SYNTHESIS OF Cu_2CdSnS_4 QUATERNARY ALLOY NANOSTRUCTURES FOR DENGUE SEROTYPE-2 DNA BIOSENSOR APPLICATIONS

by

Ali Omar Ali Abu Odeh
1541711743

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy in Nanoelectronic Engineering

INSTITUTE OF NANO ELECTRONIC ENGINEERING
UNIVERSITI MALAYSIA PERLIS

2017

ACKNOWLEDGEMENT

In the name of Almighty ALLAH, the Most Gracious and the Most Merciful, that enabled me to finish this research project. Without His blessing, I would not have been able to come this far.

It would not have been possible to write this thesis without the help and support of many kind people around me, to whom it is possible to give a particular mention here.

I would like to express my deepest gratitude to my main supervisor Dr. Ramzan Mat Ayub for his dedication, support and help. Also, I would like to express my gratitude to my co-supervisor Professor Dr. Yarub Al-Douri for his support, guidance, motivation and encouragement throughout this project. Special thanks to Dr. Subash Gopinath for his guidance and help.

Sincere thanks to my wife, family members, friends and relatives for their support, spiritually and emotionally.

Lastly, I would like to acknowledge the academic and technical support of the Institute of Nano Electronic Engineering (INEE), University Malaysia Perlis.

Ali Abu Odeh

Perlis, Malaysia. October 2017

TABLE OF CONTENTS

CHAPTER 2: LITERATURE REVIEW

CHAPTER 3: PUBLISHED PAPERS

CHAPTER 4: CONCLUSIONS AND FUTURE WORKS

LIST OF TABLES

NO.		PAGE

LIST OF FIGURES

LIST OF ABBREVIATIONS

2-D	Two Dimensional
3-D	Three Dimensional
a. u.	Arbitrary unit
AFM	Atomic-force microscopy
Ag	Silver
CNTs	Carbon nanotubes
CCTS	Cu_2CdSnS_4
CIGS	$CuIn_xGa_{1-x}Se_2$
CIS	$CuInS_2$
CEs	Counter electrodes
CPs	Conducting polymers
CPV	Concentrating photovoltaic
CZTS	Cu_2ZnSnS_4
DENV	Dengue virus
DHF	Dengue haemorrhagic fever
DNA	Deoxyribonucleic Acid
DIW	Deionized Water
DF	Dengue fever
DSCs	Dye-sensitized solar cells
E_g	Energy gap
FF	Fill Factor

FWHM	Full Width at Half Maximum
FESEM	Field Emission Scanning Electron Microscope
GaN	Gallium nitride
GNRs	Gold nanorods
GNPs	Gold nanoparticles
IDEs	Interdigitated electrodes
IV	Current voltage characteristic
LED	Light-emitting diodes
LOD	Limit of Detection
LOQ	Limit of Quantification
NMs	Nanomaterials
n-Si	n-type silicon
SiO_2	Oxidized silicon
SPEs	Screen printed electrodes
Jsc	Short circuit current
VBD	Vector-borne diseases
Voc	Open circuit voltage
PVD	Physical vapor deposition
PVs	Photovoltaics
PL	Photoluminescence
QDs	quantum dots
SEM	Scanning electron microscope
RNA	Ribonucleic Acid.

RPM	revolution per minute
Si	Silicon
SiO_2	Silicon dioxide
SELEX	Systematic evolution of ligands by exponential enrichment
ssDNA	Single-stranded Deoxyribonucleic Acid
UTRs	Untranslated regions
UV-vis	Ultraviolet-visible
XRD	X-ray diffraction
SD	Standard deviation

LIST OF SYMBOLS

%	Percentages
°C	Degree Celsius
μ	Micro
m	Meter
M	Molar
cm	Centimeter
g	Gram
I	Current
L	Liter
A	Ampere
min	Minute
mm	Millimeter
V	Volt
M_s	Number of Moles
nm	Nanometer
s	Second
T	Temperature
Ω	Ohm
θ	Theta
W	Watt

t	Thickness
a, b, c	Lattice Parameters
hkl	Miller Indices
d_{hkl}	Inter Planar Spacing
β	Full Width at Half Maximum
2θ	Bragg Angle
δ	Dislocation Density
K	Boltzmann's Constant
A	Absorption Coefficient
E_g	Energy gap
D	Crystallite size
hv	Photo Energy
ρ	Electrical Resistivity
I-V	Current-Voltage
eV	Electronvolt
V	Volume
W	Weight
M_m	Molecular Mass
λ	Wave Length
α	Absorption Coefficient
v	Incident Photon Frequency
h	Planck's constant

