SYNTHESIS AND CHARACTERIZATIONS OF BLACK PHOSPHORUS BY MECHANICAL BALL MILLING

This report submitted in accordance with the requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Hons.)

by

TE KE JIE

B051610116

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FACULTY OF MANUFACTURING ENGINEERING

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Disahkan oleh:

TE KE JIE

Alamat Tetap:

75, LORONG SRI DAMAK,
58, TAMAN SRI ANDALAS,
41200, KLANG, SELANGOR.

(Dr. Mohd Shahadan Bin Mohd Suan)

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DECLARATION

I hereby, declared this report entitled "Synthesis and Characterizations of Black Phosphorus by Mechanical Ball Milling" is the results of my own research except as cited in reference.

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfillment of the requirements for the degree of Bachelor of Manufacturing Engineering (Hons.). The members of the supervisory committee are as follow:

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Dr. Mohd Shahadan Bin Mohd Suan

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ABSTRAK

Fosforus hitam adalah bahan semikonduktor lapisan dua dimensi. Ciri-ciri yang unik seperti mobiliti Carrier yang tinggi dan jurang bandable telah menarik perhatian daripada saintis, pembuat kilang dan jurutera. Sintesis fosforus hitam akan dikaji dengan menggunakan fosforus merah sebagai bahan mentah melalui transformasi. Kaedah pengilangan bola mekanikal digunakan pada fosforus merah dengan pengisaran bola yang dibuat daripada besi tahan karat untuk sintesis fosforus hitam. Proses ini akan menjalani dalam masa 1 jam, 2 jam, 3 jam dan 4 jam untuk menyiasat kehadiran dan intensiti fosforus hitam dengan menggunakan kelajuan putaran yang sama dan nisbah fosforus merah dengan pengisaran bola yang betul. Kesan pada masa parameter di pengilangan bola akan dikaji untuk mengenal pasti struktur dan sifat fizikal fosforus hitam. Teknik pencirian akan dilaksanakan terhadap setiap sampel yang disinstesiskan pada setiap tempoh. Sinar-X-ray (XRD) digunakan untuk mengenal pasti fasa sampel. Selain itu, Raman Spektroskopi digunakan untuk menyiasat kualiti kristal fosforus hitam dan morfologi fosforus hitam telah dikaji dengan menggunakan elektron pengimbasan mikroskop (SEM).

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ABSTRACT

The black phosphorus is a two-dimensional layer semiconductor material. The unique properties like high charge carrier mobility and tunable bandgap seeking attraction from scientist, manufacturer and engineers. The synthesis of black phosphorus will be study by using the red phosphorus as the raw material undergo the transformation. The mechanical ball milling method is applied on red phosphorus with stainless steel grinding ball to synthesize the black phosphorus. The process will undergo in 1 hours, 2 hours, 3 hours and 4 hours to investigate the presence and intensity of black phosphorus with the constant speed of rotation and the weight powder ratio. The parameter effect which the time on ball milling will be studied to identify the structural and physical properties of black phosphorus. The characterize technique will apply on the result sample that synthesized on each period. X-Ray Diffraction (XRD) was used to identify the phase of the samples. Besides that, Raman Spectroscopy used to investigate the crystalline quality of Black Phosphorus and the morphology of the Black Phosphorus pellets was investigated using a scanning electron microscope (SEM).

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DEDICATION

This report is dedicated
to my beloved parents,
who educated me and enable me to reach this level
to my honoured supervisor,
Dr. Mohd Shahadan Bin Mohd Suan
for his advices, support and patience during completion of this project
and to all staffs & technicians,
for their advices and cooperation to complete this project
Thank You So Much & Love You All Forever

