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**SURFACE PRESSURE-AREA ISOTHERM, OPTICAL AND ELECTRICAL
PROPERTIES OF P3HT/NANOPARTICLES THIN FILMS BY
MODIFIED LANGMUIR-BLODGETT TECHNIQUE**

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ABSTRACT

Hybrid organic-inorganic nanocomposite materials have emerged as one of the most potential alternative candidate to silicon as future optoelectronic material due to their unique optical and electrical characteristics. However, current fabrication process involving synthesizing the pre-made nanoparticles inside the polymer matrices is tediously complex, costly and time consuming. In this research, two approaches in preparing nanocomposite thin films, *in situ* hybridization and *ex situ* hybridization, were studied and the results were compared. *In situ* hybridization, a novel method, where the nanoparticles were grown directly in the Poly(3-hexylthiophene) (P3HT) mixed with stearic acid layers by exposing the films to either H₂S or H₂Se gas. *Ex situ* hybridization were done by mixing pre-made CdS or CdSe quantum dots into P3HT solution. For both approaches, depositions of thin films on the solid substrate were done by employing modified Langmuir-Blodgett technique. Studies on Langmuir layer found that the film is very sensitive towards its environment where the amount of solutions, the weight percentage, and the subphase affecting the gas-liquid-solid transformation. Absorbance spectra show higher polymer crystallization for thin films exposed to H₂S or H₂Se gas. The peak shifting and depreciation of absorption intensity indicates the quantum confinement effect of nanoparticles formed. Photoluminescence intensity decreased with the increment of gas exposure time and quantum dots' weight percentage. The current density-voltage measurement revealed open circuit voltage for *in situ* hybrid thin film nucleating CdS and CdSe is 0.56 V and 0.72 V respectively. Thin films fabricated by *ex situ* method possess lower Johnson noise than that of *in situ*. Overall, *in situ* hybridization has shown a better performance as compared to hybrid nanocomposite thin films fabricated using *ex situ* approach. These findings have given a promising future for gas exposure method to be further studied in the fabrication of hybrid organic-inorganic nanocomposite thin films for optoelectronics application.



PENCIRIAN ISOTERM TEKANAN PERMUKAAN-LUAS, OPTIK DAN ELEKTRIK BAGI FILEM TIPIS P3HT/NANOPARTIKEL MENGUNAKAN KAEDAH UBAH SUAI LANGMUIR-BLODGETT

ABSTRAK

Bahan komposit nano hibrid organik-tak organik telah menjadi salah satu calon alternatif kepada silikon sebagai bahan optoelektronik disebabkan oleh ciri-ciri optik dan elektrik yang unik. Walau bagaimanapun, proses fabrikasi masakini melibatkan sintesis pra-hasil nanopartikel di dalam matriks polimer adalah rumit, mahal dan memakan masa. Di dalam kajian ini, dua pendekatan dalam penyediaan filem tipis komposit nano, penghibridan *in situ* dan penghibridan *ex situ*, telah dikaji dan keputusannya dibandingkan. Penghibridan *in situ* ialah kaedah novel di mana nanopartikel ditumbuhkan secara langsung dalam lapisan Poly(3-hexylthiophene) (P3HT) yang dicampur dengan asid stearik, dengan mendedahkan filem tipis dengan gas H₂S atau H₂Se. Penghibridan *ex situ* dilakukan dengan mencampurkan titik kuantum CdS atau CdSe ke dalam larutan P3HT. Untuk kedua-dua pendekatan ini, filem tipis didepositkan ke atas substrat dengan menggunakan kaedah ubahsuai Langmuir-Blodgett. Kajian terhadap lapisan Langmuir mendapati bahawa filem tersebut sangat sensitif kepada perubahan sekeliling, di mana jumlah larutan, peratusan berat dan sub-fasa memberi kesan terhadap transformasi gas-cecair-pepejal. Serapan spektrum menunjukkan filem tipis yang didedahkan kepada gas H₂S atau H₂Se mengalami penghabluran polimer yang lebih tinggi. Anjakan puncak dan penurunan keamatan serapan menandakan kesan kekangan kuantum oleh nanopartikel yang terbentuk. Keamatan PL menurun dengan kenaikan masa dedahan dan peratusan berat titik kuantum. Pengukuran ketumpatan arus-voltan menunjukkan bahawa nilai voltan litar terbuka bagi filem tipis hibrid *in situ* menghasilkan CdS dan CdSe ialah 0.56 V dan 0.72 V. Filem tipis yang difabrikasi secara *ex situ* mempunyai ciri hingar Johnson yang lebih rendah berbanding filem tipis yang dihasilkan secara *in situ*. Secara keseluruhan, hibrid filem tipis yang terhasil dari proses *in situ* mempunyai prestasi yang lebih baik berbanding dengan komposit nano hibrid filem tipis yang difabrikasi menggunakan pendekatan *ex situ*. Keputusan-keputusan ini memberikan masa depan yang cerah untuk kaedah pendedahan gas dikaji dengan lebih lanjut untuk fabrikasi hibrid filem nipis organik-tak organik bagi aplikasi optoelektronik.