n	Refractive Index
ε	Strain
N	Number of crystallites per unit area
R	Resistance
G	Conductance
F	Farad
C	Capacitance
ε_r	Relative static permittivity
ε_0	Constant permittivity of air
A	Area of the electrodes
d	Distance between electrode fingers
Zc	Impedance
W	Omega
f	Frequency
σ	Electrical conductivity
h	hour
m	Slope of the regression line
S	Siemens
Zc	Impedance

Sintesis Struktur-Nano Aloi Kuaterner Cu_2CdSnS_4 untuk Aplikasi Sel Solar dan Biosensor DNA Denggi

ABSTRAK

Penyelidikan dan pembangunan yang berterusan terhadap bahan-bahan baru merupakan kunci ke arah kemajuan teknologi yang mampan terutamanya untuk biosensor DNA. Dalam hal ini, struktur-nano aloi kuatenari Cu_2CdSnS_4 (CCTS) yang terdiri daripada unsur-unsur berkos rendah, kaya secara semulajadi dan bebas dari kecacatan telah mendapat banyak perhatian sejak akhir-akhir ini. Ianya mempunyai sejumlah merit termasuk pekali penyerapan optik yang tinggi (> 10^4 cm^{-1}), jurang jalur tenaga yang sesuai (1.4~1.5 eV), kecekapan penukaran kuasa yang tinggi, kekonduksian jenis-p, mobiliti lubang yang tinggi dan keupayaan meningkatkan kepekaan biosensor DNA. Oleh itu, matlamat kajian ini adalah untuk meningkatkan sifat-sifat optik dan elektrik struktur-nano aloi kuatenari CCTS untuk digunakan dalam pelbagai aplikasi seperti optoelektronik dan biosensor DNA denggi. Struktur nano aloi kuatenari CCTS yang telah disintesis kemudiannya didepositkan pada jenis substrat yang berbeza menggunakan teknik salutan mejam yang murah dan mudah. Ciri optik, struktur, morfologi, topografi dan elektrik CCTS telah dikaji menggunakan substrat-substrat iaitu Si, SiO_2 dan GaN untuk memilih yang paling optimum bagi digunakan dalam aplikasi yang berbeza. Telah di dapati bahawa untuk optoelektronik, jurang jalur optikal telah meningkat dari 1.29 eV kepada 1.31 eV dengan menukar suhu penyepuhlindapan dari suhu bilik hingga 500 °C. Keputusan XRD mendedahkan bahawa sampel ultrasonik mempunyai lebih banyak puncak berbanding sampel tanpa ultrasonik. Imej morfologi dan topografi mendapati bahawa suhu penyepuhlindapan yang tinggi telah membantu menghasilkan filem tipis yang lebih konsisten disebabkan oleh peningkatan saiz bijirin. Spektrum pantulan untuk sampel ultrasonik adalah 10% lebih rendah berbanding sampel tanpa proses ultrasonik yang bermaksud bahawa menggunakan ultrasonik dalam mensintesis CCTS akan meningkatkan keupayaan penyerapannya. Sampel terbaik dari segi sifat yang berbeza adalah dengan ultrasonik pada suhu 400 °C. Selain itu, jurang jalur yang dikira telah meningkat daripada 1.25 eV kepada 1.28 eV dan pemalar kekisi di dapati menurun daripada (a = 5.26 Å, c = 10.52 Å) kepada (a = 5.23 Å, c = 10.46 Å) dengan peningkatan kepekatan tembaga daripada 0.2 M kepada 1 M. Juga, kajian morfologi dan topografi telah menunjukkan kelebihan kepekatan tembaga pada 0.6 M berbanding darjah kepekatan yang lain dari segi konsisten dan homogen. Setakat mana kajian kami mengenai pembangunan biosensor, pencirian elektrik bagi elektrod interdigitated Ag yang didepositkan pada $Si/SiO_2/CCTS$ telah menunjukkan hubungan berkadar terus antara arus dan voltan manakala kapasitans dan impedans menunjukkan hubungan songsang terhadap frekuensi. Permukaan $Si/SiO_2/CCTS$ telah difungsikan dengan menggunakan prosedur yang terdiri daripada tiga langkah iaitu pengubahan permukaan menggunakan APTES, EDC dan NHS, diikuti oleh penetapan kuar DNA, dan kemudiannya hibridisasi enam sasaran DNA yang berbeza (100 fM, 1 pM , 10 pM, 100 pM, 1 nM dan 10 nM). Kepekaan biosensor yang dikira adalah 24.2 μA nM^{-1} cm^{-2}. Manakala had pengesanan (LOD) dan had pengkuantitian (LOQ) yang dikira masing-masingnya adalah 16.9 dan 56.3 nM. Keputusan-keputusan yang telah diperolehi menunjukkan bahawa penggunaan struktur-nano aloi kuatenari CCTS dalam fabrikasi biosensor DNA denggi serotype-2 boleh dianggap sebagai pendekatan yang novel kerana kos fabrikasi yang rendah, prosedur fabrikasi yang mudah.