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LIST OF ABBREVIATIONS

BP	-	Black Phosphorus
2D	-	2 Dimensional
RP	-	Red Phosphorus
Cu	-	Copper
Sn	-	Tin
SnI4	-	Tin(IV) Iodide
SnP	-	Sodium Nitroprusside
ZnO	-	Zinc Oxide
Al2O3	-	Aluminium Oxide
DNA	-	Deoxyribonucleic Acid
RNA	-	Ribonucleic Acid
ATP	-	Adenosine Triphosphate
P	-	Phosphorus
P4	-	Tetraphosphorus
HfLaO	-	Hafnium–Lanthanum Oxide
SEM	-	Scanning Electron Microscopy
EDX	-	Energy Disperse X-Ray
XRD	-	X-ray diffraction
Ar	-	Argon
N2	-	Nitrogen

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LIST OF SYMBOLS

%	-	Percentage
mm	-	Millimetre
nm	-	Nanometer
µm	-	Micrometer
GPa	-	Giga Pascal
MPa	-	Mega Pascal
° C	-	Degree Celsius
°	-	Degree
θ	-	Theta
N	-	Newton
ml	-	Millilitre
K	-	Kelvin
λ	-	Lambda
kV	-	Kilovolt
Å	-	Angstrom

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CHAPTER 1

INTRODUCTION

This chapter introduces the subject matter and problems being studied and indicates its importance and validity. The chapter comprises of research background, problem statement, objectives, and research scope of the work.

1.1 Research Background

Phosphorus is one of the most common elements on Earth, containing a proportion of as much as 0.1% of the Earth's crust according to (Chemical Society Review, 2014). Phosphorus basically has three white, red and black phosphorus allotropes. Black phosphorus is the least reactive allotrope among these three forms of phosphorus and has higher electrical conductivity compared to white and red phosphorus. (The History and Use of Our Earth Chemical Elements, 2006)

Red phosphorus is a more stable allotrope that displays in some semiconducting properties. Normally used in the production of semiconductors, safety matches, smoke bombs and incendiary shells in organic. (Red Phosphorus Uses) Meanwhile, white phosphorus will auto-ignite and burn fiercely in air when heated to 30°C, which limits its use in pure form to explosives. (Niosh, 2018) It is a wide bandgap insulator. Moreover, the army used white phosphorus mainly as an obscurant. If phosphorus ignites, white phosphorus pentoxide clouds are formed, which may be sufficiently thick to be opaque to hide on the battlefield.

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Black phosphorus is likely to be the layered semiconductor material with the highest carrier mobility at room temperature, making it promise for high-performance electronic applications. According to the Xu *et al.* (2018), black phosphorus (BP), also known as phosphorene, has attracted recent scientific attention owing to its unique structure and properties. BP has interesting physical properties, such as high load carrier mobility, large on - off ratio, major anisotropy, and layer-dependent bandgap, as a direct-bandgap layered 2D semiconductor. In field-effect transistors, photoelectric systems, lithium-ion batteries, phototherapy, photovoltaics, sensing, and catalysis, it has also shown great application potential. In addition, BP bode well for biomedical applications for biodegradability and biocompatibility.

Based on Yaris (2015), stated that a new experimental revelation about the potential application of this highly promising material to mechanical, optoelectronic and thermoelectric devices should be enabled by black phosphorus nanoribbons. A team of researchers at the U.S., Lawrence Berkeley National Laboratory (Berkeley Lab) of Department of Energy (DOE) has experimentally confirmed strong in-plane anisotropy in thermal conductivity, up to a factor of two, along the zigzag and armchair directions of single-crystal black phosphorous nanoribbons as shown in the figure 1.1. Moreover, black phosphorus, named for its distinctive color, is a natural semiconductor with an energy bandgap that enables its electrical conductance to be switched "on and off." It has been theorized that black phosphorus has opposite anisotropy in thermal and electrical conductivity as opposed to graphene.

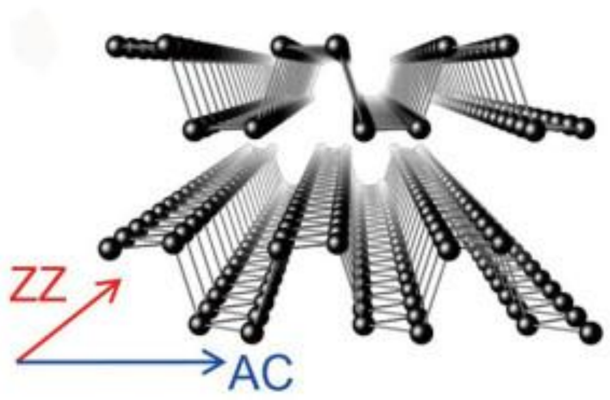

Figure 1.1: The strong in-plane anisotropy in thermal conductivity along the zigzag (ZZ) and armchair (AC) directions of single-crystal black phosphorous nanoribbons.

