THEORETICAL STUDY OF STRUCTURAL, ELECTRONIC AND OPTICAL PROPERTIES OF BISMUTH-SELENIDE, BISMUTH-TELLURIDE AND ANTIMONY-TELLURIDE/GRAPHENE HETEROSTRUCTURE FOR BROADBAND PHOTODETECTOR

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Dedicated to

My brother, **Dr. Ibrahim L Suleman**, whose sacrifice;
My late father and mother, **Alhaji Lawal Abdullahi**, whose dream;
My late mother, **Hajiya Khadijah Hussaini**, whose dream;
My Wife, Kubra Mohammad whose patience; lead to achieving my doctoral degree
And
My children, **Ibrahim and Umar Faruq**, who always sacrificed their innocent desires and gave me time to work

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ABSTRACT

It remains challenging to produce high-performance broadband photodetector that can detect light from infrared to ultraviolet frequency range for biomedical imaging, gas sensing and optical communication applications. In particular, large energy band gap and low optical absorption in the material utilized as absorbing layer have prevented a report of high performance broadband photodetector in terms of quantum efficiency and photoresponsivity. However, integrating second generation topological insulators (2GTI), namely, bismuth selenide (Bi_2Se_3), bismuth telluride (Bi_2Te_3) and antimony telluride (Sb_2Te_3) with graphene in a heterostructure appears to be the more promising approach. In this heterostructure, optical absorption takes place in 2GTI while graphene acts as charge carrier collector owing to its high carrier mobility. Therefore, detailed knowledge of the design, as well as structural, electronic and optical properties of 2GTI/graphene heterostructures, is essential to expose their hidden potentials. Structural properties of Bi_2Se_3, Bi_2Te_3, and Sb_2Te_3 are studied by first-principles calculations within density functional theory (DFT) framework. Many-body perturbation theory (MBPT) based one-shot GW (G_0W_0) and Bethe-Salpeter equation (G_0W_0-BSE) approaches were used to compute the quasiparticle (QP) band structure, excitonic and optical properties. The DFT calculations show that inclusion of van der Waals (vdW) correction with most recent developed Coope's exchange (vdW-$DF^{C09}x$) reproduce experimental interlayer distances, lattice parameters and atomic coordinates of Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3 2GTI. The one-shot GW calculations confirm that Bi_2Se_3 and Sb_2Te_3 are direct band gap materials with band gap values of 0.36 eV and 0.22 eV while Bi_2Te_3 is indirect band gap material with 0.17 eV energy band gap. The results on the optical properties of 2GTI with inclusion of electron-hole interaction show that the exciton energy for Bi_2Se_3, Bi_2Te_3, and Sb_2Te_3 are 0.28, 0.14 and 0.19 eV respectively while their corresponding plasma energies are 16.4, 15.6 and 9.6 eV respectively. These values show that the investigated materials can absorb photons within broadband wavelengths. For the design, the energy analysis of Sb_2Te_3/graphene heterostructure reveals that the most stable configuration is the one in which the Te-1 atom of Sb_2Te_3 facing to graphene is above the hole centre of graphene's hexagonal lattice. More attractively, the system of Sb_2Te_3/graphene heterostructure shows that strong hybridization between Sb_2Te_3 and graphene at smaller interlayer distance resulted in an energy gap at the Dirac states. It is, therefore, anticipated that this heterostructure will be useful for new-generation optoelectronic applications particularly in broadband photodetectors.

