schematic have been drawn only for illustration purpose and are genuinely below the SiO_2 surface. Figure 5-1 (b) shows the optical microscopic image of processed channel. The dark lines in the image represent CNW channel which are covered by the electrodes. The bright brown lane across the channel region represents Au/Ti electrode fabricated across the CNW channel. The source and drain are either side of the channel respectively in the back gated FET structure. The heavily doped n-type Si substrate acts

as the back gate electrode. The width of line pattern is 400 nm while the space between two patterns is 600 nm as mentioned in figure 5-1 (a). Only the CNW grown at the convex-pattern in self-alignment process, are taken into account for measuring the device characteristics. Therefore CNWs grown outside the channel region, which are visible in SEM image in figure 4-2 (b) (chapter-4), were etched out by O₂ plasma. Thus the pink region in figure 5-1 (b) represents SiO₂ layer.

The reminiscence of CNWs on SiO₂ substrate was neatly removed by RIE process in order to negate any possible leakage current outside the processed channel-region. *I-V* characteristic of the device both before and after O₂ plasma processing has been shown in figure 5-2. The gate current (I_G) was measured corresponding to V_G in the step voltage of 2 V.

While the *I-V* curve remained linear prior to etching, implying the leakage current from FET structure, a reduction in I_G can be clearly seen which shows that gate leakage current was reduced after the etching by O₂ plasma. It was found that I_G can be reduced by approximately of the order of 10⁻⁶ A as shown in figure 5-2 (b). The deviation in the *I-V* curve near zero bias voltage reveals a relatively weaker contact between the electrode and channel which was induced after O₂ plasma etching. Furthermore, the number of data points decreased for a lower order of magnitude in I_G and detecting the deviation became more apparent due to detection limit of apparatus. We obtained the further reduction in leakage current by 1/3 using imprinting technology. However, a reduction of 25 pA was obtained by O₂ etching and it showed that RIE process is convenient even without the imprinting technology. Thus the above result signifies that O₂ plasma is suitable for CNW-FET process.

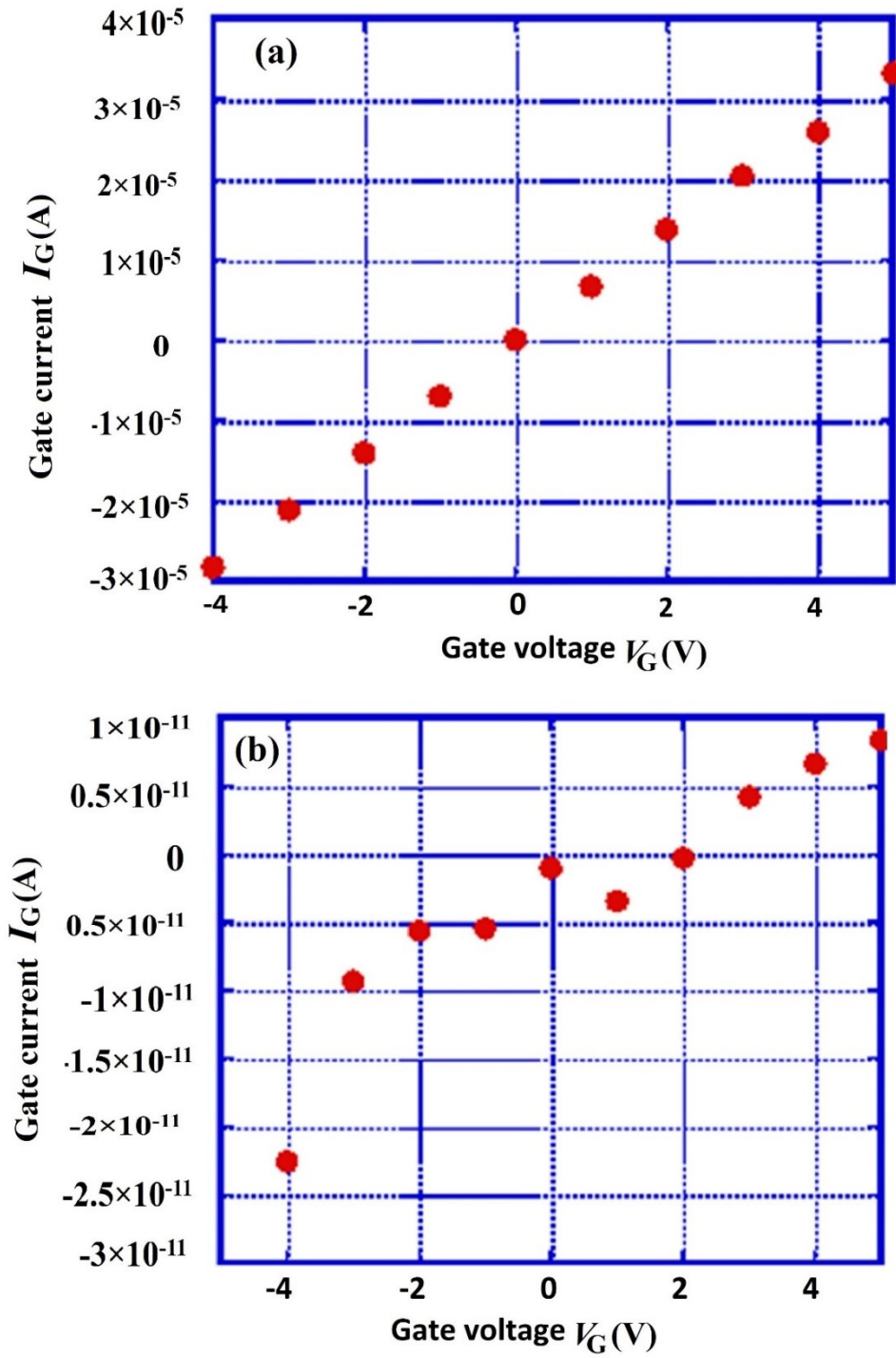


Figure 5-2 I - V characteristics of the gate. (a) denotes the gate leakage current prior to O_2 etching, and (b) after etching.

SiO_2 is often used for gate insulation and induces defects in the devices due to atomic

scale non-uniformity arisen during device fabrication [46]. This issue can be resolved by application of O₂ plasma etching in CNW-FET. The induction of defects can also be avoided using the insulating layer of h-BN.

5.3.2 Hydrogen plasma treatment

The effect of H₂ plasma in the improvement of contact resistance in CNW-FET was examined. The etching by O₂ plasma might weaken the contact between metal electrode and CNWs as previously discussed in section 5.3.1. Therefore the CNW-FET device was further processed by H₂ plasma. Previously, H₂ plasma has been used to enhance the on/off ratio in graphene based devices [194,195] and CNWs have also reportedly been treated using the same [191,196].

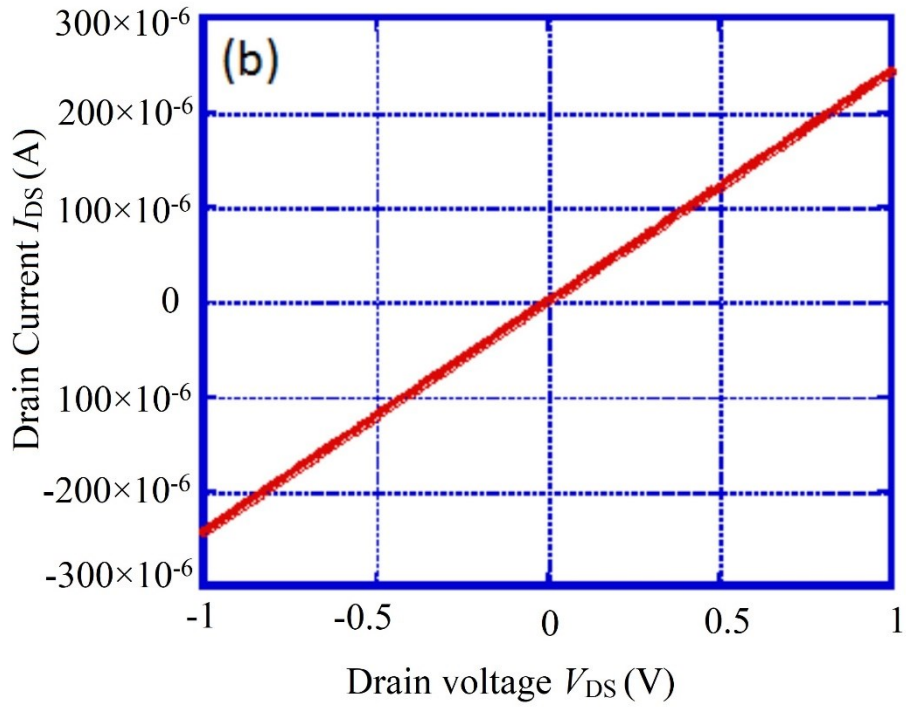
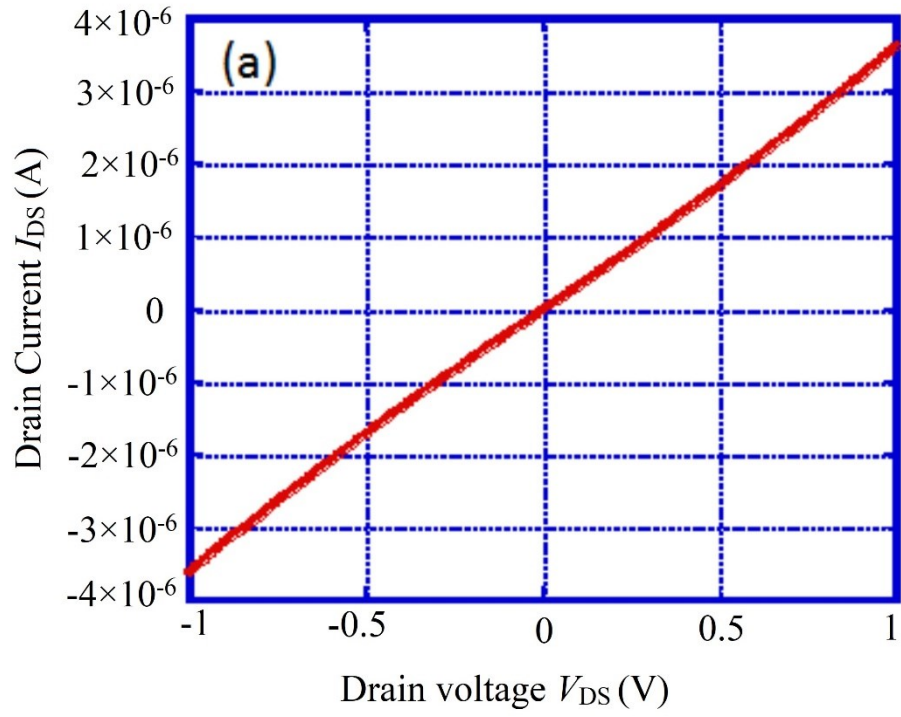


Figure 5-3 The I - V characteristics of CNW-FETs showing drain current (a) prior to H_2 etching, and (b) after H_2 etching.