Synthesis of Cu_2CdSnS_4 Quaternary Alloy Nanostructures for Dengue Serotype-2 DNA Biosensor Applications

ABSTRACT

The relentless research and development in new materials holds the key towards continuous technological advancement especially for DNA biosensor. For this purpose, Cu_2CdSnS_4 (CCTS) quaternary alloy nanostructure which regards low-cost, earth-abundant elements and defects free has received a lot of attention recently. It possesses numbers of merits including high optical absorption coefficient (>10^4 cm^{-1}), suitable energy band gap (1.4~1.5 eV), high power conversion efficiency, p-type conductivity, high hole mobility and enhanced sensitivity of DNA biosensor. Therefore, the aim of this study is to enhance the optical and electrical properties of CCTS quaternary alloy nanostructures to be used in different applications such as optoelectronics and dengue DNA biosensor. CCTS quaternary alloy nanostructures have been synthesized thereafter deposited on different types of substrates using effective-cost and simple spin coating technique. The optical, structural, morphological, topographical and electrical properties of CCTS have been investigated using varied substrates namely Si, SiO_2 and GaN to choose the best one to be utilized in different applications. It was found for optoelectronics; the optical band gap was increased from 1.29 eV to 1.31 eV with changing annealing temperature from room temperature to 500 °C. XRD results have revealed that with ultrasonic samples have more peaks than without ultrasonic ones. The morphological and topographical images have proved that high annealing temperature helps to produce more consistent thin film due to increasing of grain size. The reflection spectra for with ultrasonic samples are 10% lower than without ultrasonic ones which means that using ultrasonic in synthesizing CCTS will enhance the absorption capabilities of CCTS. The best study in terms of different properties was with ultrasonic at 400 °C. Moreover, the calculated band gap was increased from 1.25 eV to 1.28 eV and lattice constants were decreased from (a=5.26 Å, c=10.52 Å) to (a=5.23 Å, c=10.46 Å) with increasing copper concentration from 0.2 M to 1 M. Also, the morphological and topographical studies indicate the superiority of 0.6 M than the other copper concentrations in terms of consistency and homogeneity. As far as our work on biosensor development is concerned, the electrical characterization of Ag interdigitated electrodes which were deposited on Si/SiO_2/CCTS has found a proportional relationship between the current and voltage whereas, capacitance and impedance have displayed an inverse relationship with frequency. The surface of Si/SiO_2/CCTS was functionalized by using a procedure consists from three steps and they are the surface modification using APTES, EDC and NHS followed by DNA probe immobilization and then the hybridization of six different DNA targets (100 fM, 1 pM, 10 pM, 100 pM, 1 nM and 10 nM). The calculated sensitivity of the biosensor was 24.2 μA nM^{-1} cm^{-2}. Whilst the calculated limit of detection (LOD) and limit of quantitation (LOQ) were 16.9 and 56.3 nM, respectively. The demonstrated results have shown that using CCTS quaternary alloy nanostructures in the fabrication of dengue serotype-2 DNA biosensor is considered as a novel approach due to effective-cost fabrication, simple fabrication procedure, and high sensitivity.