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Black phosphorus (BP) was first discovered by Percy William Bridgman in 1914 from white phosphorus under high pressure conditions (∼1.2–1.3 GPa, 200 °C) (Two new modification of phosphorus (1914). Moreover, according to the Materials Letters (2019), which has an easy route to synthesize high-quality black phosphorus from amorphous red phosphorus. Black phosphorus was synthesized with amorphous red phosphorus using Cu as a catalyst, and Sn and SnI4 were transferred into a silica glass ampoule with a mixture of copper, tin, red phosphorus and SnI4. Under vacuum, the ampoule was sealed and put horizontally in an oven. The strong mix was in the oven's hot end. The reaction has been cooled over 3 days to room temperature, and cooling at this slow rate to room temperature allows for better growth of crystals.

Other than that, according to the Preparation of Black Phosphorus by the Mechanical Ball Milling Method and its Characterization (2018), red phosphorus successfully turned to black phosphorus by the mechanical ball milling method. Initially, the amorphous red phosphorus turns into black phosphorus nanocrystals under the action of mechanical milling. Subsequently, the grains were refined and became tiny grains under the action of many edge dislocations in the crystals.

Black phosphorus also can be synthesized by using electrochemical exfoliation. Abdelkader (2015) had mentioned the electrochemical exfoliation mechanism of BP, when a voltage is applied to bulk BP as the working electrode in a conductive solution (electrolyte), the electrical current is generated and the 2D BP nanoflakes are produced by structural deformation of the layered BP material. Besides, pulsed deposition of the laser is a method for mechanical vapor deposition. A high-power pulsed laser beam is used in this process to ablate the target material to be deposited in a chamber of vacuum. The growth of wafer-scale BP ultrathin films with tunable direct bandgap at low temperatures of around 150 ° C was demonstrated by Yang *et al.* (2015). The benefit of using PLD to prepare BP is that if the chamber is wide enough, the ultra-thin film would be collected as thick as desired.

In the application of transistor, field-effect transistors (FETs) are the most researched of the potential applications of black phosphorus, with many theoretical and experimental studies conducted over the past five years. The attractive FET features of relatively high on / off ratio and good load carrier mobility together with high conductivity will ensure fast switching with high efficiency and error-free logic according to the Li *et al.* (2014). Besides,

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based on Engel et al. (2014), black phosphorus also seeking attraction from photodetector application. The direct bandgap of black phosphorus (between 0.3eV and 1.88eV) can be tuned by changing the number of stacked layers. This makes it optically active in the red to NIR spectrum and has enabled NIR photodetectors to produce visible devices. With optical fiber networks, this region of the spectrum is essential and indicates that black phosphorus may play a role in future communication networks.

In short, the black phosphorus has been applied to many applications especially the electronic and semiconductor industry due the high carrier mobility and the widely turn able bandgap. Hence, the synthesis of black phosphorus could attract the attention from manufacturers. However, the current synthesis methods are quite complicated and high cost to implement it. The possibility of synthesizing the black phosphorus using simple and convenient way will be highly beneficial for industry.

1.2 Problem Statement

BP is a single-element crystalline substance consisting only of atoms of phosphorus. It is attracting interest from condensed matter physicists, chemists, semiconductor device engineers, and material scientists. Due to its high charge mobility and a direct gap of the order of 0.3–1.5 eV, BP presents as a very promising raw material for the electronics and energy markets. Based on Tran *et al.* (2015), BP has a mobility of 350 $cm^2 V^{-1} s^{-1}$ and at recent studies on a few layers of BP transistors have shown a thickness-dependent band gap, significantly improved mobility and higher current ON / OFF ratios. Moreover, BP also shows strong light-matter interactions in visible and infrared frequencies. This also represent at Li *et al.* (2015) whereas BP's interlayer which the distance is greater than graphite length. BP has a medium conductivity of~300 $S\ m^{-1}$, and a further transformation from semiconducting to Lithium induced metallic gives rise to good electrical conductivity. Besides, BP still has a fair anode discharge and charging potential.

