

LOW-TEMPERATURE GROWTH OF NITROGEN-DOPED
NANOCRYSTALLINE GRAPHENE FILMS BY COLD-WALL PLASMA
ASSISTED CHEMICAL VAPOR DEPOSITION FOR GAS SENSOR
APPLICATION

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UNIVERSITI TEKNOLOGI MALAYSIA

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DEDICATION

To the Prophet Muhammad, peace be upon him and loves of my live

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ABSTRACT

Our surrounding is containing high mixture of hazardous gases which had brought severe problem environment and human's health. Recently, nanomaterial particularly graphene has been extensively studied as one of the promising materials due its excellent sensing capabilities. Nevertheless, due to the physisorption of adsorbates which lead to false alarm detection and the absence of bandgap in most of the graphene devices, nitrogen (N) heteroatoms substitution is introduced. The specific bonding configuration in N-Gr i.e., pyridinic-N is believed have predominant effect on chemisorption between CO and the surface due to the presence of single lone pair which resulting highly selective and sensitive CO sensors. Whereas, predominant pyrrolic-N is experimentally approved for enhancement of NO₂ detection. The substitution of N atoms also will tune the band gap of the graphene. Thus, we report a viable method to produce nanocrystalline graphene films on polycrystalline nickel (Ni) with enhanced N doping at low temperatures by a cold-wall plasma-assisted chemical vapor deposition (CVD) method. The growth of nanocrystalline graphene films was carried out in a benzene/ammonia/argon (C₆H₆/NH₃/Ar) system, in which the temperature of the substrate heated by Joule heating can be further lowered to 100 °C to achieve a low sheet resistance of 3.3 kΩ sq⁻¹ at a high optical transmittance of 97.2%. The morphological, structural, and electrical properties and the chemical compositions of the obtained N-doped nanocrystalline graphene films can be tailored by controlling the growth parameters. An increase in the concentration of atomic N from 1.42 to 11.28 atomic percent (at. %) is expected due to the synergetic effects of a high NH₃/Ar ratio and plasma power (RF). The possible growth mechanism of nanocrystalline graphene films is also discussed to understand the basic chemical reactions that occur at such low temperatures with the presence of plasma as well as the formation of pyridinic-N- and pyrrolic-N-dominated nanocrystalline graphene. In this work, the N-doped nanocrystalline graphene films dominated by pyridinic-N and pyrrolic-N exhibit n-type semiconductor behaviour with a strong asymmetry in electron-hole conduction under ambient air conditions. The realization of nanocrystalline graphene films with enhanced N doping at 100 °C may open great potential in developing future transparent nanodevices.

ABSTRAK

Persekitaran kita mengandungi campuran gas berbahaya yang tinggi yang membawa masalah kepada persekitaran dan kesihatan manusia. Yang terbaru, bahan nano khususnya grafin telah dikaji secara meluas sebagai salah satu bahan yang berpotensi kerana keupayaan mengesan yang sgt baik. Namun begitu, disebabkan oleh keupayaan serapan secara fizikal terhadap penjerap yang membawa kepada kesilapan pengesanan dan ketiadaan jurang tenaga dalam kebanyakan peranti grafin, kemasukan atom asing nitrogen (N) diperkenalkan. Konfigurasi ikatan khusus dalam N-Gr iaitu, pyridinic-N dipercayai membawa kepada serapan secara kimia di terhadap CO disebabkan oleh kehadiran pasangan tunggal yang menghasilkan alat pengesan CO yang sangat selektif dan sensitif. Manakala, pyrrolic-N yang dihasilkan dominan dalam eksperimen, berjaya meningkatkan pengesanan terhadap NO₂. Kemasukan atom N juga akan merubah jurang tenaga pada grafin. Oleh itu, kami melaporkan kaedah yang baik untuk menghasilkan grafin berbentuk nano kristal pada Nikel (Ni) dengan peningkatan kemasukan atom N yang dihasilkan pada suhu rendah dengan kaedah pemendapan wap kimia (CVD) dengan bantuan tenaga plasma. Pertumbuhan bahan telah dijalankan dalam sistem benzena/ammonia/argon (C₆H₆/NH₃/Ar), di mana suhu substrat yang dipanaskan oleh tenaga Joule boleh direndahkan kepada 100 °C dapat mencapai rintangan elektrik yang rendah iaitu sebanyak 3.3 kΩ persegi-1 pada perpindahan optik yang tinggi sebanyak 97.2%. Morfologi, struktur, sifat elektrik dan komposisi kimia bahan ini yang diperolehi boleh diubah dengan mengawal parameter pertumbuhan. Peningkatan kemasukan atom N daripada 1.42 kepada 11.28 at. % dijangka disebabkan oleh pendedahan NH₃/Ar dan kuasa plasma yang tinggi. Mekanisme pertumbuhan yang mungkin bagi bahan ini dibincangkan untuk memahami tindak balas kimia asas yang berlaku pada suhu yang begitu rendah dengan kehadiran plasma serta pembentukan konfigurasi ikatan pyridinic-N- dan pyrrolic-N. Dalam kerja ini, bahan ini yang didominasi oleh pyridinic-N dan pyrrolic-N mempamerkan tingkah laku semikonduktor jenis-n dengan asimetri yang kuat dalam pengaliran lubang elektron di dalam udara. Realisasi bahan ini dengan peningkatan kemasukan N pada suhu 100 °C boleh membuka potensi besar dalam membangunkan peranti nano telus masa hadapan.