CHAPTER 1

INTRODUCTION

1.1 Overview

Due to the rapid universal energy crisis, the search for new materials that have optimum characteristics such as environment friendly, cost-effective and highly efficient to evolve the renewable energies turn into a very important issue to replace the fossil-based energy. Many researchers study different quaternary alloys to enhance their structural and optical properties by making adjustments on their lattice constants, energy band gap and efficiency to use them effectively in optoelectronics and DNA biosensor applications. Also, among different types of quaternary alloys, $CuInGaSe_2$ (CIGS) has attracted a lot of attention due to the high conversion efficiency, steadiness, suitable direct band gap and high absorption coefficient (Lee et al., 2010). However although, the high prices of indium and gallium slow down additional researches in this area. I_2-II-IV-VI_4 (I=Ag,Cu; II=Cd,Zn,; I =Ge,Si,Sn; VI=Se,S) chain of quaternary semi-conductors have attracted much interest due to their possible use in many applications including the thin film for photovoltaics (PVs) (Chen et al., 2010).

Recently, numerous attempts have been applied to discover cost-effective materials that consists of abundant elements from the nature. Cu_2ZnSnS_4 (CZTS), as a possible candidate to replace CIGS, has attracted a large number of researchers due to its suitable energy band gap, abundant elements in the Earth's crust and large absorption coefficient (Pawar et al., 2010; Rajeshmon, Kartha, Vijayakumar, & Sanjeeviraja, 2011;

Yakuphanoglu, 2011). Also, Cu_2CdSnS_4 (CCTS) is a quaternary alloy made up from chalcopyrite elements and it can be used as a thin film for solar cell due to its suitable energy band gap (1.4 ~ 1.5 eV) which can increase the conversion efficiency of the cells (Mitzi, Gunawan, Todorov, Wang, & Guha, 2011). The CCTS quaternary alloy nanostructures has a direct energy band gap, p-type conductivity and high absorption coefficient. Because of that, considerable efforts have been made in this project to optimize the optical and structural properties of CCTS to replace other quaternary nanostructures in optoelectronics applications.

Nanotechnology added many new tools and structures that enhanced the physical and chemical properties of biological systems, this field is called nanobiotechnology. Specially, the evolution of biosensors and quick diagnostic experiments have highly taken advantage from this field. Nanomaterials are used for signal amplification and also in the immobilization of bio-molecules. Metal nanoparticles such as gold nanoparticles (GNPs) can be used for biosensing. Also, carbon nanotubes (CNTs) shape another new type of nanostructure for using in biosensors due to their ability to bind different types of biomolecules on their surfaces using different types of immobilization (Teles, 2011). Nanomaterials have attracted a numerous attention due to their very small scale that is similar to the dimensions of the bio-molecules. Many challenges facing the use of nanostructures in biosensors due to their surface effects which can be returned to the structure of the surface, their low size, high surface to volume ratio and their charges. Currently, most evolved biosensors uses different signal detection methods such as electrochemical and electrical ones. Numerous ways have been considered for the fabrication of interdigitated electrodes (IDEs) for using in many applications including biosensors. IDEs composed of comb-like electrodes opposite to each other, whereas the distance between them is measured in micrometer or nanometer (Ahn et al., 2011). Despite the capability of biosensors and their broad application in research, just a few chips have introduced. Notwithstanding, there is an incredible interest in checking distinctive sorts of biomolecules such us cholesterol, lactate, urea, creatine and dengue DNA. There are many research papers discussed adding nanomaterials on the electrodes to enhance the performance of the biosensor hence, the synthesis of nanomaterials or the methods of modifying the electrodes are commonly complex. Occasionally, the addition of some biomolecules or polymer template in the production of nanomaterials usually leads to some unpredictable effects in DNA detection. The use of nanomaterial in several DNA biosensors didn't improve their performance, thus, there is a need to enhance the construction method of nanostructures to be used with electrodes using a simpler methods to enhance the sensitivity of the biosensors (Li Wang et al., 2011). There is a need for developing fast, cheap, easy to use and a sensitive biosensor that capable of identifying the virus of DEN-2 type.

1.2 Problem Statement

The CCTS is an important alloy among the quaternary chalcopyrite semiconductors of type I_2–II–IV–VI_4 for their suitable energy band gaps, high optical absorption coefficient, and high abundant elements for optoelectronics applications. It is crystallizing in the kesterite or stannite structure with tetragonal symmetry. There is a necessity to expand the materials range that can be incorporated into effective-cost optoelectronics devices. Hence, expensive and scarce elements such as indium and gallium are replaced by other materials such as cadmium and tin to have optoelectronics that satisfy our needs. The fabrication process of CCTS in the literature involves a complicated synthesizing method and costly deposition techniques with some limitations, such as long reaction time, complicated operations or high vacuum. (Rockett, 2010).