However, the current synthesis method is highly complex and require expensive machine and starting materials. Phosphorus mainly have three type which is red, white and black. In term of properties, the black phosphorus has the best layered dimensional structure

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and stable allotrope compare to red and white phosphorus. Although white and red does not have same properties but they can be used to produce black phosphorus. According to the Allotropes of Phosphorus (2019), white phosphorus and red phosphorus can change to black phosphorus by heating at 473K and 803K respectively. Besides, both of materials have high potential for synthesizing but in term of safety, white phosphorus is more hazardous and higher risk material. From the source of Boundless Chemistry, stated that red phosphorus will ignite at 300°C while white phosphorus will ignite at 30°C. This proved that white phosphorus will ignite at room temperature and easy to react with air. Hence, by comparison, the red phosphorus is more stable than white phosphorus. (Boundless Chemistry, 2019)

Other than that, among the three types of phosphorus which are red, white and black, the most expensive is black phosphorus. From the Ossila website, the price of black phosphorus that obtained is very expensive. With the weight of 250mg, cost about RM1200 Malaysia Ringgit. While red phosphorus, which the same sources from phosphorus but in difference microstructure and colour have huge difference price range compare with black phosphorus. Based on the Alibaba website, the price for 1 kilogram red phosphorus cost about RM16.75. Hence, from the figure 1.2 show that the black phosphorus cost about RM4.8 million while red phosphorus is RM16.75 in the comparison of price per kg. BP has 280K times than red phosphorus which is extremely high different between both phosphorus.

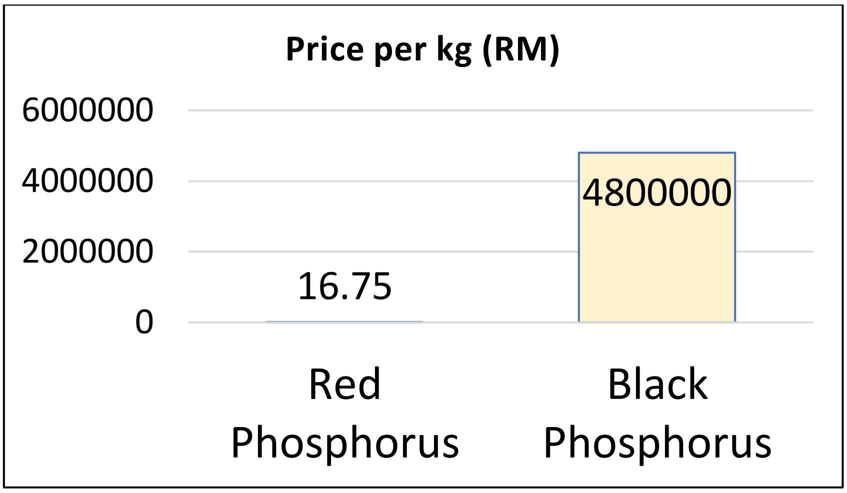

Figure 1.2: Price comparison between red phosphorus and black phosphorus. (current price from alibaba.com and oscilla.com)

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In the current synthesis method, it is complex and require many chemical substances to obtain the black phosphorus structure. Based on Wang *et al.* (2019), in the presence of various mineralizers such as Sn24P19.3I8 (21.6 mg), SnIP (10.6 mg), a mixture of Sn and I2 (Sn: 4.5–14 mg, I2: 4.8 mg) and a mixture of SnI2 and Sn (SnI2: 7.1 mg, Sn: 11.2 mg), were prepared for the presence of BP crystal and will undergo the complex of temperature heating with time duration. According to the Tiouitchi (2018), Black phosphorus has been synthesized using Cu as a catalyst from amorphous red phosphorus with the mixture of copper (22.75 mg, powder, 99.5%, aldrich), tin (42.5 mg, 99%, powder, aldrich), red phosphorus (155 mg, 99.99%, lump, acrosorganics) and SnI4 (10.0 mg). The chemical mixture need to measure and mixing in the specified quantity to successfully obtain the BP crystal structure.