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LIST OF ABBREVIATIONS

DL	-	Detection Limit
GC-MS	-	Gas Chromatography-Mass Spectrometer
ppb	-	Parts per Billion
MOS	-	Metal Oxide Semiconductor
CNT	-	Carbon Nanotubes
CO	-	Carbon Monoxide
N	-	Nitrogen
RT	-	Room Temperature
GO	-	Graphene Oxide
rGO	-	Reduced Graphene Oxide
NO ₂	-	Nitrogen Dioxide
C	-	Carbon
CVD	-	Chemical Vapor Deposition
C-N	-	Carbon-Nitrogen
C-C	-	Carbon-carbon
NH ₃	-	Ammonia
Ar	-	Argon
C ₆ H ₆	-	Benzene
FET	-	Field Effect Transistor
IDE	-	Interdigitated Electrodes
SO _x	-	Sulphur Dioxide
VOC	-	Volatile Organic Compound
Ppm	-	Parts per million
O ₂	-	Oxygen
S	-	Sensitivity
R _a	-	Resistance of sensing elements in air
R _g	-	Resistance of sensing elements in atmosphere of target gas
1D	-	One dimensional
2D	-	Two dimensional
0D	-	Zero dimensional

3D	- Three dimensional
SnO ₂	- Tin (IV) Oxides
ZnO	- Zinc Oxide
In ₂ O ₃	- Indium (III) Oxide
TiO ₂	- Titanium Dioxide
HCL	- Hydrochloric Acid
PAni	- Polyaniline
PPy	- Polypyrrole
PTh	- Polythiophene
Nn	- Nearest Neighbour
Pt	- Platinum
Pd	- Palladium
B	- Boron
SiO ₂ /Si	- Silicon dioxide/Silicon
RF	- Plasma
H ₂	- Hydrogen
Ni	- Nickel
OM	- Optical Microscope
FESEM	- Field Emission Scanning Electron Microscopy
HR-TEM	- High Resolution Transmission Electron Microscopy
XRD	- X-ray Diffractometer
XPS	- X-ray Photoelectron Spectrometer
SMU	- Source Meter Unit
DI	- Deionized
Cu	- Copper
T	- Temperature
t	- Time
FWHM	- Full Width Half Maximum

LIST OF SYMBOLS

A	-	Ampere
E	-	Energy
K	-	Kelvin
μ	-	Mobility
Ω	-	Ohm
σ	-	Sigma
$^{\circ}\text{C}$	-	Degree Celcius
kV	-	Voltage
π	-	pi
v	-	Velocity
Pa	-	Pascal
cm	-	Centimeter
s	-	Second
λ	-	Lamdha
Q	-	Heat
at. %	-	Atomic Percent
A	-	Ampere

CHAPTER 1

INTRODUCTION

1.1 Research Overview

In this new era, with the increasing demands of living standard, increasing number of manufacturing industry and the emphasis on the environment, the air around us is containing high mixture of hazardous gases known as primary pollutants and secondary pollutants that causing irrevocable environmental damage. The continuous release of various chemical pollutants from industry emission, household waste, vehicle exhaust and so forth brought severe problem not only to environment but also to human's health. According to World Health Organization (WHO), long term exposure to certain pollutants could lead to to severe disease such as cancer and chronic respiratory disease [1]. They also indicate that, air pollution had caused of approximately 4.6 million deaths in 2016. Therefore, in this era, environmental safety is a concern topic among researchers, public and political communities.