ABSTRAK

Penghasilan fotopengesan jalur lebar berprestasi tinggi yang mampu mengesan cahaya dalam julat frekuensi inframerah ke ultraungu bagi pengimejan bioperubatan, penderiaan gas dan aplikasi komunikasi optik masih menjadi cabaran. Khususnya, jurang jalur tenaga yang besar dan penyerapan optik yang rendah dalam bahan yang diguna sebagai lapisan penyerap telah menghalang penglaporan berhubung fotopengesan jalur lebar berprestasi tinggi dari segi kecekapan kuantum dan fotoresponsiviti. Bagaimanapun, gabungan antara penebat topologi generasi kedua (2GTI), iaitu bismut selenida (Bi_2Se_3), bismut telurit (Bi_2Te_3) dan antimoni telurit (Sb_2Te_3) dengan grafin dalam satu heterostruktur dilihat sebagai pendekatan yang lebih berpotensi. Dalam heterostruktur ini, penyerapan optik berlaku dalam 2GTI manakala grafin bertindak sebagai pengumpul pembawa cas disebabkan oleh mobiliti pembawanya yang tinggi. Oleh itu, pengetahuan terperinci tentang reka bentuk serta ciri struktur, elektronik dan optik heterostruktur 2GTI/grafin adalah perlu untuk mendedahkan kemampuannya. Ciri struktur Bi_2Se_3, Bi_2Te_3 dan Sb_2Te_3 dikaji secara pengiraan prinsip pertama dalam kerangka teori ketumpatan fungsian (DFT). Teori usikan banyak-jasad (MBPT) berdasarkan pendekatan satu-das GW(G_0W_0) dan persamaan Bethe-Salpeter (G_0W_0-BSE) telah diguna untuk mengira struktur jalur kuasi zarah (QP), sifat eksitonik dan optik. Pengiraan DFT menunjukkan pemasukan pembetulan van der Waals (vdW) bersama pertukaran Coope terbaharu (vdW-DF^{C09}x) menghasilkan semula nilai eksperimen bagi jarak antara lapis, parameter kekisi dan koordinat atom bagi Bi_2Se_3, Bi_2Te_3 dan Sb_2Te_3 2GTI. Pengiraan menggunakan pendekatan GW satu-das mengesahkan bahawa Bi_2Se_3 dan Sb_2Te_3 adalah bahan berjurang jalur terus masing-masing dengan nilai jurang jalur 0.36 eV dan 0.22 eV manakala Bi_2Te_3 ialah bahan berjurang jalur tidak terus dengan nilai jurang jalur 0.17 eV. Hasil bagi sifat optik bahan 2GTI dengan pemasukan interaksi elektron-lohong menunjukkan tenaga eksiton bagi Bi_2Se_3, Bi_2Te_3 dan Sb_2Te_3 masing-masing ialah 0.28, 0.14 dan 0.19 eV manakala bagi tenaga plasma masing-masing ialah 16.4, 15.6 dan 9.6 eV. Nilai ini menunjukkan bahan yang dikaji boleh menyerap foton dalam panjang gelombang jalur lebar. Untuk reka bentuk, analisis tenaga ke atas heterostruktur Sb_2Te_3/grafin mendedahkan bahawa konfigurasi paling stabil ialah konfigurasi dengan atom Te-1 dalam Sb_2Te_3 yang menghadap grafin berada di atas pusat lubang kekisi heksagon grafin. Lebih menarik, sistem heterostruktur Sb_2Te_3/grafin menunjukkan penghibridan yang kuat antara Sb_2Te_3 dengan grafin pada jarak antara lapis yang lebih kecil menghasilkan jurang tenaga pada keadaan Dirac. Oleh itu, dijangkakan heterostruktur ini bermanfaat bagi aplikasi optoelektronik generasi baharu khususnya dalam fotopengesan berjalur lebar.

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LIST OF ABBREVIATIONS

ARPES	-	Angle-Resolved Photoemission Spectroscopy
BSE	-	Bethe-Salpeter Equation
Bi_2Se_3	-	Bismuth Selenide
Bi_2Te_3	-	Bismuth Telluride
Sb_2Te_3	-	Antimony Telluride
B3LYB	-	Hybrid Functional
BZ	-	Brillouin Zone
CBM	-	Conduction Band Minimum
SCF	-	Self-Consistent Field
SOC	-	Spin-Orbit Coupling
DOS	-	Density of States
DFT	-	Density Functional Theory
e-h	-	Electron-Hole
G	-	Green's Function
GGA	-	Generalized Gradient Approximation
GW	-	Green Function and Screened Coulomb Interaction
HF	-	Hartree Fock
HK	-	Hohenberg-Kohn
KS	-	Kohn-Sham
LDA	-	Local Density Approximation
MBPT	-	Many-Body Perturbation Theory
PBE	-	Perdew-Berke-Erzndof
PDOS	-	Partial Density of States
PP	-	Pseudopotential
QE	-	Quantum Espresso
QL	-	Quintuple Layer

QP	-	Quasiparticle
RPA	-	Random-Phase Approximation
TIs	-	Topological Insulator
TDDFT	-	Time-Dependent Density Functional Theory
TMDCs	-	Transition Metal Dichalcogenides
TMOs	-	Transition Metal Oxides
UV	-	Ultra Violet
VBM	-	Valence Band Maximum
vdW	-	van der Waals
XC	-	Exchange and Correlation

LIST OF SYMBOLS

h	-	Plank's Constant
Ψ	-	Wave-function
Å	-	Angstrom
cm	-	Centimeter
Φ	-	Single Particle Wave-function
ϕ	-	Eigen-function
$\hat{\Psi}$	-	Fermionic Annihilation Operator
µ	-	Micron
σ	-	Optical Conductivity
n	-	Refractive index
ε_2	-	Imaginary Part of Dielectric Function
ε_1	-	Real Part of Dielectric Function
E_g	-	Energy Band Gap
eV	-	Electron Volt
Γ	-	Gamma
α	-	Absorption Coefficient