H₂ plasma cleaned the surface and improved the contact resistance between metal electrode and CNWs. This result was deduced after I - V measurement between V_{DS} and I_{DS} . In the measurement, the drain current enhanced from nearly 4 μ A to 200 μ A at V_{DS} =1V as shown in figure 5-3. This improved result after H₂ plasma treatment shows that the contact between source and drain electrode was improved.

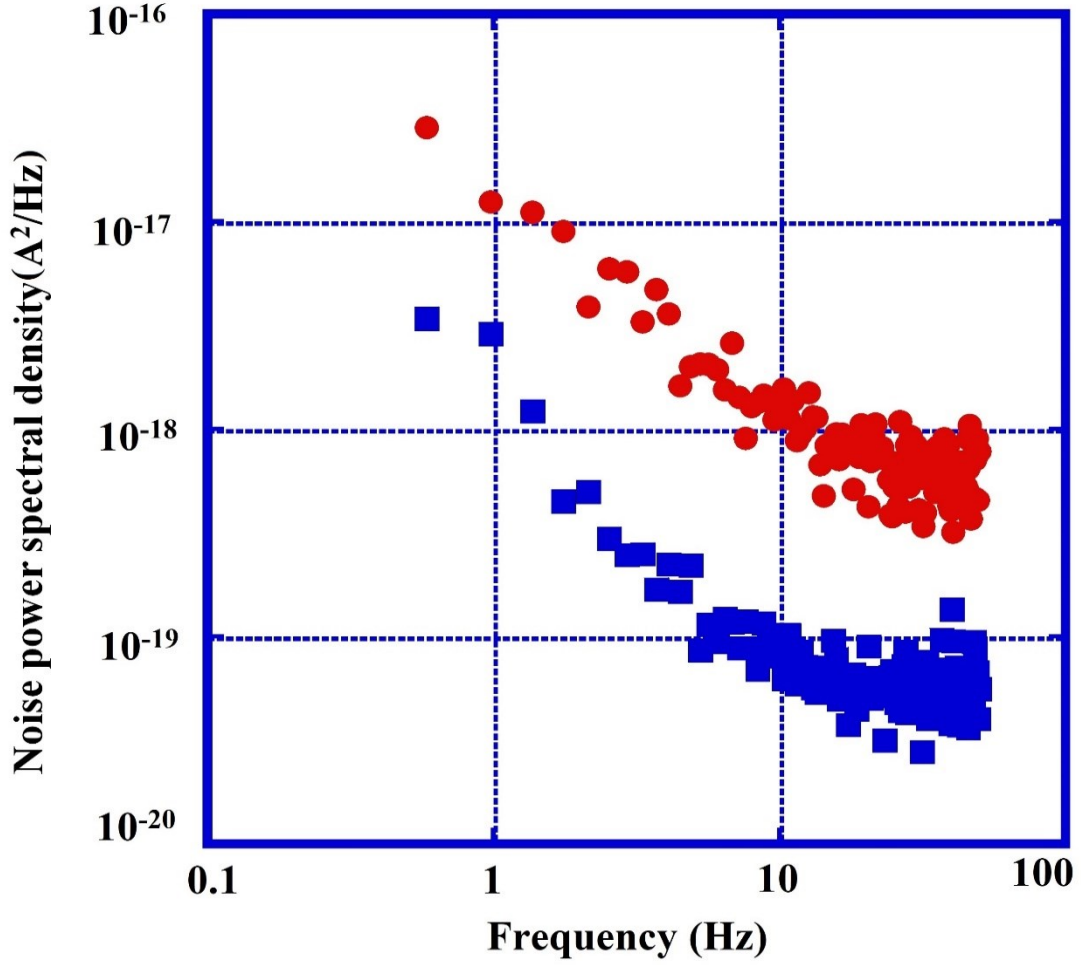


Figure 5-4 Noise power spectral density for the drain current of CNW-FETs before (red circles) and after (blue squares) H₂ etching. Noise power is reduced after H₂ etching.

The electronic property of CNW-FET is primarily dependent on the contact between of source and drain electrodes with CNW. Thus improving the contacts should lead to enhancement in noise properties in CNW-FET system. The noise spectral density of drain current is demonstrated in figure 5-4 and 1/ f type noise was obtained for the

device [175]. A decrease in low frequency for H₂ plasma treated device advocates for improved noise properties in the CNW-FET system. The possibility of carrier scattering near the junction due to weak contact was negated by H₂ plasma which resulted to reduction in noise.

The transistor properties of CNW-FET can be further improved by improving the fabrication process and introducing other components such as the insulating layer. It has been discussed previously in section 1.2 that h-BN might be a good alternative to SiO₂ layer which has charge traps and hinders mobility in graphene. The 1.7% lattice mismatch with graphene might also demonstrate altered properties in CNWs which might further improve the transistor properties. Thus in the process, synthesis of h-BN by PCVD process was performed which will be discussed later.

5.4 Conclusion

CNW-FETs were fabricated using the self-alignment process. A discussion of the plasma processes that improve the CNW-FETs has been given. Firstly, the use of O₂ plasma etching for CNW grown outside the channel region had been discussed and a reduction in gate leakage current was achieved. Secondly, the reduction in contact resistance using H₂ plasma etching was elaborated. H₂ plasma etching can also reduce the noise power spectral density of the drain current, which could improve the device properties since the electronic properties of CNW-FET are mainly dependent on the contact of the drain and source electrodes. Thus, improvements in the device properties can be achieved using O₂ and H₂ plasma treatments. These device processes can be utilized in future applications such as the development of highly sensitive biosensors and so forth.

Chapter6.

Application of carbon nanowall field effect transistor as a pH sensor

6.1 Introduction

After developing a self-alignment process wherein the position of walls was controlled using edge effect of substrate (chapter-4), the growth control of CNW channel was studied. CNW-FET was fabricated using oxygen and hydrogen plasmas for etching which enhanced the properties of channel region (chapter-5). In addition, CNWs have high asperity for liquids, like other sp^2 nano-carbon materials such CNTs and graphene, which makes the material suitable for application in pH sensors.

pH sensors, also known as ion sensitive field effect transistors (ISFETs), are one of basic step for label free biosensors and were first propounded by Piet Bergveld in 1970 [197]. The structure of ISFETs is similar to metal oxide field effect transistor (MOSFET) and are used to measure the concentration of H^+ and OH^- ions in the solution [197–200]. 2D ISFETs also work on the same principle as that of Si based ISFETs. In the basic principal of pH detection, the protonation or deprotonation of OH group at oxide layer in device depends on variation in pH values of the electrolyte which eventually changes the dielectric surface charge. The lower value of pH stimulates protonation in the solution and generates positive surface charges at the oxide/dielectric layer. The higher values of pH do exactly the opposite. The gate voltage is applied through a reference electrode and the resultant surface charge along with electrolyte voltage determines the surface potential in the system. A change in pH results to change in surface charge at oxide-electrolyte interface, which ultimately changes the conductance of the channel material, at a particular gate and drain bias in the FET. The changing conductance reflects change in sensor current and change the threshold voltage of FET.

In this chapter, I will discuss about current fluctuation in FET structure after immersing in liquids with different pH values. pH sensor is one the basic step for biosensor and hence the efficacy of device for the same purposes was investigated.

6.2 Materials and methods

The experimental procedure of sample preparation for CNW-FET fabrication has been explained in chapter 2 section 2.1 while its I - V characteristics after O_2 and H_2 plasma treatment has been discussed in chapter 5.

Going forward, the I - V characteristics of CNW-FET device was independently measured followed by the measurement in a solution of different pH. The schematic of device is given in figure 6-1 (a). After CNW-FET was covered by 300 μm thick ZEP-520A waterproof resist, a 1 μm wide groove was formed at the center of the CNW channel shown in figure 6-1 (b) and is also previously shown in figure 5-1. The waterproof resist prevents the leakage current flowing from source electrode to reference electrode. In the process, formed groove leads to formation of local electrolyte in gate solutions and acts as the sensing area for CNW-FET sensors. The pH dependence of I_{DS} for CNW-FET, having top gate Ag/AgCl reference electrode, was measured in a 3M KCl solution. Standard pH solution set (HORIBA, Kyoto, Japan) was used which contained a combination of pH 4, 7 and 9. The solutions were added on CNW channel starting with pH = 4. The measured pH values were found to be 4, 5.8 and 8.2.

6.3 Results and discussion

6.3.1 Optical microscopic observation

The schematic of the top-gate transistor has been shown in figure 6-1 (a). The dotted lines are shown only for illustration purpose of CNW channel region under measurement. An enlarged schematic of channel region is shown in chapter 5 figure 5-1. The optical microscopic image of fabricated CNW-FET has been shown in figure 6-1(b). Silicon pool was placed on CNW-FET to fill the surface of self-aligned CNW channel. A top gate voltage of 0.2 V was applied from Ag/AgCl electrode to avoid any undesirable redox reaction. The leakage current that flowed to the reference electrode

was negligible under such a small voltage.