Various types of sensors or environmental detectors are available to continuously monitor these air pollutants to prevent environmental or human health deterioration. Gas chromatography-mass spectrometry (GC-MS) has been used widely for the detection of various type of hazardous gases and volatile disease biomarkers. These analytical techniques are sufficiently accurate with detection limit (D_L) down to ppb (parts per billion) [2,3]. However, the major drawbacks for this system are high cost, importable and very complicated in gas analysis. Therefore, researchers have attempted to design an effective, cheap, high selectivity and sensitivity gas sensors for the effective qualifications of hazardous gases. Previously, there are several types of gas sensors that has been developed. Sensing technology is based on the physical properties of the sensing materials and alterations in these properties when exposed to gases. Thus, gas sensor can be classified into 4 main categories from resistive, optical, electrochemical, and catalytic. Among all, resistive gas sensors have been considered

attractive candidates since its cheap for higher production, easy to use and highly portable [4-5].

Chemo resistive gas sensors based on nanomaterials particularly semiconductor metal oxides (MOS), are commonly introduced and have provides many advantages in term of sensitivity and selectivity. Over past decades, researchers have been working to improve the current technology of MOS. The reduction of grain size to nanoscale and introduction of dopants/modifiers are the effective strategies to enhanced the sensitivity of the MOS gas sensor [6,7]. However, due to high operating temperature, these sensors hold an obvious drawback, resulting in high power consumption, which in turn adversely affects the integration and long-term stability. Furthermore, high working temperatures may give rise to safety problems for measurements in environment where explosive gases may also exist. In comparison of MOS, the sensors based on conducting polymers have many improved characteristics such high sensitivity and selectivity which operated at room temperature (RT). However, these conducting polymers exhibit disadvantages such as unstable over long periods due to environmental condition and known as poor selectivity as gas sensors due to the resistance of the device is commonly influenced by the ambient factor and the contact resistance of the electrodes [8].

Current research effort has been directed towards exploring new promising materials and improved the sensors response. Carbon based material such as pristine graphene [9], carbon nanotubes (CNT) [10], graphene oxides (GO) [11], and reduced graphene oxides (rGO) [11] were introduced and were extensively used for gas detection towards various types of toxic gases since the properties of these materials is remarkable unique in term of electrical, mechanical, optical and chemical. These materials were reported improved the response and were operated at RT [11]. However, due to physisorption of pristine graphene that leads to false alarm detection, researchers have proposed a way to enhanced the adsorption of graphene in which introducing defects, functional groups or dopants in the graphene lattice [12-15]. Later, various dopants have been reported and successfully enhanced the performance of the gas sensors [16]. Besides that, the utilization of graphene in most nanoelectronics application is restricted due to its gapless states [17,18]. To exploit possible

modifications or tailoring its properties, it is, therefore, necessary to control the charge carrier concentration by tuning the Fermi level (E_F). The method applied for band gap tuning in graphene is through doping such as surface transfer doping, substitutional doping, or chemical doping [19].

Substitutional doping of heteroatoms such as boron (B) or nitrogen (N) in the graphene is one of the most investigated methods since it is inherently stable due to the covalent bond linkage of the dopant into the graphene lattice [20]. Among B and N atoms, N substitution in graphene is most preferable due to its excellent properties such as comparable atomic size and possession of five valence electrons [21]. Particularly, N-doped graphene has three common bonding configurations known as pyrrolic-N, pyridinic-N, and graphitic-N. Pyridinic-N refers to a N atom that substitutes within the two carbon (C) atoms at the edges or defects of graphene and contributes one p electron to the π system, while pyrrolic-N refers to a N atom that substitutes into the five-membered ring and contributes two p electrons to the π system. However, graphitic-N refers to a N atom that substitutes for C atoms in the hexagonal rings [22]. For instance, these bonding configurations have a significant effect on the charge distribution of the carbon network and may work as activation sites on the graphene surface, i.e., pyridinic-N is believed to be associated with carbon monoxide (CO) detection due to the availability of a single lone pair of the electron, which is considered as an active catalytic centre [23] while graphene doping with high number of pyrrolic-N, experimentally enhanced the selectivity towards nitrogen dioxide (NO₂) detection [24,25].

