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Simon Forster

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THÈSE

Pour obtenir le grade de

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Spécialité : 2MGE : Matériaux, Mécanique, Génie civil,
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Présentée par

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Matériaux et Procédés**
dans l'**École Doctorale I-MEP2 - Ingénierie - Matériaux,
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Production**

**Nouveau matériau semi-conducteur à large
bande interdite à base de carbures ternaires
- Enquête sur Al₄SiC₄**

**Novel wide bandgap semiconductor material
based on ternary carbides - An investigation
into Al₄SiC₄**

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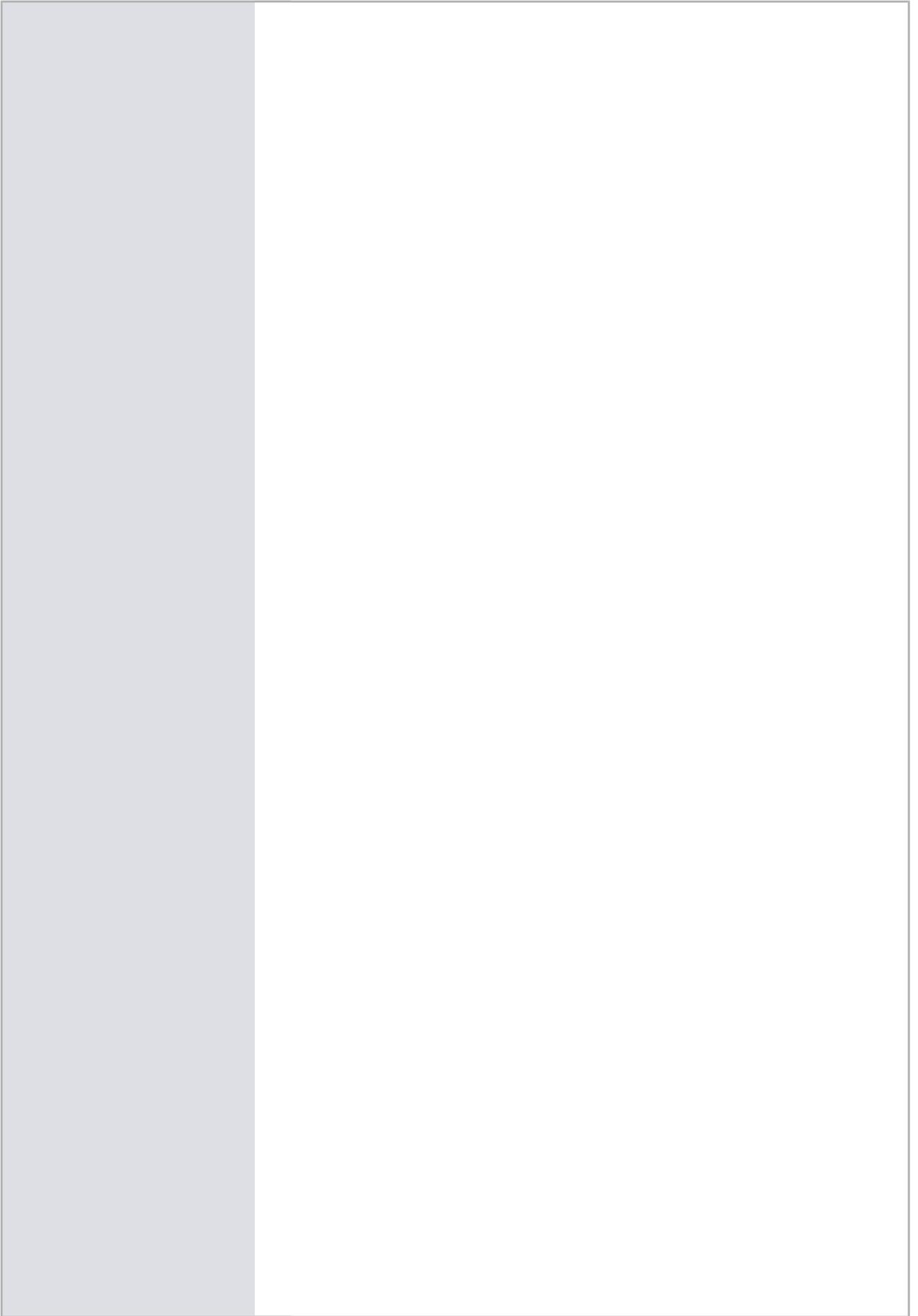
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Novel wide bandgap semiconductor material based on ternary carbides

An investigation into Al_4SiC_4

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ABSTRACT

Wide bandgap semiconductor materials are able to withstand harsh environments and operate over a wide range of temperatures. These make them ideal for many applications such as sensors, high-power and radio-frequencies to name a few. However, more novel materials are required to achieve significant power efficiency of various applications or to develop new applications to complement current wide bandgap semiconductors such as GaN and SiC.

In this dissertation, three different methods are used to study one of these novel materials, aluminium silicon carbide (Al_4SiC_4): (1) ensemble Monte Carlo simulations in order to study the electron transport properties of the novel ternary carbide, (2) experimental studies to determine its material properties, and (3) device simulations of a heterostructure device made possible by this ternary carbide. All these methods interlink with each other. Data from each of them can feed into the other to acquire new results or refine obtained results thus leading way to attractive electrical properties such as a bandgap of 2.78 eV or a peak drift velocity of $1.35 \times 10^7 \text{ cm s}^{-1}$.

Ensemble Monte Carlo toolbox, developed in-house for simulations of Si, Ge, GaAs, $\text{Al}_x\text{Ga}_{1-x}\text{As}$, AlAs, and InSb; is adopted for simulations of the ternary carbide by adding a new valley transformation to account for the hexagonal structure of Al_4SiC_4 . We predict a peak electron drift velocity of $1.35 \times 10^7 \text{ cms}^{-1}$ at electric field of 1400 kVcm^{-1} and a maximum electron mobility of $82.9 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$. We have seen a diffusion constant of $2.14 \text{ cm}^2\text{s}^{-1}$ at a low electric field and of $0.25 \text{ cm}^2\text{s}^{-1}$ at a high electric field. Finally, we show that Al_4SiC_4 has a critical field of 1831 kVcm^{-1} . In the experimental part, Al_4SiC_4 semiconductor crystals are used that had previously been grown at IMGP, one by solution grown and the other by crucible melt. Three different experiments are performed on them; (1) UV, IR and Vis Spectroscopy, (2) X-ray Photo Spectroscopy, and (3) Two- and four-probe measurements where metal contact are grown on the crystals. Here we have found a bandgap of $2.78 \pm 0.02 \text{ eV}$ UV, IR and Vis Spectroscopy and a thick oxide layer on the samples using XPS. Unfortunately the Two- and four-probe measurements failed to give any results other than noise, most likely due to the thick oxide layer that was found on the samples.

In the device simulations, a commercial software Atlas by Silvaco is utilized to predict performance of heterostructure devices, with gates lengths of $5 \mu\text{m}$, $2 \mu\text{m}$ and $1 \mu\text{m}$, made possible by the ternary carbide in a combination with SiC. The $5 \mu\text{m}$ gate length SiC/ Al_4SiC_4 heterostructure transistor delivers a maximum drain current of $1.68 \times 10^{-4} \text{ A}/\mu\text{m}$, which increases to $2.44 \times 10^{-4} \text{ A}/\mu\text{m}$ and $3.50 \times 10^{-4} \text{ A}/\mu\text{m}$ for gate lengths of

2 μm and 1 μm , respectively. The device breakdown voltage is 59.0 V which reduces to 31.0 V and to 18.0 V for the scaled 2 μm and the 1 μm gate length transistors. The scaled down 1 μm gate length device switches faster because of the higher transconductance of $6.51 \times 10^{-5} \text{ S}/\mu\text{m}$ compared to only $1.69 \times 10^{-6} \text{ S}/\mu\text{m}$ for the largest device. Finally, a sub-threshold slope of the scaled devices is 197.3 mV/dec, 97.6 mV/dec, and 96.1 mV/dec for gate lengths of 5 μm , 2 μm , and 1 μm , respectively.

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AUTHOR'S DECLARATION

I declare that the work in this dissertation was carried out in accordance with the requirements of the University's Regulations and Code of Practice for Research Degree Programmes and that it has not been submitted for any other academic award. Except where indicated by specific reference in the text, the work is the candidate's own work. Work done in collaboration with, or with the assistance of, others, is indicated as such. Any views expressed in the dissertation are those of the author.

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LIST OF CONTRIBUTIONS

Journal Publications

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S. FORSTER, B. UBOCHI, AND K. KALNA, *Monte Carlo Simulations of Electron Transport in Bulk GaN*, in Proceedings of IWCN, pp. 135-137, 2017.

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APPLICATIONS OF WIDE BANDGAP SEMICONDUCTORS

This chapter gives an introduction on the topic of wide bandgap semiconductors and the motivation behind why we want to use them over standard semiconductors. The latter part of the chapter will give details on the aims of this thesis and an overview of what to expect in each of the upcoming chapters.

1.1 What are Wide Bandgap Semiconductors

Wide bandgap (WBG) semiconductors are named after their relative wide energy bandgap in comparison to silicon. This energy bandgap is an electronic gap between the top of the valence band and the bottom of the conduction band in a material, see Figure 1.1.