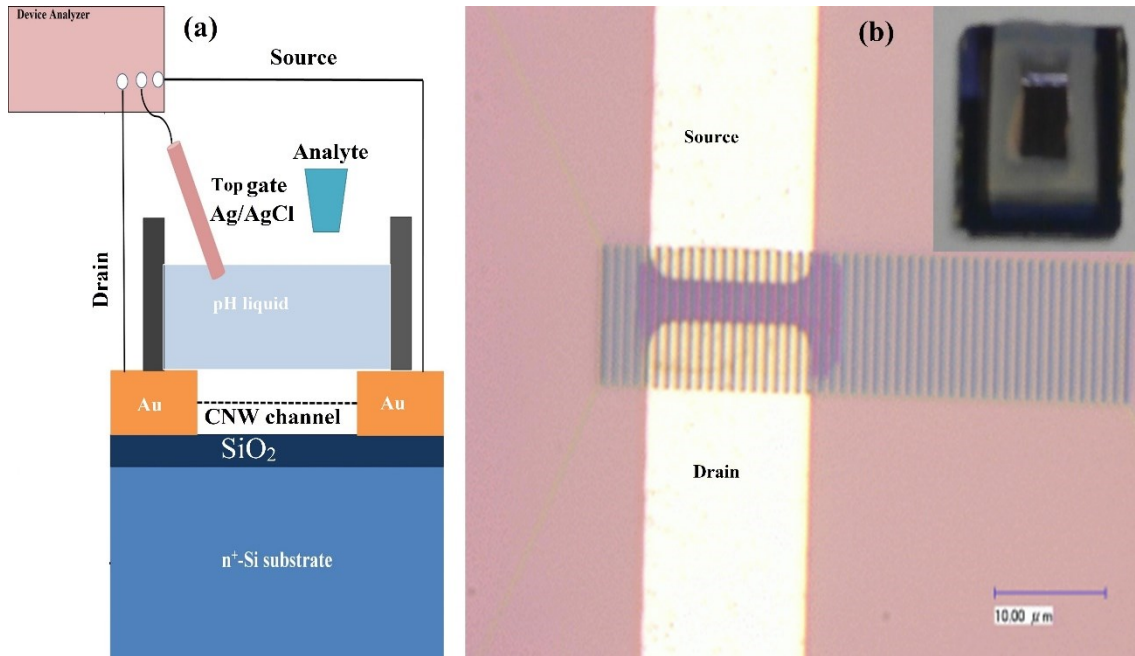


Figure 6-1 (a) Schematic of CNW-FET pH sensing device. (b) Optical microscopic image of CNW-FET. The inset shows the photograph of actual device surrounded by Silicon rubber pool.

6.3.2 SEM observation

The distribution of CNWs in the convex region of patterns was investigated by SEM analysis as shown in the figure below.

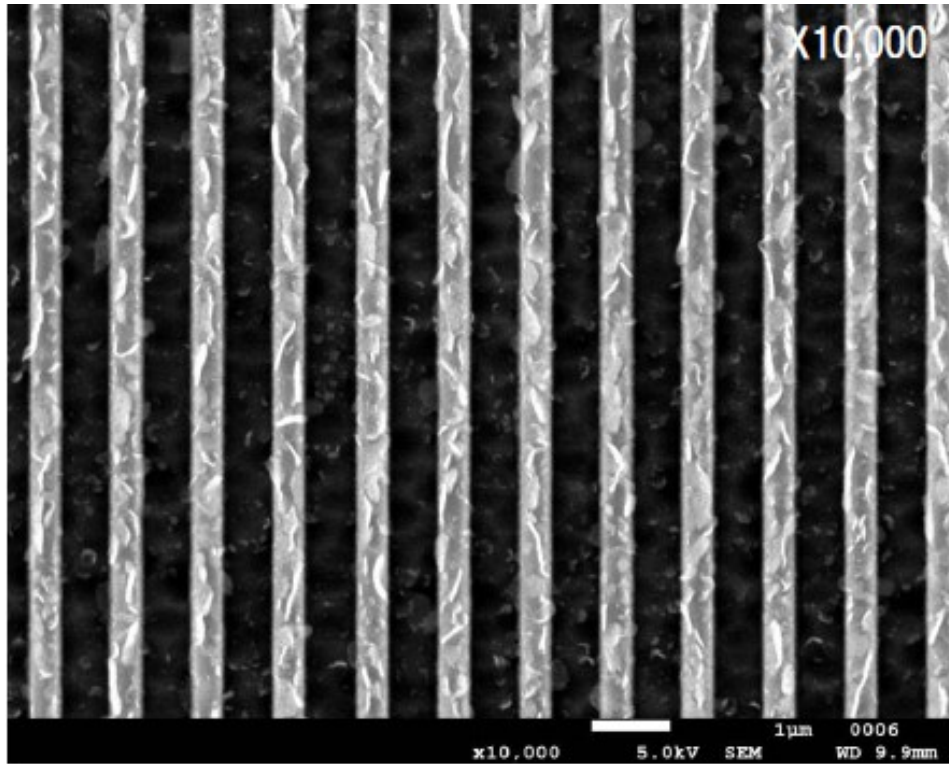


Figure 6-2 SEM image grown on patterned substrate by self-alignment process. The small flakes of CNW can be observed on in white patches aligned along the pattern.

6.3.3 Current-Voltage characteristics

Prior to putting the CNW-FET system under pH solution, the I - V characteristics of CNW-FET were independently measured. In the measurement, the channel showed nearly linear characteristic as shown in figure 6-3. However, the drain current was found to be varying when the sample was put under pH solution. The non-linearity in I - V curve can be seen for sample of higher pH in figure 6-4 (a) in which drain current was seen changing values. The small non-linearity is observed based on metallic property of the channel. The non-linearity in both the pH solutions pertains to carrier scattering at grain boundaries in the channel where ionic migration in the liquid seems to have changed the carrier flow across the channel [201,202].

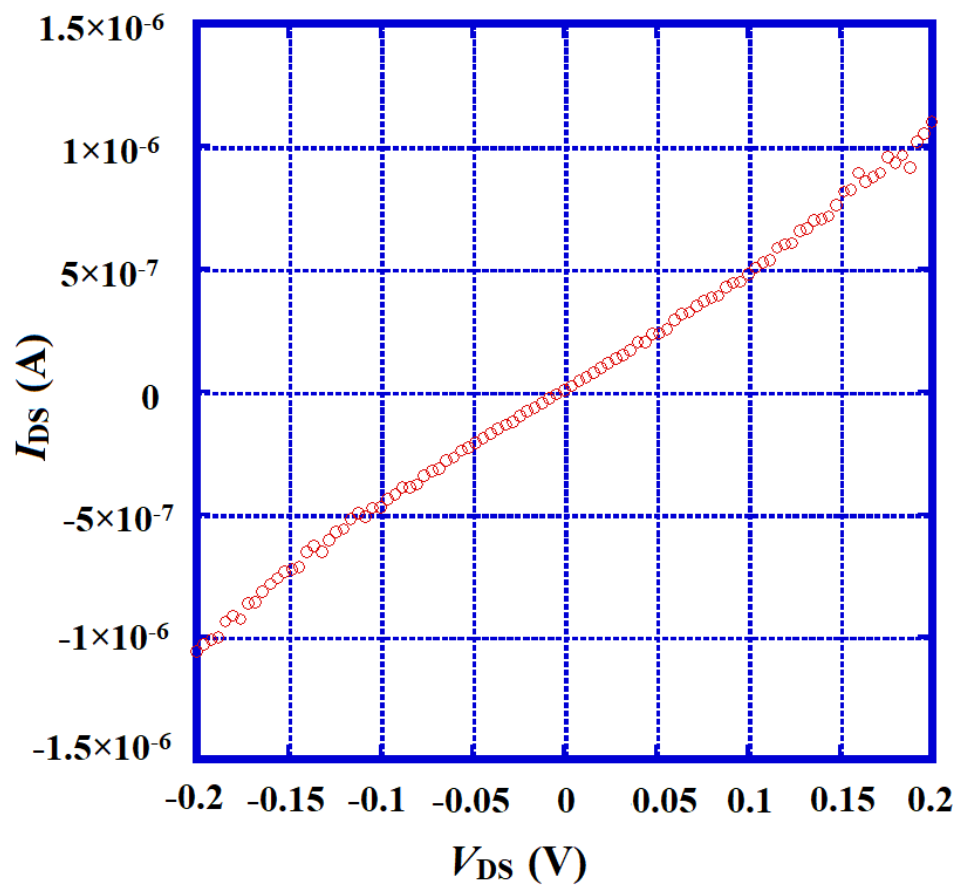


Figure 6-3 I - V characteristic of CNW-FET device under atmospheric conditions. The nearly linear curve can be seen showing metallic nature of CNW synthesized at 600 °C.