On the other hand, the spreading of diseases causes a major fear to both population and governments. As of late, developing infections have attracted much interest (e.g. dengue infection, West Nile infection, Influenza infection). One of the most dangerous diseases is the dengue fever specially in the tropical regions where water lakes are located and here it comes the importance of developing biosensors using a simple fabrication procedure that can detect dengue DNA in a timely manner (Kiilerich-pedersen, Poulsen, Jain, & Rozlosnik, 2011).

1.3 Research Objectives

The objectives are as follows:

1. To improve the optical, structural, morphological and topographical properties of CCTS quaternary alloy nanostructures deposited on p-type silicon substrates using spin coating technique by optimizing the different deposition process parameters such as ultrasonic and annealing temperature for using CCTS in optoelectronics and dengue DNA biosensor applications.

2. To investigate the effect of using different copper concentrations on the optical, structural, morphological and topographical properties of CCTS quaternary alloy nanostructures deposited on p-type silicon substrates using spin coating technique to be used in optoelectronics and dengue DNA biosensor.

3. To evaluate the analysis and characterization studies of the optical, structural, morphological, topographical and electrical properties of CCTS for using the optimized CCTS quaternary alloy nanostructures in Ag-based Interdigitated Electrodes of dengue serotype-2 DNA biosensor.

1.4 Research Scopes

The scope of this research is divided into three main tasks that must be completed successfully. The first scope of this research project is to synthesize CCTS quaternary alloy nanostructures and divide it into with and without ultrasonic. The deposition is to perform on silicon substrates via spin coating technique within a wide annealing temperature range (room temp., 200, 300, 400 and 500 °C). Afterward, to characterize optical, structural, morphological and topographical properties of CCTS.

The second scope is to synthesize CCTS from multiple copper concentrations (0.2, 0.4, 0.6, 0.8 and 1 M) and separate them into with and without ultrasonic. Silicon substrates are used for the deposition via spin coating technique and at annealing temperature 300 °C.

Finally, to characterize optical, structural, morphological and topographical properties of CCTS.

The third scope is to deposit the synthesized CCTS on SiO_2 substrate using spin coating technique at annealing temperature 400 °C. Afterward, the different properties of CCTS such as optical, structural, morphological and topographical have to be done. Also, to deposit Ag IDEs on CCTS and the electrical characterization of the device have to be carried out after the immobilization and hybridization processes to examine the capability of the device to detect dengue serotype-2 DNA.

1.5 Research Novelty

The structural, optical, morphological and topographical properties of the synthesized CCTS nanostructures have been investigated using various techniques for developing optoelectronics and dengue serotype-2 DNA biosensor applications. UV–vis measurements revealed that energy band gaps were changed from 1.29 to 1.31 eV with changing the annealing temperature from room temperature to 500 °C. Also, energy band gaps were changed from 1.25 to 1.28 eV with changing copper concentration from 0.2 M to 1M, whereas, topographical and morphological images indicated the superiority of 0.6 M on the other copper concentrations in terms of structural characteristics, regularity of granular structure and moderation of their sizes. Electrical characterization of the Ag IDEs showed a direct correlation between current and voltage. The calculated LOD and LOQ for the biosensor were 16.9 and 56.3 nM, respectively. The sensitivity of the biosensor was 24.2 $\mu A\ nM^{-1}\ cm^{-2}$. The novelty of this study was the fabrication and characterization an efficient and low-cost biosensor that capable of identifying dengue DNA serotype-2 in a timely manner.

1.6 Thesis Outline

This thesis is arranged into four chapters. The first chapter introduced an overview on different types of quaternary alloy nanostructures including CCTS and its use in different applications. In this chapter also, problem statement, research objectives, research scopes, and research novelty were addressed and discussed.

The second chapter represents the literature review, which introduce the materials abundance, other quaternary alloys, physical properties of CCTS, evaluation of CCTS quaternary alloy nanostructures for optoelectronics, IDEs, characteristics of dengue DNA, DNA immobilization, DNA hybridization detection techniques, and the characteristics of Biosensors.