When a material has a bandgap, the electrons can jump from the valence band to the bottom of the conduction band by means of thermal or optical excitation. This means that the material can conduct current or not conduct under externally adjusted conditions hence the name semi-conductor. The existence of the bandgap allows suitably designed semiconductor devices to be used as switches, diodes and other electronic components, due to the ability to switch currents on and off as desired based on the electrical function they perform. The higher this energy gap, to an extent, leads way to the WBG characteristics that allow the WBG materials perform more efficiently than silicon in power applications. Well designed WBG devices can achieve characteristics such as higher tolerance to high operating temperatures and other harsh environments like high radiation or high voltage environments. Popular WBG materials in use today are 4H-silicon carbide (SiC)

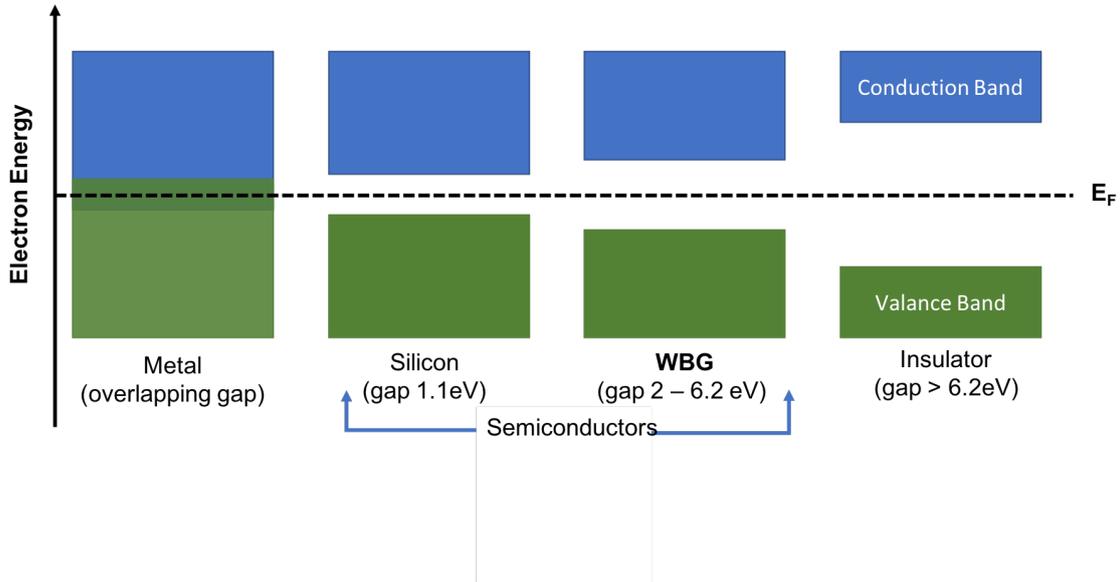


FIGURE 1.1. Energy Band Gaps in Materials.

and gallium nitride (GaN) with a bandgap of 3.3 eV [28] and 3.4 eV [19], respectively. However, there is still a need for more novel WBG materials. This work aims to examine and characterize one of these novel materials, aluminum silicon carbide (Al_4SiC_4), to see if the properties are suitable for use in electronic, opto-electronic or power applications.

1.2 Why Do We Want Wide Bandgap Semiconductors?

The invention of silicon (Si) integrated circuit over half a century ago laid the foundations of modern computing, communication, and data handling creating nowadays electronics era. Circuits made of silicon transistors are now the predominant commercial semiconductors material option for the majority of power diodes and switches used in power electronic systems. This has been mainly due to abundance of silicon, as it is seen in dusts, sands, planetoids and planets as a multitude of forms such as silica or silicates. On Earth alone, 90% of the crust is comprised of silicate minerals, thus making it the second most abundant element on Earth after oxygen (O), see Figure 1.2.

Further more, the electronic properties of silicon make it an ideal material to use for diodes and switches. However, in many modern applications and, especially, in those environments classed as harsh, silicon has reach its physical limits [54]. This serious

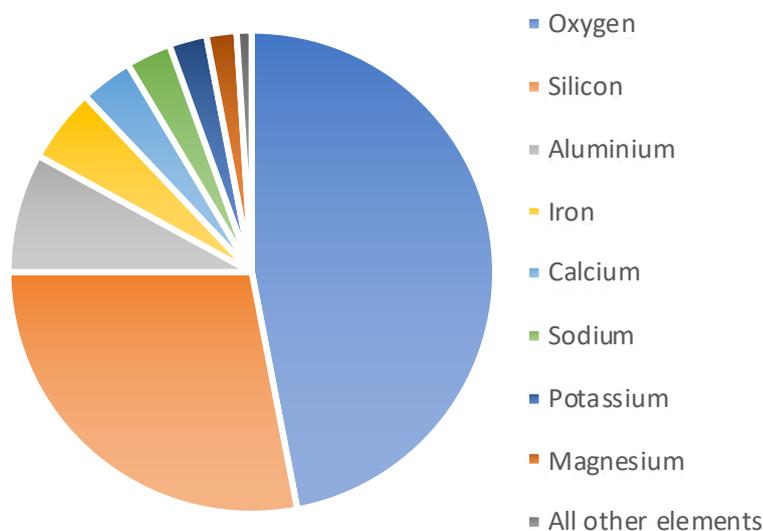


FIGURE 1.2. Pie chart of the elements in the Earth's crust data. From M. Fleischer [30].

limitation of silicon electronics had lead to impending end of the dominance that silicon has had over the modern computing and electronics era, giving way to explore novel semiconductor materials.

Harsh environments:

The environments as high temperature, low temperature, corrosive, high radiation and high voltage.

Such novel WBG semiconductors with include SiC, GaN, AlN, indium gallium nitride (InGaN), diamond and beta gallium oxide ($\beta\text{-Ga}_2\text{O}_3$) [33] to name a few. These WBG semiconductors have extended properties over silicon and therefore do not break down in the extreme environments and allow the operation of electronics to continue even under these conditions. There are many applications for these WBG electronics from electric and hybrid cars, buses and lorries, domestic appliances, energy distribution, ocean mining to space, and planetary exploration to nuclear reactors to X-ray detection.

Silicon is unable to be used indefinitely because of operational issues such as adverse heating resulting from increasing population density of transistors as well as ever increasing leakage current due to the short channel effects occurring with transistor scaling. The transistor self-heating has become very challenging to create new transistor

chips with greater power density and energy efficiency to meet market demands.

The WBG semiconductor search to replace silicon technology in power applications and harsh environments sees materials such as SiC and GaN emerging as front runners to compensate for the slow-down in silicon in the high power, higher temperature domains. These two WBG materials have roughly ten times better conduction and switching power to that of silicon and so WBG materials look to be the natural route to go for future power electronics. WBG materials also look to be able to produce devices that are smaller and more efficient along with having the ability to withstand harsh environments. Research in WBG materials estimates that replacing silicon with SiC or GaN can enhance many power electronic device metrics such as the increased DC-DC conversion efficiency from 85 to 99% [69, 85], AC to DC from 85 to 98% [119], and to optimize the efficiency of DC to AC from 96% to 99% [23]. Not only do power electronics benefit from the properties of WBG materials, but also radio-frequency (RF) applications. Where WBG semiconductor materials overcome the issues that the telecommunications industry face today with silicon-based RF power transistors.

Further more, WBG materials can also emit light. Therefore, WBG materials are suitable for various opto-electronic applications especially in the solid-state lighting industry, where GaN-based light emitting diodes (LEDs) provide energy-saving, durability and a long-life alternative to the old incandescent light bulbs. GaN has also become the choice for laser diodes, especially with the ever increasing popularity of Blu-Ray technology.

1.3 Wide Bandgap Semiconductor Applications

1.3.1 Wide Bandgap Semiconductors in High Power, High Temperature Electronics

Power electronics is ubiquitous today, as the majority of devices that use electricity, employ a power management unit such as ICs, PMICs or PMU, all of which are integrated circuits or system-on-a-chip devices. It was not until 1992 that WBG semiconductors [12] made their debut. Prior to this, silicon devices such as bipolar transistors were used. WBG semiconductor materials bring many advantages for power electronics when compared to mature semiconductor materials such as silicon. Such advantages are lower losses for higher efficiency, high switching frequency, volumetric efficiency, higher operating temperature (in excess of the maximum for silicon, 150°C), robustness in harsh environments, and high breakdown voltage. Such advantages lead way to lower

capacitance and inductance which are ideal for filters. WBG materials can achieve a larger effective heat removal from devices which is necessary due to the self-heating that occurs at higher switching frequencies. Lower intrinsic carrier concentration at room temperature giving a greater thermal control before devices become overwhelmed with thermally generated carriers. These WBG semiconductor materials are also shown to work at low temperatures (-50°C), making them suitable over room temperatures and beyond. High power, high temperature electronics device applications span a wide range of uses from industrial uses to automotive and transport systems to wireless communications to clean energy generation. Such advantages, as mentioned above, are now enabling an almost unlimited number of device applications especially in the field of power electronics, where inverter yields have increased in excess of 2% due to the ability of these devices working at high frequency with low switching losses and ultra-fast switching regardless of temperature. Comparing a WBG semiconductor device such as a SiC diode to a silicon bipolar diode a reduction in turn-on losses of 70% [26] can be seen for the SiC diode.

1.3.2 Wide Bandgap Semiconductors in Radio-Frequency Applications

As we all become more and more connected with each other, the need for better communication devices, RF devices, is needed. Unfortunately, Silicon-based RF devices such as power transistors have almost each their limits of power density, breakdown voltage and operating frequency to name a few. Therefore, a new material is needed in order to take RF devices further, this is where WBG semiconductors come into it. Comparing the most common WBG semiconductor, GaN, to silicon-based RF power transistors, the advantages seen are larger power densities and therefore reduced input and output capacitance, increased bandwidth, easier impedance matching, high breakdown voltage, lower losses for high efficiency, and high temperature operation. These advantages it is allowing telecommunication industries to make considerable performance enhancements, taking RF devices into the next generation.

1.3.3 Wide Bandgap Semiconductors in the Opto-Electronics and Lighting Applications

More and more of our electronic devices are using LEDs from TV displays, to mobile phones to traffic lights. This has all become possible due to WBG semiconductors, mainly

GaN and InGaN, taking the industry away from incandescent and filament-based lighting. Comparing LEDs to incandescent lighting we see LEDs convert 90% of their energy into light and only 10% into heat [42], where incandescent convert only 10% of their energy to light and 90% to heat [18] and so are extremely inefficient. Both the life expectancy and brightness of LEDs also surpasses that of incandescent lighting where LEDs last around 40 times longer [96] and produce 10 times more light (lumens) per watt [122]. These advantages result in high efficiency, ultra-fast switching, durability of devices based on WBG semiconductors which are also environmentally friendly (mercury-free). Significant savings through energy costs can be made and further applications beyond lighting are coming to fruition. Without the LEDs, the TV industry would not be where they are today, and we would not have ultra-thin TVs and Blu-ray players.