Direct synthesis through the chemical vapor deposition (CVD) method is widely used to produce N-doped graphene because of its economic efficiency, scalability, and acceptance by the semiconductor industry. A typical CVD route to produce N-doped graphene has been reported using various carbon precursors such as methane, acetylene, or pyridine at high temperatures in the range of 800–1050 °C [26–29]. In most cases, high-temperature processes (optimum) mostly result in dominant graphitic-N configuration over the large-area graphene while when its overheating, pyrrolic-N and pyridinic-N will be predominant [26, 30]. It is speculated due to the break of C-C bonds at the graphene lattice, resulting low coverage of N-doped graphene over the substrate. Besides that, high temperature growth was reported lead

to insufficient of N atoms concentration in the graphene lattice. It is difficult to realize since there's competition between the formation of C-C and C-N network to achieve at minimum internal energy [31].

At the same time, great deal of effort is always required in limiting the high-temperature processes due to severe physical damage to the substrates or devices, especially during the integration of graphene onto the nanoelectronics platform. Therefore, low-temperature growth of graphene is highly desirable as it is a more economical and convenient process on any low-temperature substrate. To achieve this, Ni and alloy metals have been reported as suitable catalysts for further reduction of the growth temperature while maintaining the same graphene quality as compared to that obtained by high-temperature processes [32,33].

On the other hand, one promising way to realize the low-temperature growth of N-doped graphene is employing plasma-assisted CVD [34-48]. It is believed that the plasma does not only further lower the temperature for the growth of N-doped graphene but also can provide substantial free radicals for highly efficient N substitution in the direct growth of nanographene films. Meanwhile, several groups have demonstrated that the reduction of the growth temperature can be achieved using polyhalogenated aromatic compound [miza, 26] or heteroatoms containing carbon sources such as pyridine [39,40] that possess a similar structure to benzene for producing high-quality graphene [40]. A few studies have also been demonstrated that the growth temperature of N-doped graphene can be lowered to 435 °C, in which the N atoms are mainly incorporated in the pyridinic-N form [36,37]. Meanwhile, at a much lower temperature of 300 °C, a recent study of N-doped graphene grown on Cu foils using liquid pyridine via two-step CVD demonstrated high-quality graphene films with dominant graphitic-N, but the N atomic concentration was low at around 1.6 at. % [40]. Although the growth of N-doped graphene has been reported previously, none of the systematic studies were focused on achieving nanographene films with high N doping concentration with high number of pyridinic N or pyrrolic-N at low temperatures, particularly below 200 °C for cost-effective advanced electronic applications such as sensors [41].

In this study, we report a viable method to extend the growth capabilities of N-doped nanocrystalline graphene films with enhanced N doping at low temperatures as low as 100 °C using a cold-wall plasma-assisted CVD system. This is the lowest temperature that has been reported to date for the growth of N-doped nanocrystalline graphene. In this method, we combine Joule heating and the plasma-assisted growth process at low-temperature regimes and use a mixture of benzene/ammonia/Argon ($C_6H_6/NH_3/Ar$) system to produce large-area N-doped nanocrystalline graphene films on a polycrystalline Ni catalyst in a shorter time as compared to the existing hot-wall CVD method. The influences of the NH_3/Ar ratio and RF on the morphological, chemical composition, structural, and electrical properties of N-doped nanocrystalline graphene films are systematically studied. The findings suggest that the strong synergetic effects of the NH_3/Ar ratio and RF are key to this synthesis route and offer fine-tuning control over macroscopic features to enable substantial N doping into the graphene lattice. The possible growth mechanism with pyridinic-N- and pyrrolic-N-dominated nanocrystalline graphene at low-temperature regimes is also discussed to demonstrate the tunability of N doping concentration.