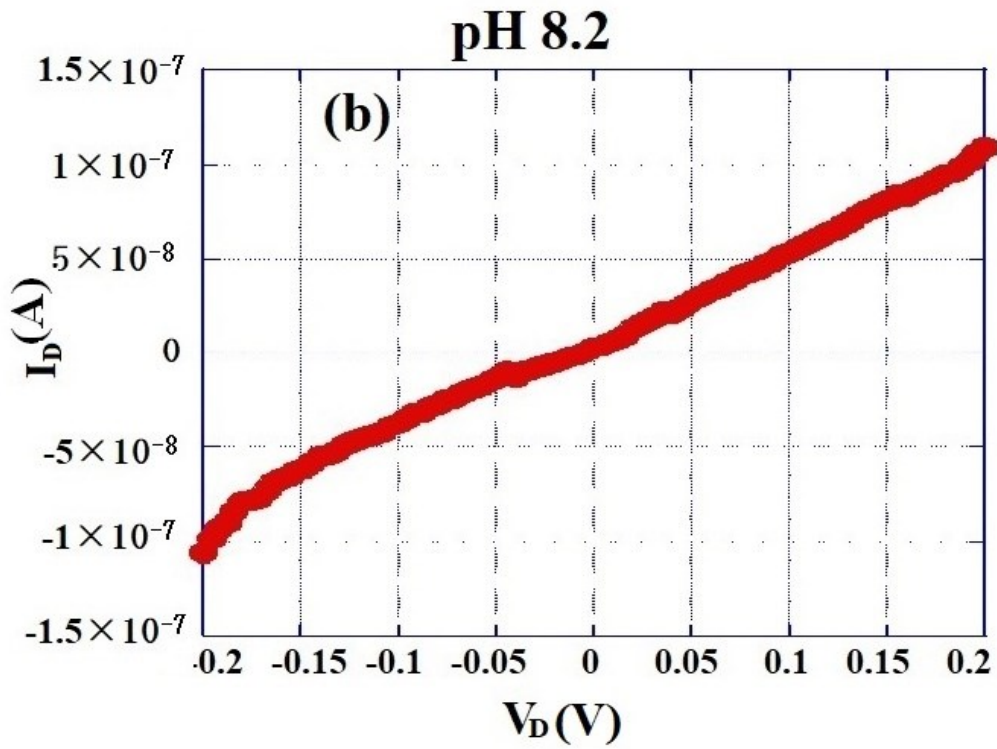
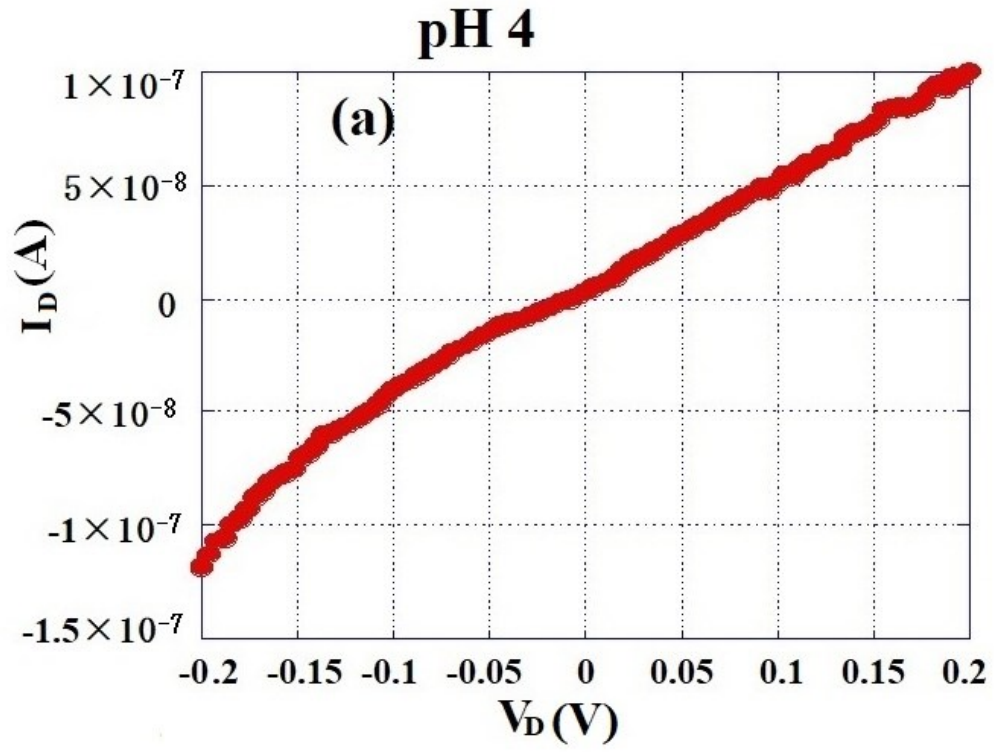


Figure 6-4 I - V characteristic of CNW-FET device under different pH values in the solution. The deviation from linearity can be clearly observed for both pH values.

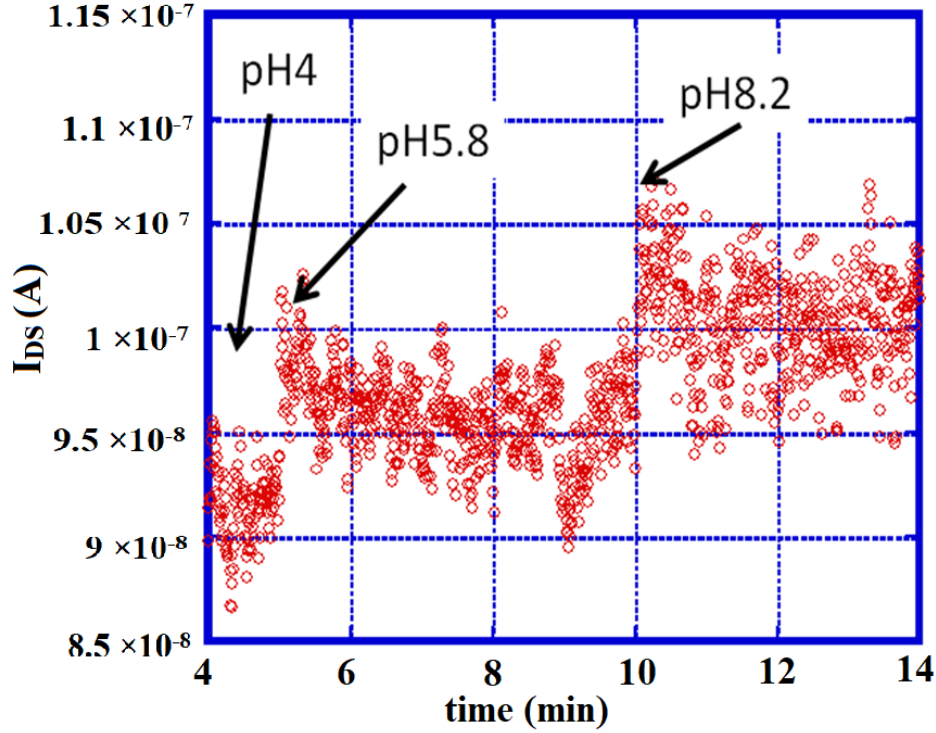


Figure 6-5 Time dependence for drain current at $V_{DS} = 0.2$ V under different pH values in a liquid.

The same was further confirmed by time dependent drain current measurement of the CNW-FET sensor. During the monitoring of drain current fluctuation, pH of the buffer was changed from 4 to 9 through 5.14 pH value. The arrows indicate the point adding different buffers solutions. The value of current is higher at the point of addition of buffer solution which decreases and saturates with increasing time. The drain current of solution was increased with increasing pH value. It can be seen that the noise in the system is increased with increasing pH and noise frequency matches at 9.5×10^{-8} A. However the average value of drain current can be seen increasing on very minute scale.

The conductivity of CNWs changes based on the hydrogen and hydroxyl ions present in base or acid i.e. change in pH. Hydrogen ion being smaller in size seems to have least affected the drain current and also scattering is low for lower pH values. This result is also due to the interaction between the CNW and the oxygen atoms because the p_x orbital of oxygen and the p-orbital of one carbon atom form a bond, which splits the

degenerate levels in the CNW. The OH^- group possesses an unpaired electron, which actively participates in hybridization near the carbon atom when it (the OH^- group) is attached to the wall. OH^- group can form an acceptor level and enhance the conductivity of the CNW, i.e. the OH^- group can be a good acceptor for hole doping. Thus the reactive binding group i.e. the hydroxyl ions, may play a key role in electron acceptance [202]. CNWs may facilitate electron transfer between a donor and an acceptor by increasing the reaction cross section, i.e. the conductivity of CNW increases with the appearance of OH^- group.

The FET structures made from CNTs have a history of exhibiting noisy properties owing to their uneven structural defects such as surface states [175,203]. CNWs, also being the sp^2 carbon structure, have a tendency to demonstrate the noise in the system due to graphitic edges and difference in the flake size during the formation of walls [166]. Thus in the process of device characterization, noise in the system was also measured and $1/f$ noise was found to be present in the system.

Higher pH values showed the pink noise in relatively lower values of frequency wherein the noise distribution observed spreading out as shown in figure 6-6. The noise in the system was separately measured according to figure 6-6. The noise distribution can be seen to be increasing with increasing value of pH. The large surface area of CNWs might lead such a large noise in the system since it is also made up of graphene sheets like CNTs [175,188,204,205]. Environmental molecules attached to the surface also increase the noise in the system.

The characteristics of CNW-FET as a pH sensor are still in developing stage as compared to CNTs and other similar materials used as a channel. However, it would be fascinating to examine the device performance of CNW-FET after altering the characteristics of device components such as thickness of the insulator or even a replacement by h-BN. An atomically flat surface of h-BN which is free of dangling bonds might change the both I-V characteristics and noise in CNW-FET system.