1.3.4 Wide Bandgap Semiconductors in Sensors

In recent years, there has been much interested in the use of surface functionality of thin film and nanowire WBG semiconductors to produce sensors [80]. Such WBG semiconductors, that are of interest for sensing applications, are GaN, InN, ZnO and SiC. This is due to the need for chemical sensors to detect a target with high specificity and great sensitivity. The WBG materials can be tuned for sensing gases [15, 70, 80, 112], heavy metals [21, 80], UV photons [21, 80], and biological molecules [21, 80] and can be used in a variety of applications from homeland security, medical, and environmental monitoring to food safety.

Through tuning these materials, electro-chemical measurements based on impedance and conductance and, in some cases, electrical measurements of micro-cantilever resonant frequency, changes in their operation can be measured. Quite often these materials are coated with a catalyst such as Pd or Pt in order to increase their detection sensitivity [1, 22, 62, 91]. There are however other way of increasing detection sensitivity and functionality of the surface by use of oxides [3], polymers [58] and nitrides [17] depending on the application. Another type of sensors, that are in demand, are those for detecting X-rays and gamma rays [117] with WBG semiconductor materials such as CdTe [9] and CdZnTe [68] being used. The reasons for WBG semiconductors becoming popular choice for sensors is due to their ability to withstand harsh environments, ability to work in a wide range of temperatures, and the ability to integrate with existing GaN-based UV light-emitting diodes, UV detectors, and wireless communication chips. There is, however, still a lot of research needed as the majority of these devices are not ready for commercialization. This is due to numerous issues these device have regarding

signal-to-noise ratio, size, and the time taken to make a detection, in a lot of cases this exceeds 2 hours [80].

1.4 Aim and Objectives of the PhD Thesis

This thesis focus is aimed at the characterization of Al_4SiC_4 through three main methods:

1.4.1 Ensemble Monte Carlo Simulations

The Monte Carlo (MC) simulations aim to provide an insight into the electronic properties of Al_4SiC_4 through computationally calculating the mobility of electrons through the material. These simulations use known parameters taken from currently literature in order to undertake these calculations. Where parameters are unknown, 4H-SiC has been chosen as a material to take parameters assuming that SiC material properties are close to material properties of Al_4SiC_4 . The unknown parameters which will be looked at experimentally will be then used in the MC simulations in order to provide as accurate simulations as possible.

1.4.2 Experimental Methods

UV/Vis/NIR Spectroscopy was performed in order to ascertain the bandgap of Al_4SiC_4 as it can directly link the transmission of light to photon absorption. X-ray Photoelectron Spectroscopy (XPS) was also performed on samples of Al_4SiC_4 . Here we looked at the workfunction of the material, valence band position, and the structural make-up of the Al_4SiC_4 material. The final experiments performed on samples of Al_4SiC_4 was 2- and 4-probe DC current voltage measurements. This was done in order to try and determine the resistivity of Al_4SiC_4 by use of the Van der Pauw method.

1.4.3 Technology Computer Aided Design Device Simulations

Commercial Technology Computer Aided Design (TCAD) device simulation tool Atlas will be used within a software package by Silvaco [67]. A heterostructure transistor designed using the novel ternary carbide in combination with established SiC is simulated to predict device characteristics such as DC current–voltage (I-V), transconductance, and device breakdown. Through the device simulation there is also a comparison between three devices scaled laterally. Similar to the MC simulations, material parameters for

the device simulations are taken from literature, current experiments, or from 4H-SiC where parameters are unknown.

1.5 Layout of the PhD Thesis

The subsequent six chapters of this thesis contain the following:

Chapter 2: Current knowledge of Al_4SiC_4 is over-viewed in a literature review. This chapter also provides details of the structure of Al_4SiC_4 .

Chapter 3: Background information that was needed throughout this thesis is given in this chapters. The information details the underlying equations that are used in the simulators along with providing information behind the experiments that were undertaken.

Chapter 4: The methodology for each of the three sections is detailed in this chapter. Here, working material parameters are given along with machines that are used in the experiments that are undertaken.

Chapter 5: Computational results are detailed in this chapter. Here, the MC simulations are detailed followed by the device simulations. A conclusion to the computational findings is also detailed in this chapter.

Chapter 6: Experimental results are detailed in this chapter. Conclusions of the experimental finding are also detailed in this chapter.

Chapter 7: Summaries the work in this thesis and then draws an overall conclusion.

ALUMINUM SILICON CARBIDE

Aluminum silicon carbide (Al_4SiC_4) has undergone little investigation since it was first detailed in a paper in 1961 [6, 74] which looked at optical and X-ray powder diffraction. The primary interest of Al_4SiC_4 to date has been in the refractories and high temperature corrosion [46, 114, 115]. Although this is of interest, especially, for use in harsh environments, the electrical properties of Al_4SiC_4 are of most interest to the work being carried out in this thesis. Over the past half century Al_4SiC_4 has been classified as a ceramic material with only the past decade or so having a shift towards an electronic classification. In this research, we are looking into how Al_4SiC_4 was characterized in the past, utilising the obtained experimental and theoretical data into both our computational work and device modeling. We also look at how Al_4SiC_4 has been characterized as a semiconductor material rather than a ceramic material.

2.1 History of Calculations of Material Properties

In 1995, Grobner et al. [36] optimized the thermodynamic modeling of Al-Si-C ternary systems to produce phase diagrams of the systems. They modelled both Gibbs energies along with a five binary parameter model. In their work, they have used experimental data both in their model and as a comparison to the outcome of their model.

Computational research into the characteristics of Al_4SiC_4 started around 2006 when T. Liao et al. [61] looked at the structural and mechanical properties giving details on the stress and strain, elastic stiffness, bonding strengths under various hydrostatic

pressures, and atomic deformation. The work used a combination of the first-principle pseudo-potential total energy method, generalized gradient approximation (GGA), plane-wave pseudo-potential total energy, Vanderbilt-type ultra-soft pseudo-potential and the Monkhorst pack method. As any many body system, the calculations of material properties of Al_4SiC_4 requires ab-initio methods such as density functional theory (DFT) in order to predict electrical or optical properties.

It was not until Hussain et al. [43] in 2008 who first investigated the electronic structure of Al_4SiC_4 through ab-initio calculations to give the first predictions for the band gap based upon the local density approximation (LDA). The LDA predicted Al_4SiC_4 to have a indirect band gap of 1.05 eV. However, LDA is known to underestimate band gap [83]. The shortcomings of LDA can be greatly improved with the addition of extra terms such as the use of a Hubbard term or by combining the method with other approximations such as the self-consistent many-body (scGW) model.

In 2015, computational modeling of the electronic structure of Al_4SiC_4 was improved by Pedesseau et al. [82] with the implementation of a DFT and scGW model. The calculations confirmed Hussain et al. [43] results for Al_4SiC_4 , that the first band is an indirect band. However, the calculations predict a higher energy gap for the first band of 2.5 eV. Pedesseau et al. [82] also predicts a second direct band at 3.2 eV and reveals that the carbon atom plays an important role in the crystal structure, whereby it connects the distorted silicon and aluminum atoms. Lastly, this paper reports on the piezoelectric constants for the first time.

Most recently in 2016, two publications into the computational study of Al_4SiC_4 with publications by Li et al. [60] and Sun et al. [102] occurred. Using first principle DFT calculations, Sun et al. [102] investigated and reported on the structural stability, bonding characteristics, and anisotropic mechanical and thermal properties of Al_4SiC_4 . The bulk modulus was reported as 171.9 GPa leading in a prediction that high temperature and high pressure would be needed in order to produce Al_4SiC_4 . Li et al. [60] used a hybrid density function HSE06 to study the polarized optical dielectric functions of Al_4SiC_4 in multiple crystal orientations to report on the longitudinal-optical–transverse-optical (LO-TO) phonon splitting, the Born effective charges, and phonon eigen-vectors for all IR-active modes. The work reported that the Al-C bonding is mainly ionic while the S-C bonding is covalent in Al_4SiC_4 along with the LO-TO splitting resulting in large mode-effective charge vectors and mode-dissociated static dielectric constants. Finally, they reported that the IR response of phonon modes is strongly dependent on crystallographic direction.

2.2 History of Experimental Measurements

Experimental research into Al_4SiC_4 has been going on since it was first report in 1961 by Barczak [6] who look at optical and X-ray power diffraction data on Al_4SiC_4 that was grown via sublimation of Al_4C_3 and SiC in a vacuum furnace. They noted two phases of Al_4SiC_4 , α and β , a yellow colour of their samples and a hexagonal lattice for $\alpha\text{-Al}_4\text{SiC}_4$ with lattice parameters of $a = 6.55$ a.u. and $c = 10.80$ a.u.

In 1979, Schneider et al. [94] found the compound Al_4SiC_4 while looking at the binary system SiC- Al_4C_3 . Schneider [94] compared their findings with the only other report of Al_4SiC_4 , that being Barczak [6]. They found differences in the lattice parameters giving $a = 0.3281$ nm and $c = 2.167$ nm, compared with $a = 0.655$ nm and $c = 1.080$ nm that Barczak [6] found. Schneider et al. also found discrepancies with the X-ray measurements of Barczak [6] where an additional fourteen reflections due to d spacing were observed between 0.13 nm and 0.15 nm.

The following year (1980), Inque et al. [47] reported on a new phase of aluminum silicon carbide, that being $\text{Al}_4\text{Si}_2\text{C}_5$ along with further data on $\alpha\text{-Al}_4\text{SiC}_4$. Inque et al. [47] synthesised $\alpha\text{-Al}_4\text{SiC}_4$ by melting powered silicon carbide with Al_4C_3 before being headed up to 2000°C before being cooled. The lattice parameters of the Al_4SiC_4 crystals were measured and found to be in agreement with Schneider et al. [94]. Inque at al. [47] postulated on the space groups for Al_4SiC_4 with the possibilities of it being either P63 mc or P63/mmc, where X-ray diffraction data confirmed the space group as P63 mc.