1.2 Problem Statement

Graphene is a novel nanomaterial with two-dimensional form of carbon packed in hexagonal lattice. Due to its unique properties in terms of mechanical, chemical, optical and electronic, it has received great attention among researchers as sensing elements in chemo resistive gas sensors [16]. However, due to physisorption of pristine graphene that leads to false alarm detection, researchers have proposed defects, functional groups or dopants in the graphene lattice for strong adsorption as reported in theoretical studied [12-15]. Besides that, the utilization of graphene in most nanoelectronics application is restricted due to its gapless states [17,18]. To exploit possible modifications or tailoring its properties, it is necessary to control the charge carrier concentration by tuning the Fermi level (E_F). The method applied for band gap tuning in graphene is through doping such as surface transfer doping, substitutional doping, or chemical doping [19]. N atoms substitution in graphene is most preferable due to its excellent properties such as comparable atomic size and possession of five valence electrons [21]. Particularly, N-doped graphene has three common bonding

configurations known as pyrrolic-N, pyridinic-N, and graphitic-N. Among these bonding configurations, pyridinic-N is believed to be associated with CO detection due to the availability of a single lone pair of the electron, which is considered as an active catalytic centre [23] while N-doped graphene with high number of pyrrolic-N, experimentally enhanced the selectivity towards NO detection [24,25].

A typical CVD route to produce N-doped graphene has been reported using various carbon precursors such as methane, acetylene, or pyridine at high temperatures in the range of 800–1050 °C [26-29]. In most cases, high-temperature processes (optimum) mostly result in dominant graphitic-N configuration over the large-area graphene while when its overheating, pyrrolic-N and pyridinic-N will be predominant [26, 30]. It is speculated due to the break of C-C bonds at the graphene lattice, which had resulting low coverage of N-doped graphene over the substrate. Besides that, high temperature growth was reported lead to insufficient of N atoms concentration in the graphene lattice. It is difficult to realize since there's competition between the formation of C-C and C-N network to achieve at minimum internal energy [31].

At the same time, great deal of effort is always required in limiting the high-temperature processes due to severe physical damage to the substrates or devices, especially during the integration of graphene onto the nanoelectronics platform. Therefore, low-temperature growth of graphene is highly desirable as it is a more economical and convenient process on any low-temperature substrate. A few studies have also been demonstrated that the growth temperature of N-doped graphene can be lowered to 435 °C, in which the N atoms are mainly incorporated in the pyridinic-N form [36,37]. Meanwhile, at a much lower temperature of 300 °C, a recent study of N-doped graphene grown on Cu foils using liquid pyridine via two-step CVD demonstrated high-quality graphene films with dominant graphitic-N, but the N atomic concentration was low at around 1.6 at. % [40]. Although the growth of N-doped graphene has been reported previously, none of the systematic studies were focused on achieving nanographene films with high N doping concentration at low temperatures with tuneable bonding configurations (predominant pyridinic-N or pyrrolic-N), particularly below 200 °C.

1.3 Research Objectives and Scope

In regard to the highlighted challenge, the objective of this study is to synthesize N-doped nanocrystalline graphene film at low temperature regime with high N-atoms concentration and tunable bonding configurations of pyridinic-N or pyrrolic-N by plasma-assisted CVD system.

- 1) To investigate the effect of low temperature (100-400°C), RF (10-50W) and NH₃-Ar flow rates ratio towards the morphological, compositional, structural, optical and atomic properties of grown N-doped nanocrystalline graphene film.
Scopes: Mixture of Ar, C₆H₆ and NH₃ at 8: 1: 1 are exposed during growth process. Ni substrate is used as the metal catalyst.
- 2) To propose the reasonable growth mechanism based on the obtained results.
Scopes: The propose idea were based on the effect of temperature, RF and precursor concentration towards grown of N-doped nanocrystalline graphene sheet properties.
- 3) To fabricate the back-gated N-doped nanocrystalline graphene field effect transistor (FET).
Scopes: The fabrication process involved in designing mask, metal deposition, resist coating, exposure and development process of interdigitated electrodes' (IDE) structure on 8-inch wafer and conventional wet transfer process of grown N-doped nanocrystalline graphene films on back-gated FET devices.
- 4) To investigate the electrical properties of back-gated N-doped nanocrystalline graphene FET.
Scopes: It consist the investigation of sheet resistance of grown N-doped nanocrystalline graphene film, Ohmic contact, N atoms concentration (at. %) towards sheet resistance of the grown samples, the effect of N doping concentration towards electron density distribution, electron-holes mobilities of the devices, and types of the band-gap tuning.