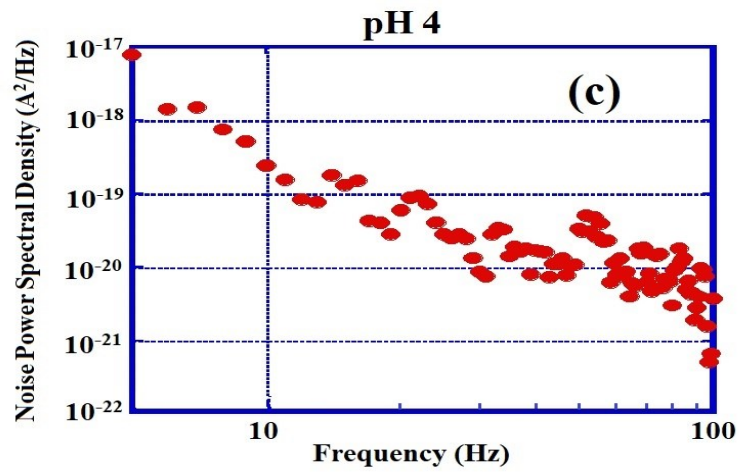
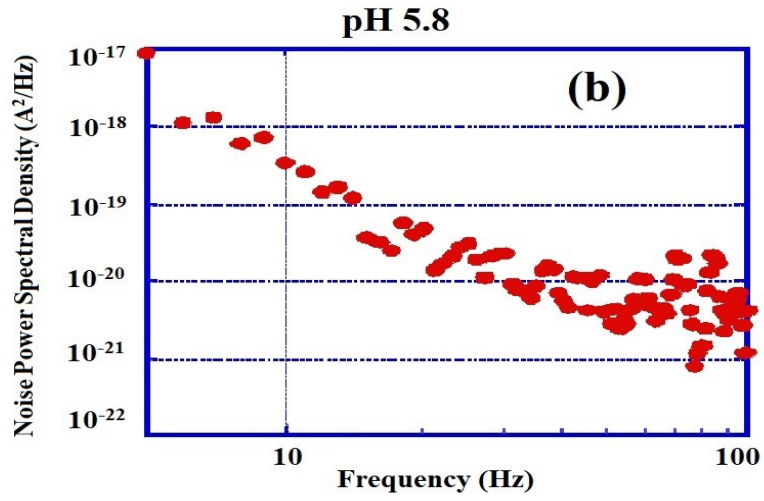
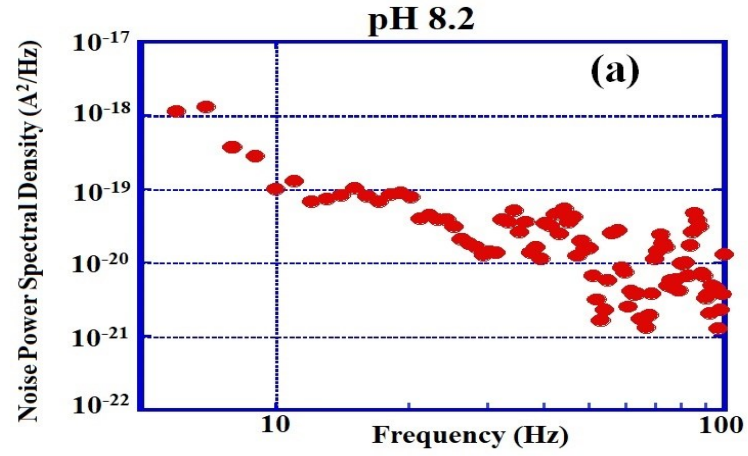


Figure 6-6 Power spectral density (PSD) analysis of CNW-FET system under different pH values. The increasing value also increased the noise in the system.

6.4 Conclusion

The pH sensing ability of the CNW-FET fabricated by self-alignment method was measured in the pH range from 4 to 9. A deviation in the linearity of I - V characteristics was observed. The real time measurement of drain current showed a change in its value with increasing pH and noise were found to be increasing. The obtained noise was recognized as $1/f$ noise. The noise in the system was predicted to be caused by ionic migration in the liquid with increasing pH. Such a pH sensitivity of device could be utilized for the application in biosensors.

Chapter7.

Synthesis of hexagonal boron nitride by microwave assisted surface wave plasma chemical vapor deposition

7.1 Introduction

Hexagonal boron nitride (h-BN), with a wide band gap (~ 6 eV) is a polymorph of BN among wurtzite, cubic and hexagonal structures [59,206–208]. With a lattice mismatch of 1.7%, the lattice parameters for both h-BN and graphite are nearly the same since both these materials possess intra-layer hexagonal lattice [46,209]. The chemical and physical properties of h-BN have been previously discussed in section 1.2 [150,210–216]. The wide band gap and p-type semiconducting nature doping enable h-BN for application in ultraviolet light emitters and deep ultraviolet light detectors [217,218]. Moreover, p-type conductivity of h-BN can be significant as most of the nitrides are normally n-type semiconductors [147,219]. The p-type conductivity in h-BN makes it a special wide band gap semiconductor since other nitride semiconductors show n-type behavior. h-BN has been explored as an excellent gate dielectric in FET devices fabricated using materials such as graphene, TMDC and other 2D materials [220–227].

The planer hexagonal lattice structure of h-BN with atomically smooth surface is free of dangling bonds, surface charged traps and other impurities. This has enabled fabrication of graphene FETs on h-BN layer achieving carrier mobility significantly higher than conventional devices on silicon dioxide (SiO_2) [46]. Moreover, the atomically thin layer can be assembled with various other 2D layers to fabricate tunneling based devices, vertical or in-plane hetero-structures and bi-stable memory devices [224,228–232]. It will be fascinating to examine the p-type behavior of an insulator in CNW-FET transistors and alteration in the properties of these materials.

Ammonia borane (AB) is a widely investigated solid precursor for h-BN growth as an

alternative to NH_3 and Tri-ethyl borane gases [87, 213,219,233–238]. In the developed process, AB has been decomposed by surface wave plasma and forms boron and nitrogen radicals independent of the substrate temperature. MW-SWP can produce dense plasma even at low gas pressure without using magnetic field and can also be enlarged by employing a large dielectric window at multi slot antenna facilitating uniform wafer scale growth [142]. The synthesis of h-BN was aimed to be used as an insulating layer for graphene and CNW growth. The synthesis independent of the catalytic behavior of the substrate can also open various possibilities of transfer-free application of h-BN for electronics device fabrication.

7.2 Materials and methods

The experimental set up and procedure has been discussed in chapter 2 section 2.2.1-2.2.3.

7.3 Results and discussion

7.3.1 Surface study

7.3.1.1 Heating test

The properties of MW-SW-PCVD system having 18 cm chamber's diameter is mentioned in chapter 2 section 2.2.1. The low electron temperature in the technique is advantageous in keeping the substrate's surface undamaged

After the growth of h-BN film by MW-SW-PCVD method, the samples were primarily brought under heating test to confirm the formation of an insulating BN film above the Cu/SiO₂/Si substrate as previously shown in figure 2-3. Figure 2-3 (a) and 2-3 (b) show photograph of the BN film coated and uncoated Cu/SiO₂/Si wafer after the heating test. Formation of a chemically inactive layer at the top of Cu/SiO₂/Si substrate was confirmed as the Cu surface remains un-oxidized as shown in figure 2-3 (a). The h-BN film protected the Cu surface from being oxidized while non-deposited Cu/SiO₂/Si substrate was oxidized [150]. The possibility of non-catalytic growth of h-BN layer on SiO₂/Si wafer was also studied. Figure 7-1 (c) shows the h-BN film coated SiO₂/Si wafer.

7.3.1.2 Optical microscopic observation

The morphology of BN film was investigated for both the catalytic and non-catalytic growth process. The deposition of BN layer was confirmed by optical microscopic analysis. Figure 7-1(a) shows an optical micrograph of BN layer directly deposited on Cu/SiO₂/Si wafer wherein a uniform deposition can be seen. The catalytically grown film was chemically etched and transferred on SiO₂/Si substrate. Figure 7.1 (b) shows optical microscopic images confirming a continuous film structure, with folded edges. The yellow patches show folded edges wherein the flakes were flipped due to viscosity of water. The dark colored layer in figure 7-1 (c) can be identified from the image confirming the non-catalytic growth. The uniform deposition covered the entire Si-wafer substrate therefore a deliberate scratch was made in order to distinguish between h-BN film and SiO₂/Si substrate.

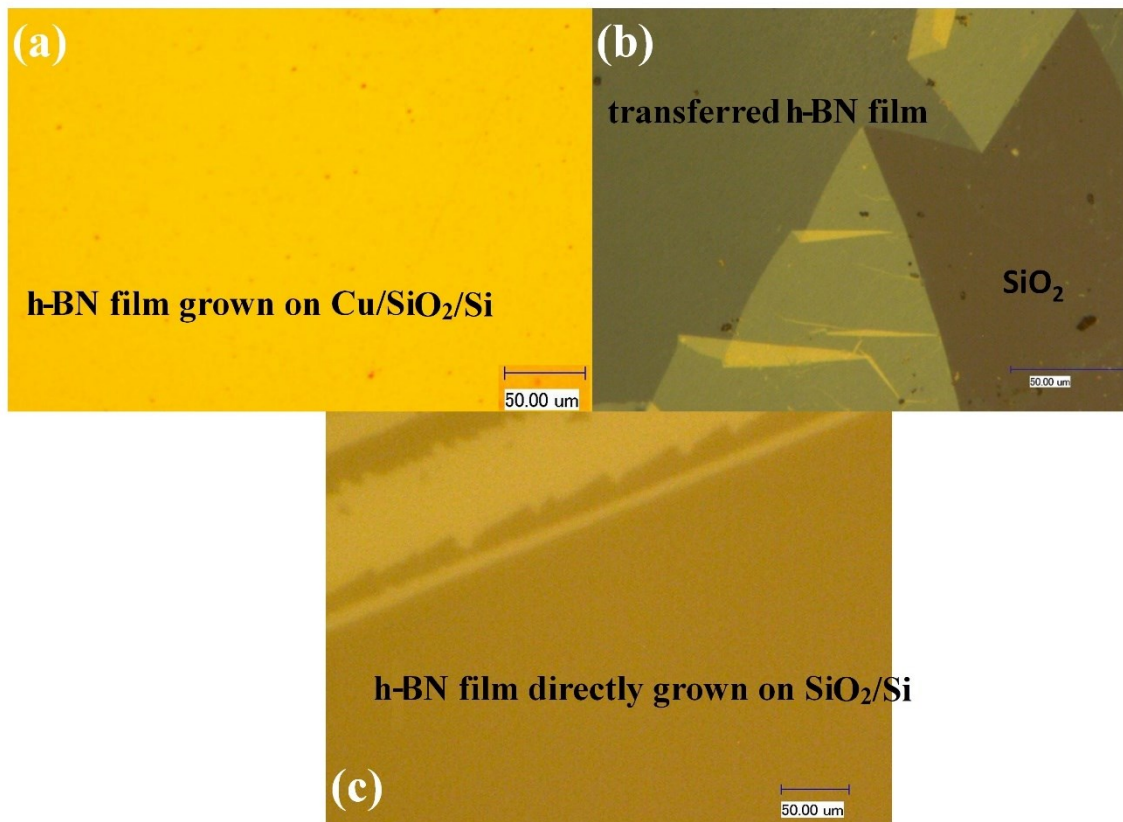


Figure 7-1 Optical micrograph of: (a) h-BN film grown on Cu/SiO₂/Si wafer, (b) h-BN film transferred on SiO₂/Si substrate after by wet-etching method. The yellow patches are folded film during the transfer. (c) Directly grown h-BN film on SiO₂/Si wafer. The lines were deliberately made by scratching the substrate to distinguish between film and the substrate.