Several years later, a paper by Schoennahl et al. [95] in 1983 gave an account of a method of preparation for Al_4SiC_4 along with crystallographic information on the structure of Al_4SiC_4 detailing the lattice parameters: $a = 0.328$ nm and $c = 2.172$ nm as well as confirming a hexagonal lattice for the material. The paper went on to give a detailed description of $\alpha\text{-Al}_4\text{SiC}_4$ but no description of a β phase of Al_4SiC_4 . Finally, they noted the possible existence of a family of compounds with the formula $\text{Al}_4\text{C}_3(\text{SiC})_n$.

Three papers came out the following year (1984), one by Beyer et al. [10] and the other by Behrens et al. [8] and a final one by Kidwell et al. [55]. Beyer et al. [10] looked at the head capacity of Al_4SiC_4 over a range of temperature from 5.26 to 1047 K. They synthesized Al_4SiC_4 from powers of Al_4C_3 and SiC. What they found was that the standard molar enthalpy of formation is 203.3 ± 4.9 kJ mol⁻¹ at 298.15 K. Behrens et al. [8] looked at the vaporization thermodynamics and enthalpy of the formation of Al_4SiC_4 . Al(g) was the only vapor present in the equilibrium vapor of ($\text{Al}_4\text{SiC}_4 + \text{SiC} + \text{C}$) up to 1784 K. Ref. [8] found a formation of a micro-layer on the Al_4SiC_4 of ($\text{SiC} + \text{C}$) and

that the enthalpy formation for Al_4SiP_4 being $-187 \pm 34 \text{ kJ mol}^{-1}$ at 298.15 K which is similar to that of Beyer et al. [10]. Kidwell et al. [55] presented a short communication into a new intermediate phase in the Al-SiC system. Several ternary phases were looked at during this work where they show the existence of $\text{Al}_4\text{C}_3\text{-SiC}$ and a new ternary intermediate phase $2\text{Al}_4\text{C}_3\text{-SiC}$. However, they could not confirm the previously reported existence of $\text{Al}_4\text{C}_4\text{-SiC}$.

Later in the 80's, Yamaguchi et al. [114] (1987) looked at the synthesis and some properties of Al_4SiC_4 . The paper noted that the addition of Al_2O_3 during synthesis helps to facilitate the formation of Al_4SiC_4 . The paper looks at two main properties of Al_4SiC_4 , the hydration resistance and oxidation resistance. The hydration resistance was found to be admirable and sufficient for practical use and oxidation resistance was shown to be good up until 750°C where it started to oxidize as the temperature increased. The same year, the alloying of aluminum, silicon, and carbon was studied by Oden et al. [73]. Here, they used various methods to determine the isopleth of $\text{Al}_4\text{C}_3\text{-SiC}$ at 2000°C and 2150°C . They also report on the solubility of carbon in aluminum and silicon at high temperature as well as the decomposition temperatures for Al_4C_3 among other Al-Si-C systems.

Oden et al. carried on the research on Al-Si-C systems and Al-C-N systems and published further works in 1990 [74]. The refractory nature of aluminum silicon carbonitrides was confirmed and the decomposition temperature for the two systems was measured to be 2265°C for $\text{Al}_4\text{C}_3\text{-AlN-SiC}$ phases. One thing that restricted practical information was the formation of liquid phases on the AlN side at 2175°C and on the SiC side at 2070°C . This work also looked to the isothermal sections and, at 1860°C , indicated a pseudo-binary compound, $\text{Al}_3\text{C}_3\text{-AlN}$, in the $\text{Al}_4\text{C}_3\text{-Al}_n$ subsystem along with two compounds $2\text{Al}_4\text{C}_3\text{-SiC}$ and $\text{Al}_4\text{C}_3\text{-SiC}$ in the $\text{Al}_4\text{C}_3\text{-SiC}$ system and, finally, $\text{AlC}_3\text{-AlN}$ and $\text{Al}_4\text{C}_3\text{-AlN-SiC}$ in the $\text{Al}_4\text{C}_3\text{-AlN-SiC}$ system.

Almost ten years later in 1996, Grobner et al. [36] looked at the phase diagram of Al-Si-C systems optimizing it using past experimental data [7, 11, 16, 37, 38, 56, 66, 71, 72]. Grobner et al. [36] also gave an account of previous investigations from Barczak et al. [6] through to Oden et al. [74]. The optimized calculation of the phase diagram found small deviations which was put down to incompatibility between established solubilities in the binary subsystems and measured solubilities in the ternary system.

In 2002, Yamamoto et al. [115] looked at synthesizing Al_4SiC_4 from a powder mixture of aluminum, silicon and carbon black. It was noted that a small amount of triethanolamine (TEA) was needed in order to form Al_4SiC_4 as without TEA the mixture seem to form Al_4C_3 and SiC instead. The paper discusses the oxidation resistance of

Al_4SiC_4 at various temperatures up to 1450°C . Yamamoto et al. [115] found that Al_4SiC_4 has superior oxidation resistance below a temperature of 850°C . The same year, Inoue [46] also looked at the fabrication and oxidation resistance of Al_4SiC_4 . Syntheses of Al_4SiC_4 was done by mixing powders of aluminum, silicon and carbon together before sintering by pulse electronic current. The work also reported on oxide grow at high temperature of $1250\text{-}1500^\circ\text{C}$ and showed that the oxide layer grows exponentially as the temperature increases.

The following year (2003), Inoue et al. [45] looked at the electrical resistivity of Al_4SiC_4 sintered bodies at various temperatures. Inoue et al. [45] found that the material gave slightly insulating electrical properties. They also showed that the current-voltage characteristics followed a linear relationship and have an ohmic region. The same year, Inoue et al. [44] carried out further studies into the synthesis of Al_4SiC_4 . They synthesized Al_4SiC_4 with a powdered mixture of aluminum, silicon and carbon together as well as amounts of kaolin powder. They discussed the various intermediate stages for synthesizing Al_4SiC_4 as well as the Gibbs energy of formation, which changes from positive to negative at a temperature of 1106°C .

Further works into the synthesis and the oxidation behavior were reported on by Wen et al. [113] in 2005. The process for synthesis that Wen et al. [113] used was by hot pressing aluminum, graphite powders and polycarbosilane (PCS). They report that the use of PCS helps promote the formation of Al_4SiC_4 and its densification into one event, rather than having intermediate stages. Further works were carried out by Wen et al. [113] on Al_4SiC_4 giving the first accounts into the mechanical and thermal properties. The same year came first reports of the compression and pressure behavior of Al_4SiC_4 by Solozhenko et al. [101]. The quasi-hydro-static compression of Al_4SiC_4 was studied up to a pressure of 6 GPa at room temperature. Through their work they were able to determine a bulk modulus, B_0 , of $182(10)$ GPa and an anisotropic nature of compression.

2007 came with further works into the synthesis of Al_4SiC_4 , where Zhao et al. [120] studied the various factors that influenced the synthesis. The methods that were studied included heating mixtures of Al_2O_3 , SiO_2 and graphite in an argon atmosphere. Zhao et al. [120] noted that the optimum molar ratio of carbon, Al_2O_3 and SiO_2 was 8:2:0.8, where by pure Al_4SiC_4 was formed. Within the works they also give a discussion about the formation mechanism of Al_4SiC_4 .

Several years later, in 2010, Deng et al. [24] produced further information into the synthesis of Al_4SiC_4 and $\text{Al}_4\text{O}_4\text{C}$. This work introduced the idea of using an Fe_2O_3 additive in the synthesis process along with flint clay, activated carbon and aluminum

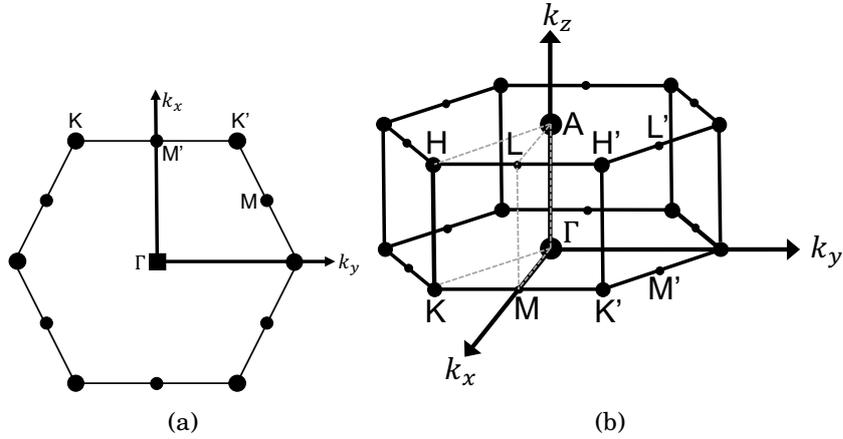


Figure 2.1: (a) 2D hexagonal (0001) plane showing the location of the M valleys within the Al_4SiC_4 hexagonal structure and (b) a 3D hexagonal structure showing locations of principal valleys.

powders. They report that the use of an Fe_2O_3 additive promotes the nucleation and grain refinement of Al_4SiC_4 phase and leads to Fe_3Si coating Al_4SiC_4 grains. This giving way to fine granules structure instead of fibrous-like structures.

Come 2015, Zevgitis et al. [118] look at characterizing Al_4SiC_4 and compared it with Al_4C_3 [103]. Here they presented results from synthesising material by cooling an aluminium-silicon melt in a graphite crucible. Raman spectroscopy was used to determine the vibrational modes, where 18 Raman lines in the $80\text{-}920\text{ cm}^{-1}$ were found in Al_4SiC_4 which fell short of the 25 that were predicted hexagonal $\text{P6}_3\text{mc}$ structure. UV-Vis-NIR spectroscopy was also performed on samples of Al_4SiC_4 to determine the band gap which presents itself around 2-2.5 eV. The crystal structure was confirmed in this paper by both XRD and TEM and was in agreement with past examinations of Al_4SiC_4 showing the same hexagonal structure, an orange coloured crystal and a crystal orientation of $\text{P6}_3\text{mc}$.