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LIST OF ABBREVIATIONS AND SYMBOLS

μA	microampere
2D	Two-dimension
3D	Three-dimension
A	Area per molecule
Å	Armstrong
A_i	Lift off area
Al	(Aluminum)
AM 1G	Air Mass 1 Global
A_o	Molecular area
APCVD	Atmospheric pressure chemical vapor deposition
ASTM	American Standard for Testing and Materials
c	velocity of light
Cd^{2+}	Cadmium ion
CdCl_2	Cadmium chloride
CdS	Cadmium sulfide
CdSe	Cadmium selenide
CVD	Chemical vapor deposition
D/A	Donor/Acceptor
DC	Direct current
DFT	Density functional theory



DI	De-ionized
DSA	Dynamic signal analyzer
DUT	Device under test
E	Energy
EB-PVD	Electron beam physical vapor deposition
EDX	Energy Dispersive X-ray
emf	Electromotive force
FACVD	Flame assisted chemical vapor deposition
FESEM	Field Emission Scanning Microscopy
FF	Fill factor
h	Planck's constant



H ₂ S	Hydrogen sulfide
H ₂ Se	Hydrogen selenide
HOMO	Highest occupied molecular orbital
Hz	Hertz
ITO	Indium Tin Oxide
J _{MPP}	Current density at maximum power point
J _{sc}	Short-circuit current density
J-V	Current density-Voltage
k	Boltzmann constant
kHz	kilohertz
LB	Langmuir-Blodgett
LED	Light-emitting diode





LFenM Low frequency electrical noise measurement

LN Low noise

LPCVD Low pressure chemical vapor deposition

LS Langmuir-Schaefer

LUMO Lowest occupied molecular orbital

Mma Mean molecular area

M_w Molecular weight

$N(f, T)$ Planck number

N_A Avogadro's number

OLED Organic light-emitting diode

P3HT Poly(3-hexylthiophene)



PECVD Plasma enhanced chemical vapor deposition

PL Photoluminescence

PLD Pulsed laser deposition

P_{max} Maximum power output

PSD Power spectral density

PVD Physical vapor deposition

QD Quantum dot

R Resistance

rpm Rotation per minute

SA Stearic acid

$S_I(f)$ Current noise



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SMU	Source measure unit
$S_v(f)$	Voltage noise
T	Temperature
UV-Vis	Ultraviolet-visible
V_{MPP}	Voltage at maximum power point
V_{oc}	Open-circuit voltage
wt%	Weight percentage
γ	Surface tension of water covered by film
γ_o	Surface tension of pure water
λ	Wavelength
ν	Frequency

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CHAPTER 1

INTRODUCTION



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1.1 Research Background

Semiconductor materials have been an important catalyst in tremendous progress of electronic and microelectronic devices. Semiconductor is a group of materials whose conductivity lies between conductor and insulator, ranging from 10^5 S/cm – 10^{-8} S/cm (Czichos, Saito & Smith, 2007). It exhibits an energy bandgap, where the states below the gap are fully occupied by electrons whilst the upper state is empty. At absolute zero, the semiconductor carries no net current hence acts like an insulator.



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The most dominant material for semiconductor devices is silicon, a single-element from group IV, which is abundantly and cheaply available all around the world. One main advantage of silicon general properties is its ability to be doped to tune the types of conductivity in order to fabricate high quality substrates. Silicon semiconductor industry is a matured technology that began in 1947 when silicon-based transistors were invented in Bell Laboratories (Zekry, 2014). The rapid progress in silicon technology enabled Bell Lab to invent photovoltaic device with efficiency around 6% in 1954 (Chapin, Fuller & Pearson, 1954). However, the substrate fabrication is very expensive as compared to the cost of overall device. For example, in order to fabricate photovoltaic panel, around 50% of overall fabrication cost is due to cost of silicon substrate production (Aberle & Widenborg, 2011). Thinner wafers are produced to lower the cost, but it causes the wafer to break easily at minimum achievable thickness. Thinner substrates also lead to fractional loss due to sawing damage. Thus, among possible approach to address this issue are by using alternative semiconducting materials, thin film technology, or the combination of both.