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Conversion of light into electrical signals is at the heart of researchers due to their significant impacts on every aspect that affects our lives. Applications, like laser photonic, optical communication, biomedical imaging, homeland security, gas sensing, remote sensing, quantum computing and motion detection have reached a high level of maturity due to the development of integration technology, large-scale production, and development of high-performance materials. Although optoelectronic technology is growing, the need of efficient photodetector that can absorb light within wide energy range (ultraviolet, visible and infrared spectra) and convert them into electrical signals, is becoming more imminent. These led to the increasing focus on searching of different source materials and the development of methods to characterize these materials. To this point, integration of 2D band gap materials with graphene appears to be more promising approach [1, 2]. Although many efforts were done on transition metal oxides (TMOs) and transition metal dichalcogenides (TMDCs) for this intention, energy band gap of 1.0 to 3.3 eV has limited their application for the detection of light in the near-infrared region [3]. However, a narrow band gap second generation topological insulator (2GTI) mainly Sb_2Te_3, Bi_2Te_3, and Bi_2Se_3 would be a better choice [1, 4-6]. In the heterostructure, optical absorption takes place in 2GTI while graphene acts as charge carrier collector owing to its high carrier mobility. Therefore, detailed knowledge of the design, as well as structural, electronic and optical properties of 2GTI, is essential to expose their hidden potentials.

Experimental measurements and theoretical investigations using various ab-initio methods are the two possible ways of analysis in condensed matter physics. Though physical properties of materials can be characterized experimentally, in some cases it is difficult to furnish experiments with the required conditions for characterization or synthesis. An experimental investigation at atomic scale level is also difficult to execute even with modern experimental techniques. The second option is to solve many-body problems by solving quantum mechanical equations and this also takes a long time. First-principles or ab-initio calculation is an approach that relies on well-established fundamental laws that do not rely on any fitting techniques, special model or suppositions. In this present era, computational methods based on the first-principles approach have gained great attention due to advancement in computer processing technology, which enables simulation and modeling of materials to be performed under diverse conditions in a short time. Computational techniques are the easiest and cheapest way of discovering new materials for device applications. The valuable properties of materials which are not yet explored experimentally can be accurately predicted through simulation techniques. On the other hand, approaches based on computational techniques provide an exact description of various physical properties of materials such as structural, electronic and optical properties and sometimes replace experimental methods within a short time at low cost.

First-principles calculations within the framework of density functional theory (DFT) is the method of choice for investigating material properties at the ground state. This method was proposed by famous Hohenberg and Kohn in 1964 as an approach to determine the electronic structure of a system at the ground state. DFT in principle provides an exact description of material physical properties at ground states although approximations become necessary. Calculations based on DFT are distinguished from other ab-initio methods as first-principles calculations with an approximate error of 10^{-3} eV [7]. Despite the fact that this approach gives an accurate description of material properties at ground states but it has some shortcomings. The limitation of this approach is the failure to give correct information about material properties associated with the excited states. In particular, it is well known that Hartree-Fock (HF) approximation and DFT are not suitable for

accurate prediction of electronic band gap especially for narrow band gap semiconductor materials like 2GTI because Hartree-Fock and DFT Kohn-Sham energy cannot predict the quasiparticle (QP) band structure precisely [8]. This limitation could be overcome by using GW approach. GW calculation can be performed either self-consistently or nonself-consistently. However, full self-consistent GW approach is prohibitively expensive and impractical for bulk and surface state calculations of insulators and semiconductors [9-11]. Consequently, coupling DFT with many-body perturbation theory (MBPT) within nonself-consistent GW approximation, G_0W_0, is a better choice for accurate prediction of the fundamental band gap, this approach is also practicable for surface state calculations to examine the topological nature of Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3 TIs [8, 12-14].

For a few decades, optical properties of materials have been investigated extensively with standard DFT using independent particle approach of Ehrenreich and Cohen [15, 16] and one-particle Green's function approach within GW approximation [17]. However, neither of these methods provides a correct evaluation of optical spectra, because the optical spectrum and the shape of the calculated dielectric function show significant differences from those obtained experimentally [18-21]. The limitation of standard DFT and one-particle Green's function is their failure to describe the excitonic effect of electron-hole interaction which requires two-particle approach. It has been known that two-particle approach provides a correct description of optical properties of a number of systems due to the influence of electron-hole correction in the optical spectra [19, 22, 23]. For optical properties calculations, we adopted an approach that provides a correct description of optical spectra in better agreement with experimental data [24], via the solution of two-particle BSE based on GW corrections.