Besides, there are also synthesis method is expensive at starting material or machine. Pulsed laser deposition method is the one of the costly methods to start up the experiment. Based on Kuzanyan *et al.* (2016), the pulsed laser deposition can be high cost when manufacture in a large size. Moreover, there is the price of pulsed laser deposition machine from mcallister.com as show Figure 1.3, the machine price is nearly to RM45,000.00. Hence, from the starting material in high cost with the manufacturing cost, it may affected the price for the final product that produced.

Figure 1.3: Price for Pulsed Laser Deposition.

Regarding from the problem statement that founded, it show that black phosphorus is the expensive produce and need the complex method to synthesis it. Upon from that, there is one of the method to yield nanoparticle is using ball mill. The method have been reported to successfully yield various types of nanoparticles includes ZnO, Al2O3, etc based on Salah *et al.* (2011) The temperature created during the process is expected to transform the red

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phosphorus into the black phosphorus. In order to obtain high purity of black P, the milling parameters include milling speed, ball size and quantity need to be optimized. Hence, this study is conducted to achieve the black phosphorus structure from red phosphorus by mechanical ball milling method.

1.3 Objective

I. To synthesize black phosphorus from red phosphorus by using mechanical ball milling method.
II. To analyse the structural and physical properties of the black phosphorus.
III. To investigate the effects of the milling time on the structural and physical properties of black phosphorus.

1.4 Research Scope

The scopes of research are as follows:

a) Synthesize the black phosphorus by using red phosphorus with mechanical ball milling.
b) Duration of milling time will be varied of 1 hour, 2 hour, 3 hour and 4 hour.
c) Milling speed is 400r.p.m. and ratio of grinding ball to red phosphorus powder is 500g to 1g. The quantity of stainless steel grinding ball is 25 which 16.4mm diameter and 20g for each.
d) Sample preparation of red phosphorus mix with grinding ball will be prepared in argon atmosphere glove boxes and put in the stainless steel jar after weighting.
e) The sample that done milling process will be stored in the glove box for 2 days for cooling down.
f) The morphology of the black phosphorus pellets was investigated using a scanning electron microscope (SEM).
g) X-ray diffraction (XRD) was used to identify the phase of the samples.
h) Raman Spectroscopy used to investigate the crystalline quality of black phosphorus.

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CHAPTER 2

LITERATURE REVIEW

This chapter is mainly describing the theory and important research finding related to this project, which have been defined and done by various researcher years ago.

2.1 Phosphorus

Phosphorus is the atomic chemical element number 15, a radioactive, non-metal combustible element that occurs in two common allotropic forms. According to Royal Society of Chemistry (2019), in the natural abundance, phosphorus is not found in nature, but is commonly present in mineral compounds. Phosphate rock, which contains the minerals of apatite and is found in large quantities in the world now and is an important source. Nowadays, many people are concerns that around in 2050, ' peak phosphorus' will occur, whereas our resources will reduce. Meanwhile, in biological role, phosphorus is important for all living things. They will in the forms of base of DNA and RNA in sugar-phosphate. As part of ATP (adenosine triphosphate), it is important for the transfer of energy in cells and is present in many other biologically important molecules.

In the 12th century, the Arab alchemists may have the chance become the first person intentionally founded phosphorus, but the records are uncertain. However, in 1669, Hennig Brand, a German merchant whose hobby was alchemy, has successfully discover phosphorus. Nevertheless, phosphorus remained a chemical mystery until it turned out to be a part of bones about a century later. Phosphoric acid was produced by digestion of bones with nitric or sulfuric acid, from which phosphorus could be purified by charcoal heating. Finally, in the late 1800s, Edinburgh's James Burgess Readman developed a method of electric furnace

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