The most popular choice of alternative semiconducting material is conjugated polymer, owing to its relatively lower cost as compared to silicon (Gaudiana & Brabec, 2008). While semiconducting properties of silicon depending on its crystal structure, conjugated polymer semiconductivity depends on its chemical structure. Conjugation in polymer is due to alternating single and double bonds between the carbon atoms on its backbone. Single bond comprises of strong covalent bond called sigma (σ) bond only, whilst double bond is constructed by both σ bond and a pi (π) bond. The π bond is due to

weak overlapping of unhybridized p-orbital electron. Electrons in π bond are known as π electrons, delocalized along carbon backbone. Atomic orbitals overlapping also creating occupied π -bond and unoccupied π^* -anti-bond molecular orbital. The filled π band is called the highest occupied molecular orbital (HOMO) and the empty π^* band is called the lowest unoccupied molecular orbital (LUMO). This is analogous to silicon band gap, where HOMO is equivalent to valence band and LUMO is called conduction band.

Among interesting characteristic of conjugated polymer are it has strong absorption and high quantum yield in the solid state that make it a promising material for optoelectronic devices (Brandão, Viana, Bucknall & Bernardo, 2014), exhibits molecular wire properties and highly fluorescent (Y. Liu, Lam & Tang, 2015) and it can be easily processed (Gaudiana & Brabec, 2008) and deposited on a wide range of substrates (Levell, Giardini & Samuel, 2010). The deposition of conjugated polymer is generally done by means of thin film technology.

Thin film technology henceforth became the basis in the development of solid state electronics, in which the properties of functional materials are significantly different when analyzed in the form of thin films as compared to their bulk materials. Thin film is a solid layer of a material, adhered to a substrate that possesses different properties of the said film, with the thickness ranging from tenths of nanometers to micrometers. The processing of materials into thin film allows easy integration into many types of applications in various industries (West, 2003).



The major application of thin film is in microelectronic field (Lazar, Tadvani, Tung, Lopez, & Daoud, 2010), with growing applications in other areas like optoelectronics, magnetic devices, electrochemistry, and protective and decorative coatings. Studies on thin films have advanced and combined many new area of research, particularly in solid state physics, chemistry and biophysics. One of the leading reasons behind thin film advancement is the miniaturization of electronic devices towards cheaper and faster gadget but with lower power consumption and higher efficiency.

The manufacturing technique plays important role in determining thin films' properties (Vilarinho, 2005). There are varieties of thin film deposition techniques available and in use today which originate from purely physical or chemical processes. However, recently many studies combined different well developed process to get more defined control and properties of the thin films. Generally, the deposition technique affects the morphology, adhesion, crystallinity, and growth rate of thin film, in which necessitate direct control of materials on molecular and atomic scale (Mallik & Ray, 2011). Hence the appropriate deposition method selection is vital in order to control the properties of the resultant film.

Thin films deposition can be categorized into one of three approaches: physical vapor deposition, chemical vapor deposition and wet chemical deposition. Each of the categories and several common techniques are described in the next subtopics.



1.2 Physical Vapor Deposition (PVD)

Physical vapor deposition (PVD) methods are a range of techniques used to fabricate thin films using purely physical process. The technique involves the condensation of a solid or liquid source material that is vaporized under vacuum, onto a substrate (Pulker, 1999). The evaporation of the source either by evaporation, or sublimation of ions impinge on a target, depending on the technique to excite the source atoms to the vapor phase. The main PVD techniques are vacuum thermal evaporation, sputter deposition, cathodic arc deposition and pulse laser deposition.

The first system called vacuum thermal evaporation is the easiest system among PVD technique. Due to its low cost and maintenance, most university research laboratories use this system in work of materials science and related field (Stagon, 2013). The evaporation of material occurs inside a vacuum chamber, in which a conductive heating element used to vaporize the materials, and allowed to deposit onto a substrate. This technique generally is performed in high to ultra-high vacuum condition because the vapor atom will not leave the liquid melt if the minimum required pressure is not met (Stagon, 2013).