7.3.1.3 SEM and AFM observation

Figure 7-2 (a) shows the SEM image of the transferred h-BN film. The optical microscopic and SEM images confirm catalytic growth of BN layer at a significantly lower temperature than that of thermal CVD process using the AB precursor. The thickness measurement of the film was carried out using atomic force microscopy (AFM). The red arrow in figure 7-2 (b) shows the point of measurement from SiO₂ substrate to the film. Yellow lines indicate the wrinkles arose in the film during transfer process. The thickness of the film after multiple scanning was obtained as 12.0 nm which substantiates more than 20 layers of h-BN. Controlling the growth duration and amount of precursor might facilitate in controlling the thickness of material during its synthesis.

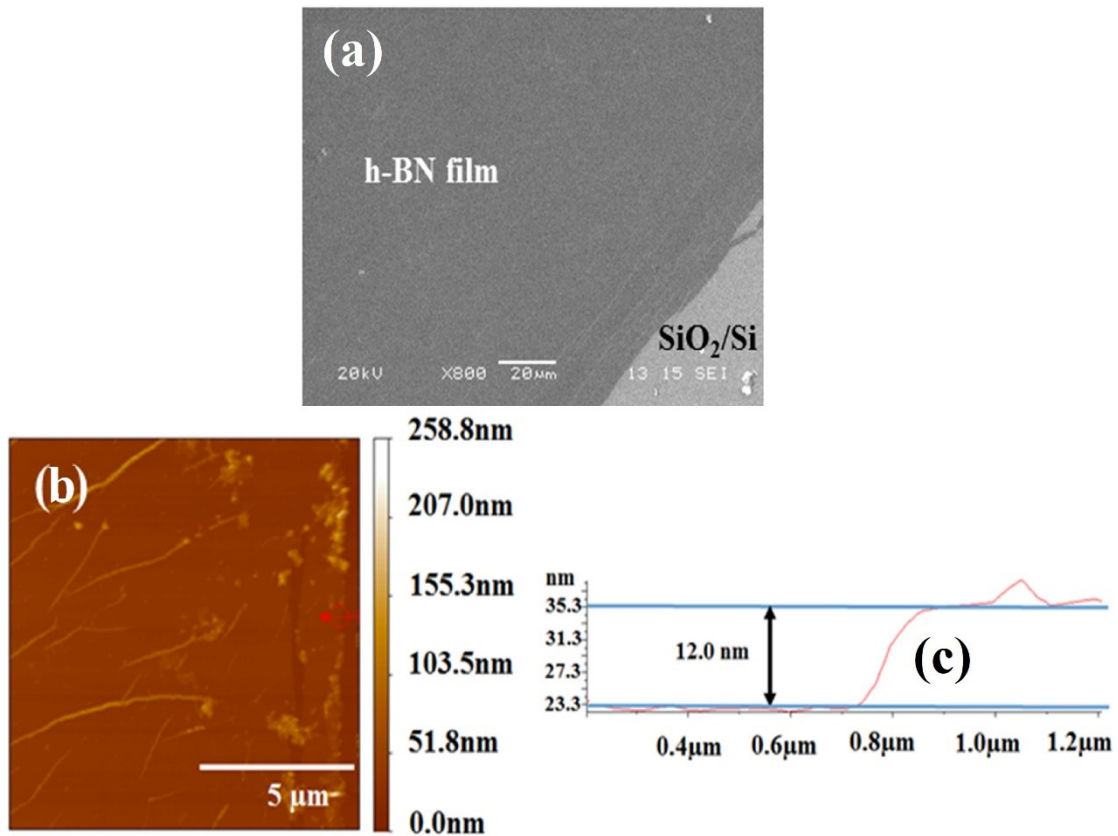


Figure 7-2 (a) SEM image of h-BN film transferred on SiO₂/Si substrate, (b) AFM image of the same sample. The red arrow head indicates the two different surfaces of h-BN and SiO₂ and (c) Line profile of the previous image.

7.3.2 Crystallinity study

7.3.2.1 FT-IR study

Both the crystallinity of film and the bonding character between B and N were characterized using FT-IR spectroscopy. Figure 7-3 shows the comparative FT-IR spectra of h-BN film synthesized on SiO₂/Si and bare SiO₂/Si substrate. A strong peak appears for the BN coated sample at 1385 cm⁻¹, which corresponds to the transverse optical (TO) vibrations for in-plane B-N bond stretching in sp² bonded h-BN. The FT-IR result clearly showed formation of h-BN structure rather than the other forms of BN [150].

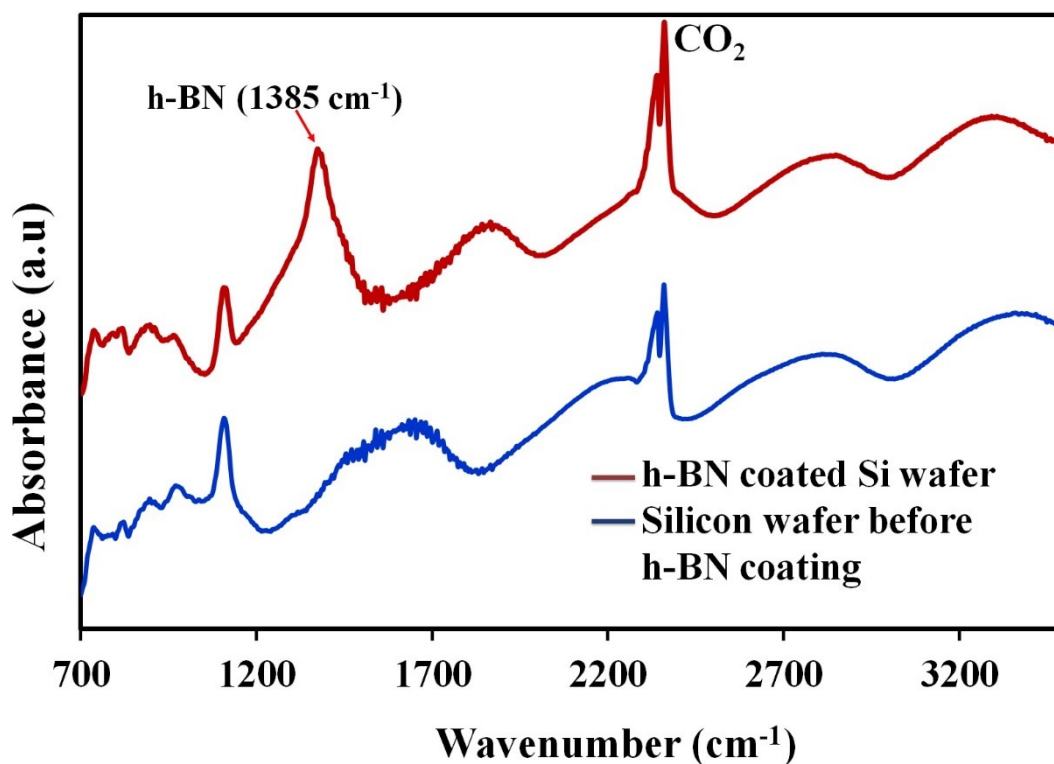


Figure 7-3 FT-IR spectra of h-BN grown using MW-SW-PCVD process transferred on Si/SiO₂ compared to bare Si-wafer.