2.3 Material Properties

Al_4SiC_4 belongs to a family of aluminium-silicon ternary carbides with the general formula $(\text{Al}_4\text{C}_3)_x(\text{SiC})_y$ ($x, y = 1$ or 2) and exhibit a hexagonal structure, see Figure 2.1. Al_4SiC_4 in particular is a stacked unit of two-unit cells, that being Al_4C_3 and SiC , see Figure 2.2.

It has a group spacing of $\text{P6}_3\text{mc}$ [43, 47, 73, 82] with lattice parameters $a = b = 3.2812$

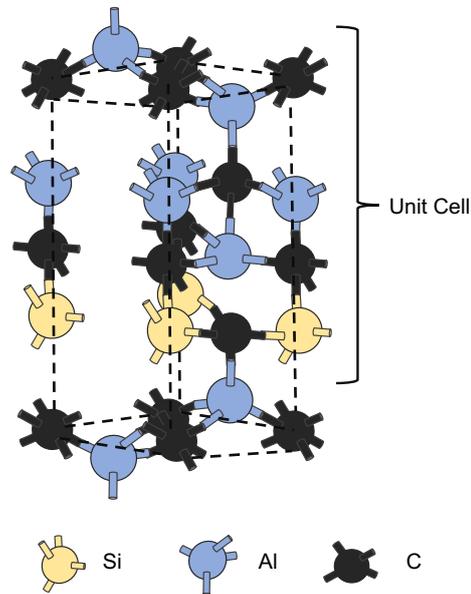


FIGURE 2.2. Crystal structures of Al_4SiC_4 . The blue, yellow, and black spheres represent Al, Si, and C atoms, respectively.

\AA [82] and $c = 21.7042 \text{ \AA}$ [82] and a mass density of 3.03 g/cm^3 [82]. Other parameters that are of use to this work are listed in a comparison of Al_4SiC_4 to other semiconductor material parameters like the piezoelectric constant, acoustic deformation potential, and the longitudinal and transverse acoustic velocities in Table 2.1.

Parameter	Si [99]	SiC [34] (3C / 4H / 6H)	GaN [34] (Wurtzite)	AlN [34]	Al ₄ SiC ₄
Mass (g/cm^3)	2.32	3.21 / 3.211 / 3.21	6.15	3.23	3.03 [82]
Lattice Constant (Å)	5.43	4.36 / 3.07 / 3.07	3.16	3.11	3.28 [82]
Longitudinal Acoustic Velocity ($\times 10^5 cm/s$)	2.32	9.50 / 12.50 / 12.50	7.96	10.97	10.577 [102]
Transverse Acoustic Velocity ($\times 10^5 cm/s$)	5.34	4.10 / 7.10 / 7.10	4.13	6.22	6.431 [102]
Electron Effective Mass	0.916 m_0 0.190 m_0	0.68 m_0 / 0.29 m_0 / 0.20 m_0 0.25 m_0 / 0.42 m_0 / 0.42 m_0	0.20 m_0	0.4 m_0	M_{long} 0.5678 m_0 ^(a) M_{trans} 0.6952 m_0 ^(a) K_{long} 1.0569 m_0 ^(a) K_{trans} 0.9360 m_0 ^(a)
Optical Phonon Ener- gies (meV)	63.00	102.80 / 104.20 / 104.20	91.2, 40.00	99.2	80.59 ^(b) , 86.79 ^(b)
Band Gap (eV) Direct(D)/Indirect(I)	1.12 I	2.40 – I / 3.26 – I / 3.02 – I	3.40 – D	$E_{g1} = 6.2 \Gamma_1$ Valley – D $E_{g2} = 6.9$ M-L Valley – I $E_{g3} = 7.2$ K Valley – I	$E_{g1} = 2.78$ M Valley – I ^(c) $E_{g2} = 3.30$ K Valley – D [82]
Acoustic Deformation Potential (eV)	9.0	12.6 / 11.6 / 11.2	8.16	9.5 [52]	11.4 ^(d)

TABLE 2.1. A comparison of Al₄SiC₄ to other semiconductor material parameters. References for the parameters are listed in the top of the column unless otherwise stated, (a) calculated values based on the DFT data that was received from L. Pedesseau [82], (b) calculated values based on the Raman and IR experiments at LMGP/Grenoble INP [81], (c) values calculated in this work, and (d) average taken from Ref [49].

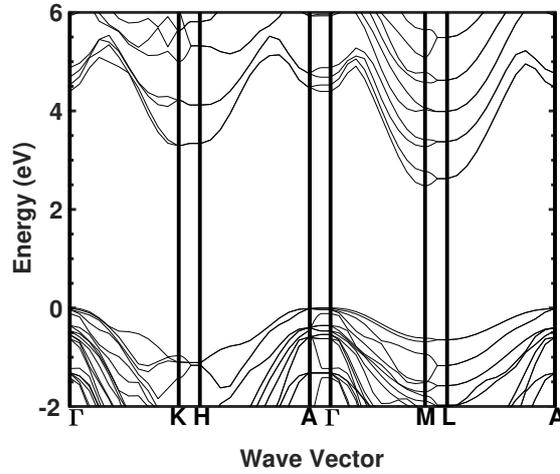


FIGURE 2.3. Re-scaled Al_4SiC_4 bandstructure obtained from Pedesseau et al. [82] density functional theory (DFT) calculations.

From the hexagonal crystal structure, Figure 2.1, and the band diagram, Figure 2.3, we have determined the following valleys, Γ , A, L, H, M and K. Not all of these valleys are of importance to the electronic properties as we shall see later on in Chapter 5.1.

There have been several predictions for a bandgap of this material starting with Hussain et al. [43] in 2008 at a value of 1.05 eV and the most recently in 2015 at 2.48 eV [82], the various bandgaps have been detailed in Table 2.2. The bandgap will be investigated further in this thesis.

Published Band Gap (eV)	Method
1.05	Computational (DFT)[43]
1.12	Computational (DFT)[102]
1.81	Computational (DFT)[60]
2-2.5	Experiment (UV-Vis-NIR)[118]
2.48	Computational (DFT) Experimentally (Ellipsometry)[82]
2.4-2.5	Experiment (UV-Vis-NIR and Ellipsometry)[81]

TABLE 2.2. Comparison of published energy band gaps for Al_4SiC_4 indicating a method and a source.

The works on vibration modes by Zevgitis et al. [118] and Pedesseau et al. [81] performed Raman spectroscopy measurements on Al_4SiC_4 single crystal platelets at different polarized configurations (laser propagation parallel to the c -axis and orthogonal

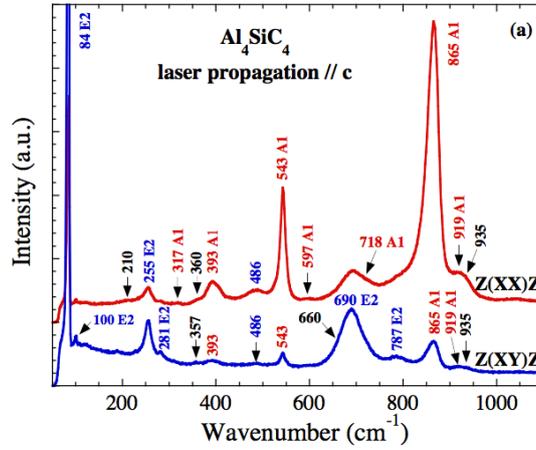


FIGURE 2.4. Polarized Raman spectra of Al_4SiC_4 single crystals. Spectra collected on the crystal surface (laser propagation along the c -axis). Image taken from [81]

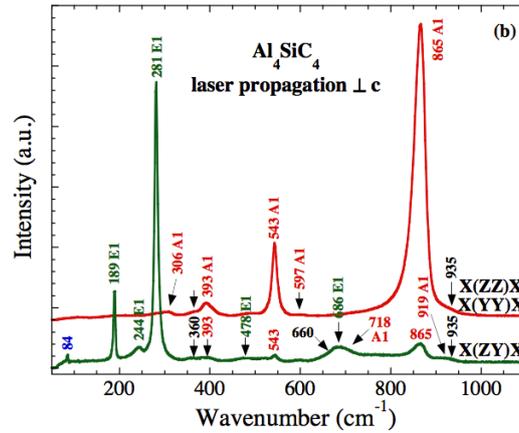


FIGURE 2.5. Polarized Raman spectra of Al_4SiC_4 single crystals. Spectra collected on the crystal edge (laser propagation parallel to the crystal surface). Image taken from [81].

to the c -axis), see Figures 2.4 and 2.5. These vibration modes of phonons are important when calculating the electronic transport properties as they determine the electron interactions with phonons. Unfortunately, there is no current literature that investigates phonon spectrum in Al_4SiC_4 and, therefore, it is still unknown as to what effect these vibrational modes of phonons have on the transport of carriers.

THEORETICAL BACKGROUND

This chapter gives background details on the methods used in this thesis. There are details on solid state physics, ensemble Monte Carlo (MC) technique employed to simulate transport properties of the bulk aluminium silicon carbide, device simulations and experiments. The main emphasis of this chapter is to give a theoretical background to the physical approaches and experimental techniques that make up the work in this thesis, from the approximation of effective carrier mass to describe a band structure of a semiconductor considering its relevance to the carrier transport, through carrier free flights assuming Newton mechanics and quantum-mechanical scattering, to Poisson's equation to self-consistently account for long-range electron-electron interactions (Coulomb scattering).

3.1 Effective Mass

When electrons and holes have a relatively small energy, they behave as free particles where their effective mass and energy dispersion follows a parabolic dispersion law. This law represents the $E - \mathbf{k}$ dispersion relation, that is, the relationship between the electron energy, E , and the crystal momentum or wave-vector, \mathbf{k} . When $\mathbf{k} = 0$, the band minima, the energy dispersion takes on the form:

$$(3.1) \quad E(\mathbf{k}) = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m^*} = \frac{\hbar^2}{2m^*} (k_x^2 + k_y^2 + k_z^2)$$

where $E(\mathbf{k})$ represents the kinetic energy of electron when measured from the band minima, m is the mass of an electron, m^* is the effective mass, x , y and z refer to the axis and are aligned to the principal axes of the ellipsoids, p is the momentum and \hbar is Plank's constant divided by 2π .