The third chapter started with a synopsis that describes briefly the published papers on the development of CCTS quaternary alloy nanostructures for using in optoelectronics and biosensor, followed by attaching published articles.

Finally, chapter 4 summarizes the output of the thesis based on the objectives of this research also the recommendation for future works to improve the finding of this project.

CHAPTER 2

LITERATURE REVIEW

2.1 Materials Abundance

Accurate consideration must be taken to select the proper elements for making a quaternary alloy. (Peter, 2011) have demonstrated the annual production of some high demand elements in the Earth's crust relevant to quaternary alloys. Current technologies may include copper zinc tin sulfide (CZTS), copper cadmium tin sulfur (CCTS) and cadmium telluride (CdTe). Figure 2.1 compares present annual production of an equivalent set of elements. The effects from production demands would be the largest for the quaternary alloys such as CIGS, because the annual production of indium and gallium elements is little compared with alternative metals like zinc, copper, cadmium and tin, that might be used as a replacement materials.

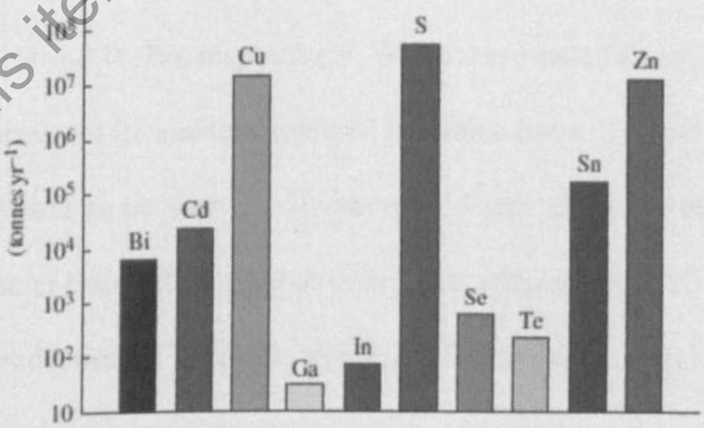

Figure 2.1: Present production of a group of elements used in photovoltaics. (Peter, 2011)

There is a necessity to extend the domain of materials that can be combined into low cost quaternary alloys. The scarce and expensive element such as indium is substituted by cadmium or zinc and gallium is substituted by Sn. Also, Se is substituted by cheap and abundant S as shown in Figure 2.2.

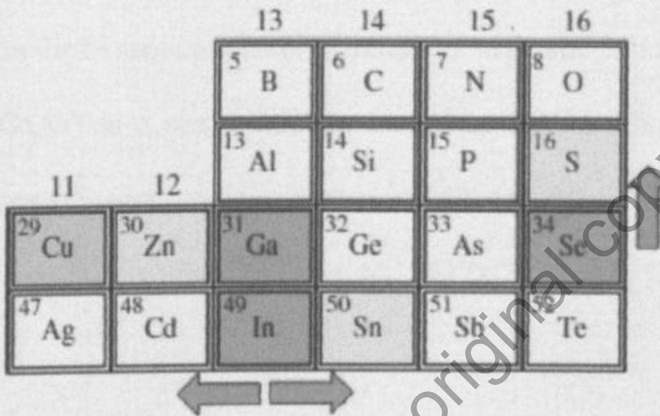

Figure 2.2: Part of periodic table describing the change from group 13 to groups 12 and 14. (Peter et al., 2011)

Advances in solar cells persists to achieve essential movement towards evolving cost-effective and efficient PVs. Specially, CuIn-GaSe$_2$ (CIGSe) and CdTe PVs have attained efficiencies of 20.3% and 16.7%, respectively. While these materials are as of now available, cost unpredictability cases (In and Ga), material plenitude cases (Te) and potential ecological cases (Cd) have raised some worries. However, if Earth abundant elements used in the manufacturing of solar cells with similar or even better efficiency to CIGS or CdTe, then this will lead to the production of cost-effective PVs (Rincón et al., 2011). PVs need a high amount of Si due to the thickness needs, half of the silicon is waste as sawdust in wafering process. It's notwithstanding, Polycrystalline Silicon is harder than single-crystalline Silicon and it can be cut into one third the thickness of single-crystalline. Many materials can be used