7.3.2.2 XPS study

The elemental composition along with the h-BN purity was investigated by X-ray photoelectron spectroscopy (XPS). Figure 7-4 (a) shows XPS survey spectra for both catalytic and non-catalytic growth h-BN samples. The XPS spectra shows clear B1s

(191 eV) and N1s (401 eV) peaks along with the C1s (284 eV) and O1s (500 eV) peaks. A comparatively stronger C1s peak for the h-BN film deposited on SiO₂/Si substrate was observed. In the process, the individual B1s and N1s peaks of h-BN film on catalytic and non-catalytic substrates were compared. Figure 7-4 (b) and 7-4 (c) show the B1s and N1s core level spectra for h-BN synthesized both on catalytic (Cu/SiO₂/Si) and non-catalytic (SiO₂/Si) substrates. The B1s and N1s peak-centers were observed at 191.1 eV and 398.5 eV for catalytic growth sample which were calibrated with C1s peak as shown in Figure 7-4 (d). In addition, the B1s and N1s peaks were observed at

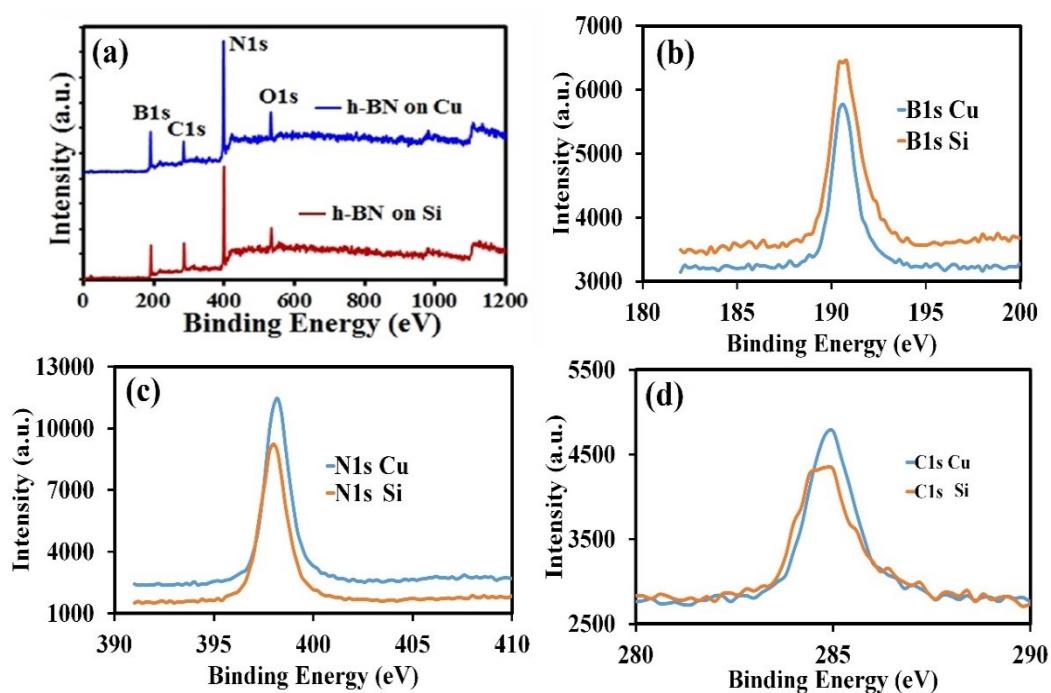


Figure 7-4 Comparative XPS spectra of h-BN grown on both Cu/SiO₂/Si and SiO₂/Si substrates by MW-SW-PCVD method. (a) Survey data, (b) Boron 1s peaks, (c) Nitrogen 1s peaks and (d) Carbon 1s peaks for calibration purposes. The B1s and N1s peaks have been calibrated considering the minimum value of binding energy obtained for carbon.

191.8 eV and 399.4 eV respectively for the non-catalytic sample. The width of N1s and B1s peaks for both catalytically and non-catalytically grown films remained nearly same which indicated no significant difference in h-BN structure. The incorporation of carbon and oxygen atoms in the film might occur during growth process and post-growth exposure to atmosphere [239, 240]. The concentration of oxygen and carbon impurities in MW-SW-PCVD grown film were found to be higher than the film

synthesized using thermal CVD process for their corresponding XPS studies.

The incorporation of carbon impurities shows that plasma CVD synthesis method can be advantageous for h-BN doping using carbon impurities. The MW-SW-PCVD growth process for h-BN can lead to synthesis of boron-carbon-nitride (BCN) and boron-carbon-nitride-oxide (BCNO) and other similar structures by incorporating the impurities and thereby can change the optoelectronic, catalytic and other physical properties of the film [241-244].

7.3.2.3 UV-Visible-NIR spectral study

The optical properties of h-BN are of prime importance due to its wide band gap which is used in deep ultraviolet (DUV) emission devices and UV-detector applications. In order to characterize the optical properties of the film, the catalytically grown film was wet-etched and then transferred on glass substrate after multiple rinsing in DIW as shown in figure 7-5 (a). The UV-Vis absorbance measurement showed an acute excitonic absorption peak at 276 nm in the UV region as shown in figure 7-5 (b). The peak might have arisen due to incorporation of carbon and oxygen impurities in the film. The second maximum was not obtained in the spectrum due to the measurement limit of the measuring apparatus to 190 nm. This result is different from widely reported results of a higher band gap (~6 eV) for h-BN which shows the change in optoelectronic properties of the film.

The optical band gap (E_g) of transferred h-BN film was derived using Tauc equation

$$\omega^2\epsilon = (h\omega - E_g)^2$$

where ω is angular frequency of incident radiation ($\omega = 2\pi\nu$), ν represents frequency and ϵ is its optical absorbance. The Tauc plot for $(ah\nu)^2$ and $h\nu$ is shown in figure 7-5 (c). A graph was plotted to find the E_g . The intersection points of $(ah\nu)^2$ with x-axis corresponding to the E_g are found to be ~4.1 eV which is less than pristine h-BN layer [148]. These results implies that both carbon and oxygen incorporated impurities can potentially be taken advantage for doping h-BN in its plasma CVD synthesis. The chemical stability and inertness of h-BN hinders the tuning of its band gap. A change in band gap of h-BN from 6.0 to 4.31 eV by the exposure of oxygen plasma is reported [244]. In the reported study, it was demonstrated that h-BN film treatment with oxygen plasma reduces band gap with increasing the exposure duration in which oxygen atom

creates N-vacancies in B-N bond and replaces N-atoms which alters the optical transition in material [243]. In BCN synthesis experiments, it was reported that the bandgap of BCN reduces from 5.3 to 3.4 eV with increasing concentration of carbon in the film [242]. In addition, the edges and grain boundaries in h-BN layer are vulnerable for impurity incorporation and which increases with increasing number of layers [245-247]. It was found in our study that the optical band gap in h-BN can be inherently changed by introducing oxygen and hydrogen impurities which appeared to have introduced during synthesis from the chamber and poor quality of Cu/SiO₂/Si substrate.

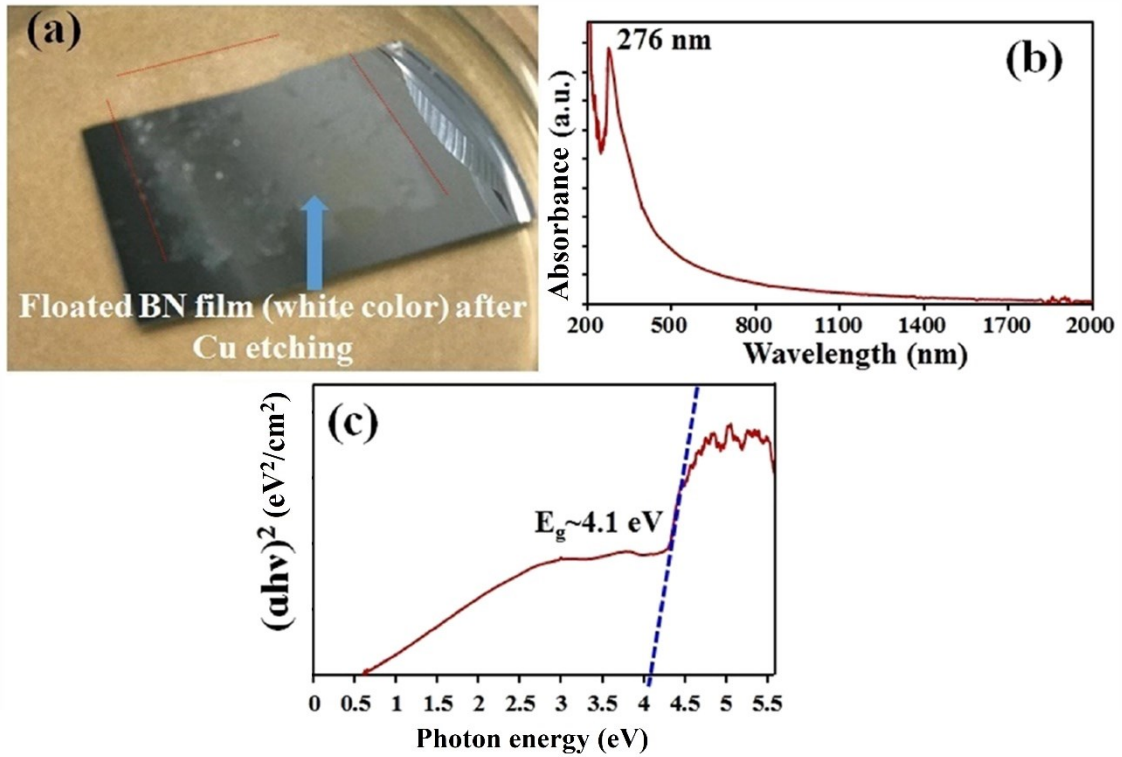


Figure 7-5 (a) h-BN film grown on Cu/Si substrate floating in DIW after wet-etching process, (b) the corresponding UV-Vis spectra and (c) the Tauc plot of h-BN showing a band gap at 4.1 eV.

7.3.2.4 TEM observation

The synthesized h-BN on catalytic substrate was further investigated by TEM analysis. Figure 7-6 (a) and 7-7 (b) shows TEM images of h-BN sheets synthesized on Cu/SiO₂/Si substrate.