We can write Equation (3.1) for the effective mass, m^* , by differentiating E twice with respect to \mathbf{k} , leading way to:

$$(3.2) \quad \frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 E(\mathbf{k})}{\partial k^2}$$

We can use this dispersion relation to calculate the effective mass from the band structure. As the conduction band has a zero slope at its minima, the dispersion is taken as a quadratic, as illustrated in Figure 3.1, and is fitted with a polynomial trend-line with the form:

$$(3.3) \quad y = a + b x + c x^2$$

where a , b and c are constants and y and x refer to the axis.

The second order derivative of the parabolic equation can be related to the energy dispersion relation as follows:

$$(3.4) \quad 2c = \frac{\partial^2 E(\mathbf{k})}{\partial k^2}$$

This equation is used to determine the effective electron mass in both the longitudinal and transverse direction of Al_4SiC_4 so that we could use them as a material parameter in the MC simulations (see Chapter 5.1).

3.2 Boltzmann Transport Equation

The Boltzmann Transport Equation (BTE) is a statistical physical model describing carrier transport in semiconductors over time, both in real space and momentum space. A distribution of electrons can be described using the distribution function, $f(\mathbf{k}, v, t)$, for an individual electron with velocity, v , moving under an external force \mathbf{F} . The BTE is given by [64]:

$$(3.5) \quad \frac{\partial f}{\partial t} = -(\mathbf{v} \cdot \Delta_{\mathbf{r}} f + \mathbf{F} \cdot \Delta_{\mathbf{k}} f) + \left(\frac{\partial f}{\partial t} \right)_{collision}$$

where f is the distribution function and t is the time variable, the subscript *collision* denotes the collision term and $\Delta_{\mathbf{r}}$ and $\Delta_{\mathbf{k}}$ are the differential operators in terms of the position and momentum vectors respectively.

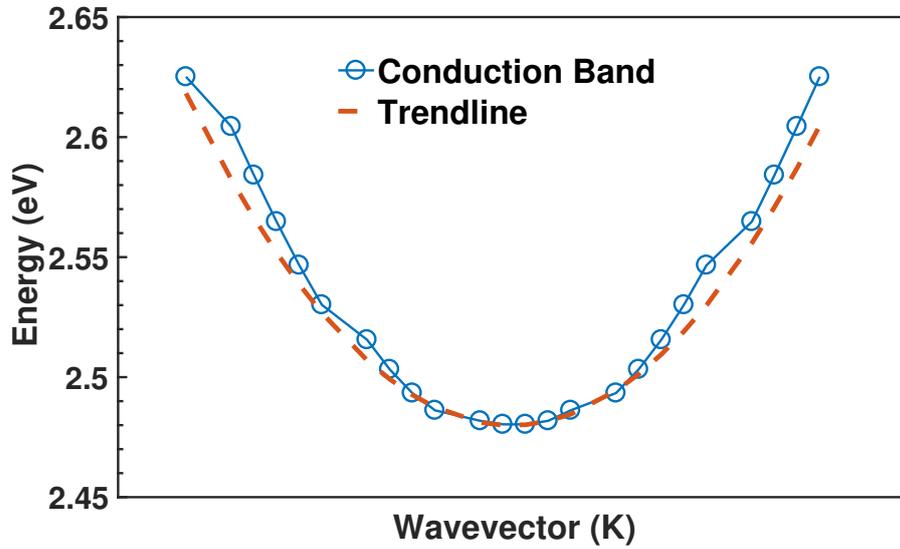


FIGURE 3.1. Dispersion relation in a conduction band fitted with a polynomial trendline.

Equation (3.5) takes into account only transport evolution of particles due to particle collisions (scattering) and their drift due to an applied external field. In other words, the BTE describes the evolution of the distribution of particles through the motion of the particles, the force acting on them, and their scattering due to collisions. The BTE is an integral-differential time-dependent kinetic equation of motion over six-dimensional position-momentum space, and finding an analytically solution is extremely difficult [5]. Prior knowledge is usually needed in order to solve the BTE analytically which sometime is not known [35, 109]. Therefore, it is usually solved numerically through such methods as a MC technique to simulate the electron transport through a many-body system [59, 78]. Details on a specific MC technique, the ensemble MC technique, which simulates a transport of carriers in condensed matter, gas or plasma, can be found in Section 3.3.

3.3 Bulk Ensemble Monte Carlo Simulations

The behaviour of any semiconductor device such as a bipolar junction transistor (BJT) and field effect transistor (FET) can be adequately described by a semi-classical model of charge transport within device domain. This is due to the fact that the characteristic dimensions in question are typically of length scales much larger than those

where quantum-mechanical phase coherence is maintained. At these length scales, a particle-based description based on the BTE framework and its approximations can be used. However, as devices continue to shrink, their channel length are approaching the characteristic wavelength of particles, the so-called de Broglie wavelength, and the quantum-mechanical effects are expected to become increasingly important. For example, a quantum-mechanical confinement affects distribution of electrons and holes in the inversion layer of FETs. However, at room temperature and under strong electric fields, such effects are usually found to be of the second order in the overall behaviour of the device. This is not to say that as spatial dimensions reduce that the consideration of quantum effects will not take precedence over other effects.

When the BTE is applied to give a classical description of charge transport in semiconductors, a probability distribution function is assumed for particles which develops in real and momentum space in time. This probability distribution function, given by $f(\mathbf{k}, v, t)$, describes movement of charged carriers in a six-dimensional phase space of a real position and crystal momentum in time. When this probability distribution function is known, any physical observable of carriers or a system such as velocity, momentum, energy, charge or current can be monitored or calculated based on the averages of f (see Section 3.2 for further details on the BTE). An expansion of the BTE over a momentum space reveals a set of approximate partial differential equations in position space, leading way to the hydrodynamic model for charge transport. A simplification of the hydrodynamic model where only the continuity equation (Section 3.10.5) and the current density (Section 3.10.6) is written in term of the local electric field and concentration gradients leads to the drift-diffusion transport model (see Section 3.10.6). This model can be reduced further if needed for the simulation of lumped parameter behaviour at a circuit level where many individual devices as well as passive elements can be simulated.

3.3.1 The Ensemble Monte Carlo Method

The ensemble MC technique [50, 51, 57, 121] has been used as a numerical method to simulate non-equilibrium particle transport in many-body systems including semiconductors, both in bulk materials and devices, for several decades now. When the ensemble MC technique is applied to a simulation of carrier non-equilibrium transport in semiconductors, the simulation is semi-classical because the carrier movement between collisions is assumed to be classical govern by Newton equations while the probability of collisions or carrier scatterings is calculated quantum-mechanically. Technically, a random path is generated to simulate the stochastic motion of particles which can be

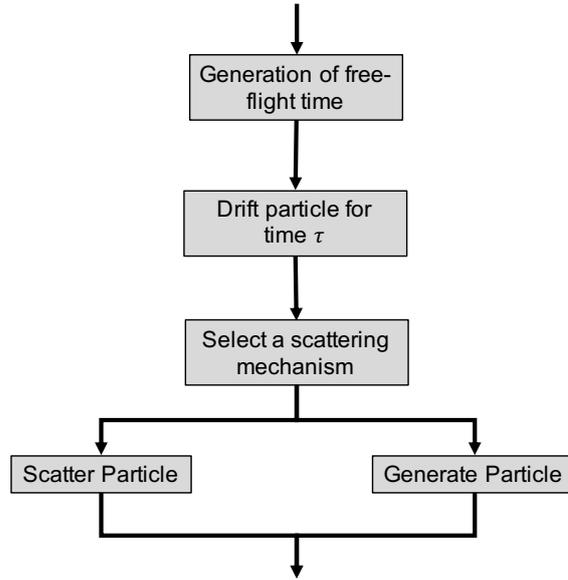


FIGURE 3.2. Evolution of a particle in a Monte Carlo simulation.

subject to randomly selected collision processes. This random path generation evaluates integral equations and is a part of the general random sampling used in the evaluation of multi-dimensional integrals. The technique simulates free flights during a particle motion that gets terminated by instantaneous scattering events occurring with a quantum-mechanical probability. The algorithm for the MC technique consists of the generation of random free flight times for each particle, the generation of a scattering process determined by the quantum-mechanical probability which will occur at the end of the free flight, and the generation of a final energy and a momentum of the particle based on probability related to the scattering. This process is repeated for the next time step as illustrated in Figure 3.2.

The MC method will sample the particles motion at various times throughout the simulation. This will allow for an approximation of physical quantities of interest such as the single particle distribution function, the average drift velocity in an applied electric field, etc. Simulation of an ensemble of particles, which is representative of a physical system of interest, can provide the non-stationary time-dependent evolution of both the electron and hole distributions under the influence of a time-dependent driving force.

3.3.2 Free Flight Generation

The ensemble MC technique models the dynamics of particle motion by assuming that the particle free flights are terminated by instantaneous scattering events, that change the momentum and energy of the particle. The selection of the time when scattering occurs, the selection of the scattering mechanism, and the selection of a final state after the scattering, as well as many steps in initialisation of a many-body system, is performed using random numbers within physically calculated probability.

In particular, the free flight is simulated with a probability density, $\mathbf{P}(t)$, in which $\mathbf{P}(t) dt$ is the joint probability. The probability that a particle will arrive without scattering at time, t , after a previous collision at $t = 0$, and then suffers a collision at the time t is given by:

$$(3.6) \quad \exp \left\{ - \int_0^t \Gamma[\mathbf{k}(t')] dt' \right\}$$

where $\Gamma(\mathbf{k})$ is the total scattering rate given by:

$$(3.7) \quad \Gamma(\mathbf{k}) = \sum_{j=1}^N \Gamma_j(\mathbf{k})$$

where j is the j -th scattering mechanisms and N is the number of all possible scattering mechanisms considered. The joint probability density is then:

$$(3.8) \quad \mathbf{P}(t) = \Gamma[\mathbf{k}(t)] \exp \left\{ - \int_0^t \Gamma[\mathbf{k}(t')] dt' \right\}$$

where the probability of scattering in the time interval dt around t is $\Gamma[\mathbf{k}(t)dt]$ and $\Gamma[\mathbf{k}(t)]$ is the scattering rate of an electron or a hole with wave-vector \mathbf{k} .