1.4 Overview of Thesis Organization

This thesis is organized into 6 chapters. Chapter 1 presents an overview of the research background and motivation. This chapter also provides the research objective and its scope of work.

Chapter 2 provides an overview of the theoretical background and literature review for the work. The explanation focuses on types of gas sensors, sensing materials and its performances as well as the sensing mechanism towards various type of toxic gases. Recent development of the promising material, graphene with the substitution of heteroatoms of N is also explained in this chapter. The previous study on low temperature growth for N-doped graphene also are also well reviewed.

Chapter 3 presents the growth process of N-doped nanocrystalline graphene film, characterization process and the equipment used. Next, the integration of N-doped nanocrystalline graphene film onto back-gated FET also is well described in this chapter.

Chapter 4 presents the result and discussion of the synthesis of N-doped nanocrystalline graphene film at low temperature regime with tunable of pyridinic-N and pyrrolic-N by cold-wall plasma assisted CVD. The result and discussion for annealing process and the effect of temperature towards growth of N-doped nanocrystalline graphene film from 500° C down to 100° C are presented. Then, the discussion on morphology, structural, elemental and atomic properties towards the lowest growth temperature of N-doped nanocrystalline graphene film also well discussed throughout this chapter. Finally, the result and discussion on the effect of NH₃/Ar flow rates ratios and RF towards the formation of N bonding configurations (pyridinic-N and pyrrolic-N) are deliberated. Lastly, this chapter also described the proposed growth mechanism of the grown N-doped nanocrystalline graphene film.

Chapter 5 presents the fabricated of standard back-gated N-doped nanocrystalline graphene FET. The quality of the transferred N-doped nanocrystalline

graphene film on IDE' structure and the electrical properties of the devices based on the N-doped nanocrystalline materials are also presented and described.

Chapter 6 concludes the main findings of the work and the direction for the future work is described accordingly.

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LIST OF PUBLICATIONS AND CONFERENCES

PUBLICATIONS

1. **Nur Hamizah Zainal Ariffin**, Muhammad Aniq Shazni Mohammad Haniff, Mohd Ismahadi Syono, Mohd Ambri Mohamed, Azrul Azlan Hamzah, Abdul Manaf Hashim. ‘Low-Temperature Nitrogen Doping of Nanocrystalline Graphene Films with Tunable Pyridinic-N and Pyrrolic-N by Cold-Wall Plasma-Assisted Chemical Vapor Deposition,’ ACS Omega 2021, 6, 37, pp. 23710–23722 (Impact Factor: 3.512, Q1).
2. Muhammad Aniq Shazni Mohammad Haniff, **Nur Hamizah Zainal Ariffin**, Mohd Ismahadi Syono, Syed Muhammad Hafiz, Poh Choon Ooi, Mohd Ismahadi Syono, Abdul Manaf Hashim. ‘Wafer-scale Fabrication of Nitrogen-doped Reduced Graphene Oxide with Enhanced Quaternary-N for High-Performance Photodetection,’ ACS Appl. Mater. Interfaces 2021, 11, 4, pp. 4625–4636 (Impact Factor: 8.91, Q1).
3. Muhammad Aniq Shazni Mohammad Haniff, **Nur Hamizah Zainal Ariffin**, Poh Choon Ooi, Mohd Farhanulhakim Mohd Razip Wee, Mohd Ambri Mohamed, Azrul Azlan Hamzah, Mohd Ismahadi Syono, Abdul Manaf Hashim. ‘Practical-Route for the Low-Temperature Growth of Large Area Bilayer Graphene on Polycrystalline Nickel by Cold-Wall Chemical Vapor Deposition,’ ACS ACS Omega 2021, 6, 18, pp. 12143–12154 (Impact Factor: 3.512, Q1).

CONFERENCE

1. **Nur Hamizah Zainal Ariffin**, Muhammad Aniq Shazni Mohammad Haniff, Sz J. Yung, Mohd Ismahadi Syono, Abdul Manaf Hashim. ‘Synthesis and Characterization of Nitrogen-doped Graphene at Low Temperatures by Cold Wall Plasma Assisted Chemical Vapor Deposition,’ Nanotechnology Malaysia Biennial Symposium 2021, 11-13 October 2021, Universiti Kebangsaan Malaysia, Selangor, MALAYSIA.