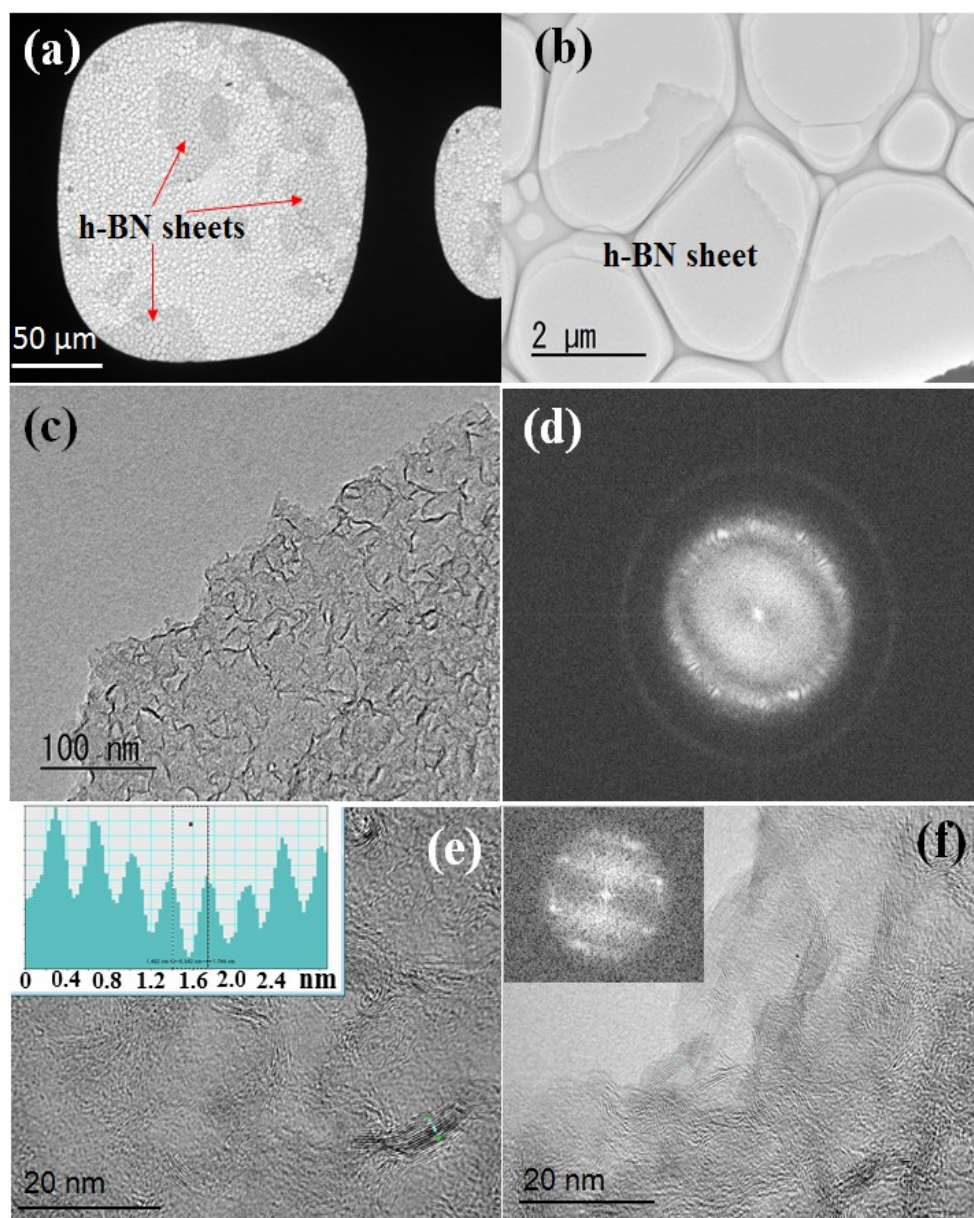


Figure 7-6 TEM analysis of the h-BN film synthesized on Cu/SiO₂/Si substrate (a) low resolution image of h-BN sheets transferred on TEM grid, (b) magnified image at the edge of h-BN sheet. (c) TEM image presenting polycrystalline like layer structure (d) corresponding FFT pattern (e) HRTEM image of randomly oriented distinct crystalline layer (inset shows interlayer spacing of 0.34 nm), and (f) HRTEM image of h-BN layer at the edge. The inset shows small area selective FFT pattern presenting hexagonal diffraction spots.

Figure 7-6 (c) shows magnified image at the edge of h-BN sheet, presenting the

polycrystalline like h-BN structure. The dark lines in image are edge of h-BN sheet with few-layered structure. It also indicates small grain structure of the synthesized h-BN on catalytic substrate by the plasma CVD process [248,249]. The polycrystalline and small grain structure of the h-BN film might have occurred due to poor crystalline quality of catalyst substrate as Cu was coated at room temperature and used without any further thermal treatment. The TEM image is presenting polycrystalline sheet like h-BN structure, corresponding to the FFT pattern. The crystalline quality of Cu thin film on Si substrate can be improved by thermal treatment to obtain larger grain structure of the h-BN film [214]. The HRTEM characterization was performed for small area as shown in figure 7-6 (e). Distinct layered structure is observed with an interlayer spacing of 0.34 nm that corresponds to the spacing between h-BN layers [148]. Figure 7-6 (f) shows HRTEM image of h-BN layer at the edge with better crystalline quality. Inset of the figure 7-6 (f) shows small area selective FFT patterns, wherein hexagonal diffraction spots are obtained. The TEM analysis also clearly shows the growth of crystalline h-BN layers by the MW-SW-PCVD technique at 500 °C using AB as solid precursors [250].

The MW-SWP-CVD growth process demonstrates the possibility for growth of h-BN both catalytically and non-catalytically wherein the catalytic behavior of the substrate can be taken advantage in low temperature growth. Thus even though the crystallinity of MW-SW-PCVD grown h-BN is not as high as compared to thermal CVD process which uses a high temperature growth, the MW-SW-PCVD system can be significant for wafer scale growth of h-BN at lower temperature on various substrates. In addition MW-SWP-CVD system can be used for impurity doping. This growth process can also be advantageous as a low temperature coating tool, as that of thermal CVD, in order to prevent a metal from degrading due to atmospheric condition. Further, the detailed investigations are ongoing to increase the crystalline quality as well understanding the effect of various impurities in the synthesized h-BN film by the plasma technique.

7.4 Conclusion

The both catalytic and non-catalytic wafer-scale growth of h-BN film at a comparatively low temperature using AB as solid precursor by the MW-SW-PCVD technique is demonstrated. The solid precursor was sublimed inside the CVD chamber and

decomposed to form plasma radicals, which allowed growth of h-BN layer at the temperature of ~ 500 °C. Heating test and microscopic analysis confirmed the growth of fully covered h-BN film with or without Cu catalyst on SiO₂/Si wafers. The growth of h-BN on a non-catalytic substrate by the plasma CVD process was confirmed by the FT-IR and XPS analysis. Optical absorption spectra was analyzed for the h-BN film synthesized on catalyst substrate, revealing excitonic absorption peak at 276 nm wavelength and the optical band gap using Tauc plot was obtained at ~ 4.1 eV. It was deduced from this result that MW-SW-PCVD growth process for h-BN incorporates oxygen and carbon impurities in the film. The addition of such impurities alters the band gap in material and can be significant for various device applications. TEM analysis clearly showed growth of h-BN multi-layers with polycrystalline and small grain structures. The finding of h-BN growth by the plasma CVD process can be significant for large area hetero-structure fabrication with other layered materials and direct integration for various device applications.

Chapter 8

Summary and future work

In this thesis, I addressed the self-aligned growth of CNWs at commonly used temperature of 500 °C. The self-alignment in the CNW film occurred due to the geometrical catalytic effect of the substrate while the patterns were fabricated in line and space form on the substrate to make CNW channels and observe its effects. The results deviated from the expectations based on previously reported data. In previously reported data, it was mentioned that CNW behave like a semiconductor due to high carrier scattering in the walls owing to uneven graphitic edges. LTB layer of CNW in its synthesis process rectified the uneven growth of edges. Furthermore, the CNWs were aligned along the edges of carved geometrical patterns. In addition, this self-alignment introduced new type of defect into the walls due to strain induced in straightening process against the natural curl structure. CNW shows metallic properties at 600 °C growth while semiconducting characteristics were obtained for 500 °C growth. The semiconducting property of CNW grown at 500 °C turned into linear or metallic characteristics when CNW film was grown above its buffer layer grown at 400 °C. The results were compared with the samples grown with buffer at 500 °C and a small difference in crystallinity was observed. Raman spectra, SEM and I - V analysis showed that CNW helped in reducing the effect of strain from the walls which had occurred in self-alignment process. The LTB was found to have worked as a catalyst on the substrate reducing the required activation energy for growth of CNW on a non-catalytic substrate.

In further process of making a transistor from CNW, the Au/Ti electrode was grown above the channel region. The walls grown outside the channel region were etched by oxygen plasma and the contact between electrode and channel was improved by H₂ plasma. The obtained results revealed that CNW demonstrates the required linear characteristics that were comparable to many other material used for the same purpose.

The same device was put for test in a pH solution and non-linear I - V characteristic was obtained as compared to the sample measured without pH. This result suggested that CNW-FET can be used as biosensor.

Hexagonal boron nitride was synthesized in another set of experiments for application as dielectric material and substrate for graphene and CNWs. The synthesis was performed by MW-SW-PCVD method using solid precursor ammonia borane at 500 °C. The obtained results showed the synthesis of polycrystalline h-BN structure grown at catalytic substrate which was confirmed by TEM and XPS analyses. The crystallinity of the grown samples varied for both catalytic and non-catalytic growth. The advantage of using this method for h-BN is the ease with which impurities can be incorporated into the film. The incorporation of oxygen and carbon impurities reduced the optical band gap of h-BN which can be significant for application in optoelectronics. Furthermore, the wafer scale growth can be fruitful for coating and deposition of insulating layer instead of SiO₂.

Future work

CNW grown by self-alignment process shows promising results and it will be great to see the application of the material grown under this method in transducers. The material has optimum height and aspect ratio for such an application. The geometrical pattern carved by electron beam evaporation can be very useful in fabricating transducer like structure and growing CNW above it by self-alignment process.

The LTB layer can be tried for growth of other material using PCVD method where the catalytic effect of substrate is negligible. This method can be tried for h-BN and other 2D film growth by the process.

Moreover the thickness control of h-BN film under MW-SW-PCVD is needed to be studied and tried. TEM, FT-IR and Raman spectra should be used to confirm the crystallinity of the film which showed uniformity in synthesis method. The *in-situ* growth of CNWs and graphene over h-BN by MW-SW-PCVD can also be tried. The success of such experiments might change the future of nano-electronics.

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