The probability density, $\mathbf{P}(t)$, can be related to a uniform random number r by:

$$(3.9) \quad \mathbf{P}(r) dr = \mathbf{P}(t) dt$$

Integrating this with regards to $\mathbf{P}(r) = 1$ gives:

$$(3.10) \quad r = \int_0^t \mathbf{P}(t') dt'$$

Substituting $\mathbf{P}(t)$ from Equation (3.8) and integrating gives:

$$(3.11) \quad r = 1 - \exp \left\{ - \int_0^t \Gamma[\mathbf{k}(t')] dt' \right\}$$

The relation for the random number r can be simplified because $1 - r$ is statistically the same as r , the uniform random number. In other words, the probability distribution will

be the same. A fundamental equation, which is needed to generate random free flight time after each scattering event, is then given by:

$$(3.12) \quad -\ln(r) = -\int_0^t \Gamma[\mathbf{k}(t')] dt'$$

The overall scattering probability Γ is generally depending on wave-vector \mathbf{k} . In order to speed up the simulation process by avoiding calculations of $\Gamma(\mathbf{k})$.

The numerical determination of the free flight time, t , from Equation 3.12 is computationally very time consuming. Therefore, a trick is used by introducing a self-scattering mechanism, first introduced by Rees [87], which leaves the state of an electron unchanged (neither the particle momentum nor energy is changed) in order to have the total scattering rate a constant. The total scattering rate, Γ , will be then given by:

$$(3.13) \quad \Gamma = \Gamma_0[\mathbf{k}(t')] + \Gamma[\mathbf{k}(t')]$$

where Γ_0 is the self-scattering rate chosen to be equal to or larger than the maximum Γ expected in the simulation as [51]:

$$(3.14) \quad \Gamma_0(\mathbf{k}) = \Gamma - \sum_{j=1}^N \Gamma_j(\mathbf{k})$$

where Γ is defined as:

$$(3.15) \quad \Gamma = \sum_{j=0}^N \Gamma_j(\mathbf{k})$$

The free flight time, t , therefore is given by:

$$(3.16) \quad t = \frac{1}{\Gamma} \ln r$$

3.3.3 Final State After Scattering

The final state after scattering is determined by the scattering mechanism that is randomly selected i.e. acoustic phonon, photon emission, etc. This scattering mechanism terminates the free flight and the final energy and momentum of a particle can be determined. The scattering mechanism is chosen using a uniform random number between 0 and Γ leading way to:

$$(3.17) \quad \Gamma = \Gamma_0[n, \mathbf{k}] + \Gamma_1[n, \mathbf{k}] + \Gamma_2[n, \mathbf{k}] + \cdots + \Gamma_N[n, \mathbf{k}]$$

where Γ_0 is self-scattering, n is the band index of the particle and \mathbf{k} is the wave-vector at termination of free-flight. The scattering rate $\Gamma_j[n, \mathbf{k}; m, \mathbf{k}']$ is the j -th scattering

mechanism, where n and m are the initial and final band indices, and \mathbf{k} and \mathbf{k}' are the wave-vectors before and after scattering.

The scattering angle here is defined by a spherical coordinate system around the initial wave-vector, \mathbf{k} , where the final wave-vector, \mathbf{k}' , is specified by $|\mathbf{k}'|$ as well as the azimuthal and polar angles, ϕ and θ around \mathbf{k} . The scattering rate only depends on the angle θ between \mathbf{k} and \mathbf{k}' and therefore, ϕ is chosen using a uniform random number between 0 and 2π , while θ is chosen according to the cross-section arising from the scattering rate. If the probability for the scattering into a certain angle, $P(\theta)d\theta$, is integrable, then random angles satisfying this probability density may be generated from a uniform distribution between 0 and 1 through an inversion of Equation (3.11). If not, then a rejection technique may be used to select the random angle according to $P(\theta)$.

3.3.4 Ensemble Monte Carlo Simulation

The above process/algorithm may be used to follow single particle over many scattering events in order to simulate the steady-state behaviour of an uniform system. However, the simulations of the realistic many-body semiconductor system require the use of an ensemble of particles where the above process/algorithm is repeated for each particle within the ensemble system of interest until the simulation is completed. This process happens by simulating a particle until the end of a time-step, Δt , then the next particle in the ensemble is treated. Over each of the time-steps, Δt , the motion of the particle is simulated independently of other particles. The nonlinear effects such as carrier-carrier interactions are updated at the end of each time-step.

The non-stationary many-body distribution function and related quantities, drift velocity, valley population, etc., are taken as averages of the time-step throughout the simulation. For example, the average drift velocity (\bar{v}) in the presence of the field given by an ensemble average of the component of velocity in the direction of the applied field is given at the n -th time-step (Δt) by [111]:

$$(3.18) \quad \bar{v}(n\Delta t) \cong \frac{1}{N} \sum_{j=1}^N v^j(n\Delta t)$$

where N is the number of simulated particles and j labels each of the particles in the ensemble. The equation thus represents an estimation of the true velocity, which has a standard error, s , of:

$$(3.19) \quad s = \frac{\sigma}{\sqrt{N}}$$

where σ^2 is the variance which may be estimates from:

$$(3.20) \quad \sigma^2 = \frac{N}{N-1} \left(\frac{1}{N} \sum_{j=1}^N (v^j)^2 - \bar{v}^2 \right)$$

A similar distribution function for both electrons and holes may be tabulated by counting the number of electrons in each of the cells defined in \mathbf{k} -space. The error that is estimated by Equation (3.19) decreased with the squared root of the number of particles in the ensemble. Typical sizes for good statistical ensemble models are in the range of $10^4 - 10^5$ particles. However, there are a variety of techniques to decrease this standard error enhancing statistically rare events such as impact ionization or electron-hole recombination [50].

3.3.5 Fermi's Golden Rule

Fermi's Golden Rule, derived from perturbation theory, is a quantum mechanical equation of the transition rates or carrier scattering process. In what follows, we will focus only on electrons because the equations for holes are identical. The j -th electron scattering rate, Γ_j , of the transition of an electron from an initial state $|\mathbf{k}_0\rangle$ to a final state $|\mathbf{k}'_0\rangle$ will occur is given by [64]:

$$(3.21) \quad \Gamma_j[n, \mathbf{k}_0; m, \mathbf{k}'_0] = \frac{2\pi}{\hbar} \left| H_{m, \mathbf{k}'_0; n, \mathbf{k}_0}^{a,e} \right|^2 \delta(E(\mathbf{k}'_0) - E(\mathbf{k}_0) \mp \hbar\omega)$$

which keeps an account of both phonon absorption (a) and phonon emission (e) energies with the $\mp \hbar\omega$. H in Equation 3.21 includes the scattering potential of the interaction, and $E(\mathbf{k}'_0)$ and $E(\mathbf{k}_0)$ are the initial and final state energies of the particles. The delta function, δ , is the Kronecker delta and results in the conservation of energy for long times after the collision. The scattering rate in Equation (3.21) can be transferred to three-dimensional (3D) space by converting it to an integral within a crystal volume, V , if required, giving the final scattering rate as:

$$(3.22) \quad \Gamma(\mathbf{k}) = \frac{V}{(2\pi)^3} \frac{2\pi}{\hbar} \int \left| H_{m, \mathbf{k}'_0; n, \mathbf{k}_0}^{a,e} \right|^2 \delta(E_{\mathbf{k}'_0} - E_{\mathbf{k}_0} \mp \hbar\omega) \delta_{\mathbf{k}' - \mathbf{k} \mp \mathbf{q}, 0} d\mathbf{k}$$

The assumption here is that any collision occurs instantaneously and had permanent effects. This is due to the amount of time of each collision being much smaller than the time between collisions. This condition is satisfied in nanoscale semiconductor devices operating at sub-terahertz frequencies as many semiconductor transistor for digital and analogue applications. [88, 89]. The typical electron scattering time at room temperature

is in the range of picoseconds ($10^{-12}s$) to which only terahertz frequencies are comparable. Naturally, this assumption will not be valid at a very low temperature, for example, close to helium temperatures. When we sum up over all final states $|\mathbf{k}'_0\rangle$ of an electron in Equation (3.21), the j -th electron scattering rate of the electron with an initial state $|\mathbf{k}_0\rangle$, the total rate used to generate the free flight, from Equation (3.17), is then given by:

$$(3.23) \quad \Gamma_j[n, \mathbf{k}_0] = \frac{2\pi}{\hbar} \sum_{m, \mathbf{k}'} \left| H_{m, \mathbf{k}'_0; n, \mathbf{k}_0}^{a, e} \right|^2 \delta(E(\mathbf{k}'_0) - E(\mathbf{k}_0) \mp \hbar\omega)$$

3.3.6 Scattering Process

Both electrons and holes, aka free carriers, interact with the crystal lattice and each other through a variety of scattering mechanisms which relax the energy and momentum of the particle. The scattering mechanism is given by Fermi's Golden rule [64] as introduced in Section 3.3.5. However, there are limitation to the use of the Fermi's Golden rule due to the effects such as collision broadening and finite collision duration time [29] but these are beyond of the scope of this work.

Scattering mechanism are roughly divided into three categories: (1) crystal defects which are primarily elastic; (2) lattice scattering between carriers and phonons which are inelastic and finally; and (3) scattering between the carrier's, carrier-carrier scattering. Phonon scattering involves different modes of vibration, acoustic or optical along with both transverse and longitudinal modes. We also designate inter- or intra-valley scattering which comes from whether the initial and final states are in the same valley or in different valleys. Once the scattering rates are calculated using on Fermi's Golden rule, they are tabulated in a scattering table in order to be selected when required.