1.2 Background of Problem

Although applications areas are growing, the need of photodetector with high performance in terms of quantum efficiency, speed, wavelength range (Ultraviolet,

visible and infrared spectra), is becoming more eminent [2, 6, 25]. Within past few years, extraordinary features of graphene, a novel two dimensional (2D) material have drawn the great attention of researchers in this regards [1, 26]. Some of its unique properties are high crystal quality, high charge carrier mobility (about 10^6 cm^2/Vs at room temperature), linear dispersion near Fermi energy level, high velocity at low density, anomalous quantum Hall effect (QHE) at room temperature and absence of energy gap [26]. Despite the outstanding characteristics of graphene, thrilling features like limited optical absorption of 2.3% over a wide energy spectrum and the absence of band gap prevented its potentiality for high-performance photodetector in terms of quantum efficiency and speed [2, 6]. These shortcomings lead to poor performance such as low responsivity, internal quantum efficiency, external quantum efficiency and detectivity [1, 27, 28]. Many efforts have been made to address this problem such as graphene nanoribbons, band gap opening by utilizing bilayer graphene. Such approaches are difficult to fabricate and due to degradation of charge carrier mobility, high performance is not guaranteed also.

On the other hand, integrating graphene with layered materials that retain their stability down to monolayers is the most promising approach. Recently, graphene was integrated with transition metal oxides (TMOs) and transition metal dichalcogenides (TMDCs) for this intention. In this respect, recently a photodetector with high performance in terms of sensitivity, responsivity, and quantum efficiency have been achieved using WSe_2-graphene and MoS_2-graphene heterostructure [29, 30]. Nevertheless, the energy gap of 1.0 to 3.3 eV limited the detection of the light near-infrared region in TMOs and TMDCs compounds [3]. To this point, integrating graphene with another van der Waals (layered) materials namely, Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3 is a better choice, because they offer some unique capabilities and characteristics as compared to other layered materials such as narrow band gap, low saturable optical intensity, protected conducting surface states, high damage threshold, large modulation depth, strong optical absorption, and low cost [31, 32]. In this heterostructure, 2GTI can be utilized as an absorbing layer (photoactive materials) while graphene layer act as work-function electrodes. Therefore, for the optimal operation of this heterostructure for device applications, accurate

measurements of the structural, electronic properties, as well as optical characteristics, are needed.

Through extensive literature review following issues were identified:

i) It is unclear if spin-orbit coupling (SOC) effect is important for predicting structural properties of Bi_2Te_3, Bi_2Se_3, and Sb_2Te_3 compounds.
ii) Although comprehensive investigations have been done using various ab-initio methods and experimental measurements on Bi_2Se_3, $Bi_2Te_3$and Sb_2Te_3 band structure, positions of the extrema of the upper valence band and the lower conduction band in the bulk Brillouin zone (BZ) has been debated in these compounds. Therefore, the basic nature of the difference between calculated band gaps and the exact values is still an open question.
iii) Optical properties calculation with the inclusion of electron-electron and electron-hole interactions on Bi_2Te_3, Bi_2Se_3, and Sb_2Te_3 compounds are not explored.
iv) Surface states band structure calculations with effects of van der Waals (vdW) correction for Bi_2Te_3, Bi_2Se_3, and Sb_2Te_3 have not reported.
v) Questions on how graphene sheet interaction with Bi_2Te_3, Bi_2Se_3 and Sb_2Te_3 layers at different positions affects the new surface states are not yet explored.

1.3 Objectives

In order to address the above-mentioned problems, following are the main objectives of this thesis:

i) To calculate structural properties of Bi_2Te_3, Bi_2Se_3, and Sb_2Te_3 compounds.
ii) To investigate electronic properties (evaluation of the band structure, total and partial density of states) of Bi_2Te_3, Bi_2Se_3, and Sb_2Te_3 compounds.

iii) To determine the optical properties (real and imaginary part of the dielectric function, refractive index, extinction coefficient, optical conductivity, reflectivity spectra and absorption coefficient) of Bi_2Te_3, Bi_2Se_3, and Sb_2Te_3 compounds.

iv) To elaborate the electronic band structure and optical properties of Bi_2Te_3, Bi_2Se_3, and Sb_2Te_3 surface states.

v) To analyse the effects of Sb_2Te_3 material heterostructuring with graphene.