A method that is categorized under thermal evaporation is electron beam evaporation (EB-PVD), in which a high energy electron beam bombards the source material causing local vaporization (Singh & Wolfe, 2005). The system is as illustrated in

Figure 1.1. With a proper pumping and slow outgassing of the source, high purity film can be achieved. This technique allows a wide range of materials to be deposited.

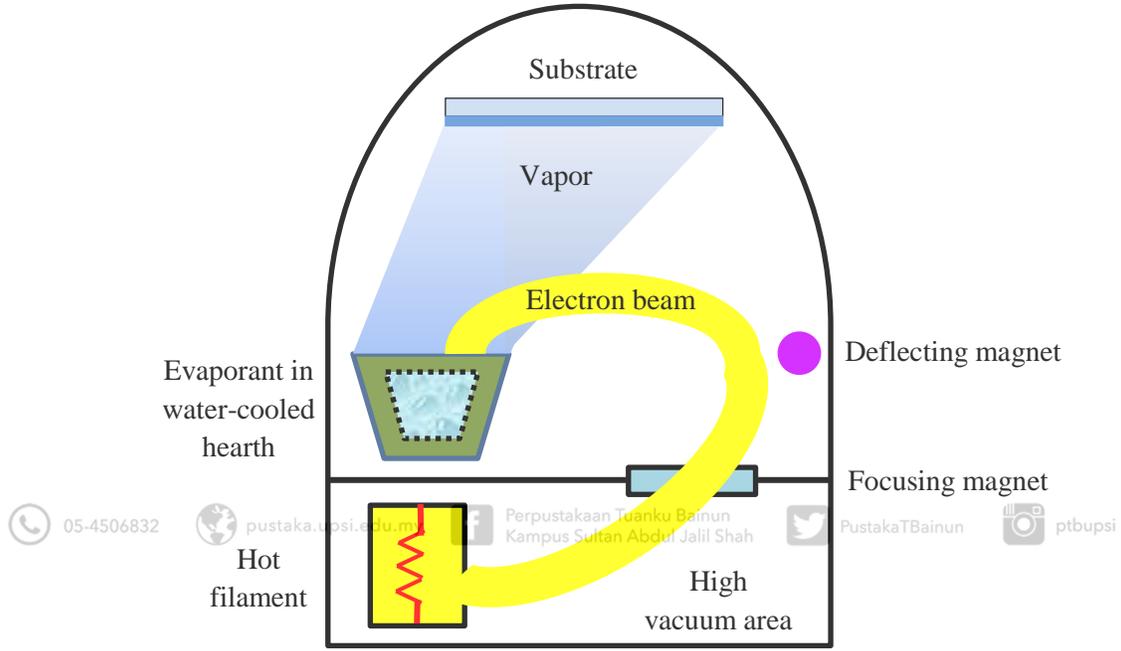


Figure 1.1. Electron beam physical vapor deposition (EB-PVD)

The second PVD technique is sputter deposition, where surface atoms are ejected from source materials by momentum transfer from energetic bombarding particles and then freed into a vacuum chamber. Since the energetic particles are usually gaseous ions accelerated from plasma, it is quite challenging to control the bombardment rate. Another setback of this method is random bombardment angle complicate the process of masking and shadowing that is usually implemented in microelectronic industry.

Cathodic arc deposition is the third system where cathodic electrode was vaporized on anodic electrode using high current, low-voltage arc. The arc beam is only a few microns in size and rapidly heats the area causing the source to evaporate and highly ionized. The ions are then accelerated to a biased substrate resulting a very hard thin film coating. Other deposition system generates a less hard coating even using the same materials because the temperature and velocity of the vapor is lower.

The fourth physical vapor technique is pulsed laser deposition (PLD) where a target is hit with a high energy laser in regular intervals causes evaporation of the source material (Park, Ikegami, Ebihara & Shin, 2006). The interaction of laser and the source not just heats the area, but also generates phonon, excites electrons, and ejects ions, molecules, and melted cluster. Hence this system is quite complicated and it is quite hard to control the deposition rate.

1.3 Chemical Vapor Deposition (CVD)

Chemical vapor deposition (CVD) is a process of formation of a thin film on a substrate by reacting chemical precursors in vapor phase. The precursors are evaporated via heating and transported into the reaction chamber. The product of the reaction is a solid material in thin film form, condenses on the surface inside the chamber. Figure 1.2 depicted the typical CVD reactor.