1.4 Scope of the Research

In this research, the structural, electronic and optical properties of the heterostructure photoactive materials namely, Bi_2Te_3, Bi_2Se_3 and Sb_2Te_3 compounds in bulk and surface states have been investigated in details using state-of-art first-principles MBPT techniques based on DFT. The effects of graphene sheets on Sb_2Te_3 material for the new physics of interacting massless Dirac fermions have also investigated comprehensively. Following approaches are adopted, in order to achieve the above objectives.

i) The structural properties (lattice parameters, interlayer distances, and atomic coordinates) of Bi_2Te_3, Bi_2Se_3 and Sb_2Te_3 are computed with and without taking into account the effects of van der Waals and SOC correction within generalized gradient approximation (GGA) and local density approximation (LDA) exchange-correlation potentials.

ii) Investigation of the electronic properties with and without SOC (band structure, total and partial density of states) of Bi_2Te_3, Bi_2Se_3, and Sb_2Te_3 compound are carried out using density functional theory approach based on GGA exchange-correlation potentials. Furthermore, to overcome the problem of underestimation of band gap one-shot GW approach has been used.

iii) Investigation of optical properties of Bi_2Te_3, Bi_2Se_3 and Sb_2Te_3 materials are carried out using three different approaches: Random-phase approximation (RPA) based on PBE (DFT+RPA) without taking into account the effects of electron-electron and electron-hole interaction, RPA based on one-shot GW

approximation (G_0W_0+RPA) which neglects electron-hole interaction and by solving BSE (G_0W_0+BSE) to include excitonic effects of electron-hole interaction.

iv) Surface states band structure and optical properties calculations of Bi_2Te_3, Bi_2Se_3, and Sb_2Te_3 compounds are performed using density functional theory approach based on GGA exchange-correlation potentials.

v) Effects of graphene sheets on the Sb_2Te_3 compound investigation for the new physics of interacting massless Dirac fermions were carried out using DFT based on GGA exchange-correlation potentials.

1.5 Significance of the Research

Although extensive studies have been performed for 2GTI namely, Bi_2Te_3, Bi_2Se_3 and Sb_2Te_3, most of the studies focused of their potentiality of converting heat to electrical energy, whereas their optoelectronic behaviour is scarcely studied. This research offers comprehensive study on optoelectronic properties of these compounds using first-principles MBPT approach, in order to spawn a new generation broadband photodetector for our daily lives benefits. The highly accurate first-principles MBPT technique will certainly contribute in removing the discrepancies between theoretical and experimental measurements. This study is intended to demonstrate that these materials have the capability of absorbing light within a wider range of wavelengths (ultraviolet, visible and infrared spectra). Therefore, strong absorption in 2GTI over very wide energy spectra is an exciting feature to emerge them as promising absorbing materials for broadband photodetection. However, this research expects that combination of 2GTI namely, Bi_2Te_3, Bi_2Se_3 and Sb_2Te_3 as photoactive materials and graphene layer as work-function electrodes for the broadband photodetector, the performances in terms of efficiency, speed, photoresponsivity and detectivity will improve compared to pure graphene-based devices. Furthermore, prediction of properties that have not explored experimentally yet has also been introduced with reduction of time and cost. The results of this study will certainly open a new pathway for other optoelectronic applications.

1.6 Thesis Organisation

This thesis is classified into five different chapters. Chapter 1 introduces the research work which consists of sub-headings of the background of research, the background of the problem involved in the current study, problem statement, objectives and scopes of the research, significant of the study and lastly thesis organisation. Chapter 2 describes the literature review based on the research topic. The literature reviewed covers overviews of the existing literature on graphene and 2GTI for the broadband photodetector. The chapter further describes in detail the theoretical background involved in the calculations. Chapter 3 explains the methodologies and computational details. Chapter 4 presents the investigation of structural properties of 2GTI (Bi_2Se_3, Bi_2Te_3, and Sb_2Te_3) via various exchange-correlation potentials. The effects of spin-orbit coupling (SOC) and electron-electron interactions on electronic properties of the optimized structures of 2GTI has also discussed in Chapter 4. The effects of electron-hole interactions on optical properties have been also discussed in Chapter 4. The optical properties discussed are reflectivity, refractive index, real and imaginary parts of the dielectric function, optical conductivity and absorption coefficient respectively. The results of the band structure of the surface states of 2GTI have been presented in Chapter 4. Effects of a graphene sheet on 2GTI have also discussed in this chapter. For the interfacing study, Sb_2Te_3 has been chosen. The separation distance between Sb_2Te_3 and graphene sheet was varied from 2.5Å to 5.5Å for the new physics of interacting massless Dirac fermions. Finally, general conclusions along with a recommendation for further work are presented in Chapter 5. At the end of this thesis list of references and relevant appendices are arranged.

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