In this thesis the MC simulator uses the following scattering mechanism; **(1) electron—acoustic phonon interaction; (2) electron—ionised impurity interaction; (3) electron—polar optical phonon interaction; and (4) electron—non-polar optical phonon interaction (intra-valley and inter-valley).**

(1) Electron–Acoustic Phonon Interaction. The electron interaction with acoustic phonons assumes that the charge between neighbouring cells is minimal and only introduces a small change in the lattice constant and energy band. The instantaneous change of the energy band causes scattering of the carriers with a phonon. An electron scattering rate for the acoustic potential of phonons is calculated using the following formula:

$$(3.24) \quad \Gamma(E) = \frac{\sqrt{2} m^{3/2} k_B T_L D_{acoustic}^2}{\pi \rho v_S^2 \hbar^4} \sqrt{E(1 + \alpha E)} (1 + 2\alpha E) F(E)$$

where $D_{acoustic}$ is the deformation potential, k_B is Boltzmann constant, α is the non-parabolic parameter for the initial valley, T_L is the lattice temperature, ρ is the density of the material, v_S is the velocity of sound and $F(E)$ is equal to the following:

$$(3.25) \quad F(E) = \frac{(1 + \alpha E)^2 + 1/3(\alpha E)^2}{(1 + 2\alpha E)^2}$$

This electron-acoustic phonon scattering assumes that the acoustic phonon energy $\hbar\omega_0$ is much smaller than $k_B T$ at room temperature. Therefore, assuming the elastic equilibrium approximation, the acoustic scattering in Equation (3.24) is considered to be an elastic scattering process ($\hbar\Omega = 0$, Ω is the phonon frequency) [4, 106].

(2) Electron-Ionised Impurity Interaction. Modern semiconductor devices are usually doped with either acceptors or donors or both. With these dopants a scattering is experienced due to Coulomb potential from the dopants in doped regions. An electron scattering rate for an interaction with ionised impurities with the form factor calculated using electron overlap wave-function approximation from [92]. The scattering rate can be calculated from:

$$(3.26) \quad \gamma(E) = \frac{N_i e^4}{8\pi\sqrt{2m}(\epsilon_0\epsilon_S)^2} \frac{1 + 2\alpha E}{[E(1 + \alpha E)]^{3/2}} \left(\frac{\left[1 + 2c_k^2 \frac{\beta_E^2}{4E(1 + \alpha E)} \right]^2}{\frac{\beta_E^2}{4E(1 + \alpha E)} \left(1 + \frac{\beta_E^2}{4E(1 + \alpha E)} \right)} \right) \\ + c_k^2 \left[1 + 2c_k^2 \frac{\beta_E^2}{4E(1 + \alpha E)} \right] \log \frac{\frac{\beta_E^2}{4E(1 + \alpha E)}}{1 + \frac{\beta_E^2}{4E(1 + \alpha E)}} + [c_k^2]^2$$

where N_i is the concentration of ionised impurities, ϵ_0 is permittivity of vacuum, ϵ_S is the relative static permittivity of the material, α is the non-parabolic parameter for the initial valley and c_k^2 and β_E^2 are defined as:

$$(3.27) \quad c_k^2 = \frac{\alpha E}{1 + 2\alpha E}$$

$$(3.28) \quad \beta_E^2 = \frac{\hbar^2}{2m} \frac{e^2 N_i}{\epsilon_0 \epsilon_S k_B T_L}$$

where β_E^2 is the Debye-Hückley inverse screening length in the energy form.

(3) Electron-Polar Optical Phonon Interaction. An inelastic process which is usually anisotropic in nature. A scattering rate for the interaction of an electron with polar optical phonon is found using the following [50]:

$$(3.29) \quad \Gamma(E) = \frac{\sqrt{m} e^2 \omega_{pop}}{4\sqrt{2}\pi\hbar\epsilon_0} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_S} \right) \left[\begin{array}{c} N_0 \\ N_0 + 1 \end{array} \right] \frac{1 + 2\alpha E}{\sqrt{\gamma(E)}} F(E, E')$$

where ϵ_∞ is relative high-frequency permittivity of the material, γ is defined by $\gamma(E) = E(1 + \alpha E)$, N_0 is the Bose-Einstein distribution [53], ω_{pop} is the frequency of polar optical phonons, the electron final energy E' is defined as $E' = E \pm \hbar\omega_{pop}$, and $F(E, E')$ is defined as:

$$(3.30) \quad F(E, E') = \frac{1}{C} \left(A \cdot \ln \left[\frac{\sqrt{\gamma(E)} + \sqrt{\gamma(E')}}{\sqrt{\gamma(E)} - \sqrt{\gamma(E')}} \right] + B \right)$$

where A, B, C are defined as:

$$(3.31) \quad A = \{2(1 + \alpha E)(1 + \alpha E') + \alpha[\gamma(E) + \gamma(E')]\}^2$$

$$(3.32) \quad B = -2\alpha \sqrt{\gamma(E)\gamma(E')} (4(1 + \alpha E)\{1 + \alpha E'\} + \alpha[\gamma(E) + \gamma(E')])$$

$$(3.33) \quad C = 4(1 + \alpha E)(1 + \alpha E')(1 + 2\alpha E)(1 + 2\alpha E')$$

(4) Electron—Non-polar Optical Phonon Interaction (Intra-valley and Inter-valley). The inter-valley scattering from different valleys is a very rare transition occurring with a low probability due to large energy distances between valleys but the inter-valley scattering is included in the MC simulation toolbox as the transition will play a role at large kinetic energy of an electron. An electron scattering rate for the intra-valley or inter-valley interaction with non-polar optical phonons can be found using the following:

$$(3.34) \quad \Gamma(E) = \frac{Z_{ij} m^{3/2} D_{ij}^2}{\sqrt{2} \pi \rho \omega_{ij} \hbar^3} \left[\begin{array}{c} N_0 \\ N_0 + 1 \end{array} \right] \sqrt{E'(1 + \alpha E')(1 + 2\alpha E')} F(E, E')$$

where Z_{ij} is the number of equivalent valleys, D_{ij} is the non-polar optical potential, ω_{ij} is the non-polar optical frequency, N_0 is the Bose-Einstein distribution [53], the final energy after the scattering E' is defined by $E' = E \mp \omega_{ij} - \Delta V_{ij}$, with V_{ij} being the energy difference between valleys for inter-valley transitions, otherwise $\Delta V_{ij} = 0$ and $F(E, E')$ is defined as:

$$(3.35) \quad F(E, E') = \frac{(1 + \alpha E)(1 + \alpha' E') + 1/3 \alpha E \alpha' E'}{(1 + 2\alpha E)(1 + 2\alpha' E')}$$

3.4 Beer-Lambert Law

Many materials absorb ultraviolet (UV) or visible (Vis.) light. The light radiation that passes through the material can be expressed using the rate of the intensity of the

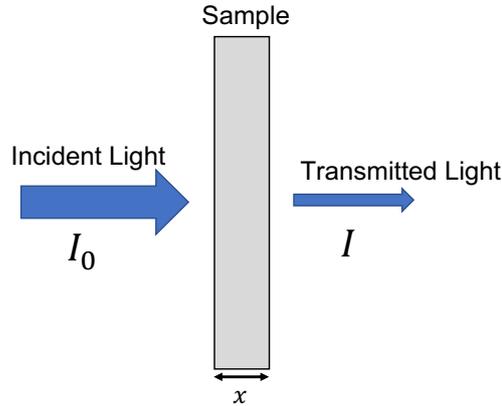


FIGURE 3.3. Beer-Lambert law schematically showing the incident light, the sample and the transmitted light.

radiation which is directly proportional to the intensity of the incident light. The rate of the intensity also relates to the attenuation of light to the properties of the sample and one can use the rate to determine such things as the concentration or the bandgap of the sample. This relationship can be expressed by the Beer-Lambert Law which provides the necessary equation to work out the absorption, A , from the following equation:

$$(3.36) \quad A = \log\left(\frac{I_0}{I}\right)$$

where I_0 is the incident light and I is the transmitted light as illustrated in Figure 3.36. The transmission, T , is $T = I_0/I$.

Beer-Lambert Law also gives the relationship between absorption coefficient, α , and light intensity, I , as [100]:

$$(3.37) \quad I_x = I_0 \exp^{-\alpha x}$$

This can be rearrange to give us an equation for the absorption coefficient in the form:

$$(3.38) \quad \alpha = \frac{1}{x} \ln \frac{I_0}{I}$$

where x is the thickness of the material and α is the absorption coefficient.

3.5 Semiconductor Light Absorption

In this section, the fundamental absorption will be discussed, and refers to band-to-band or to excitation transitions, and other types of absorption such as dopant, excitonic or

free carrier absorption will be neglected. This fundamental absorption is the process where electron-hole pairs are generated as a result of optical excitation of electrons from the valence band to the conduction band and a rapid rise in absorption can be seen. This process of light absorption must obey the conservation of energy and momentum laws. This leads to the fact that the minimum quantum energy needed to excite electrons from the valence band to the conduction band is equal to the bandgap of a semiconductor material. The fundamental absorption occurs at the red edge of the spectrum, usually within the visible and near ultraviolet spectral range, allowing the determination of a semiconductor materials bandgap energy, E_G , from UV-Vis Spectroscopy.

Semiconductor materials can be divided into two groups according the nature of their bandgap: (1) direct bandgap semiconductor materials where the position of the valence band top and the conduction band bottom coincide in \mathbf{k} -space as shown in Figure 3.4(a) and (2) indirect bandgap where the valence band top and the conduction band bottom do not coincide in \mathbf{k} -space as schematically shown in see Figure 3.4(b). Near the edge of the fundamental absorption in direct bandgap semiconductor materials only photon absorption is necessary for the transition from the valence band to the conduction band in order to conserve energy. However, in the case for an indirect bandgap semiconductor material, the addition of a particle, which changes the momentum of the electron is necessary in order to conserve energy and so a phonon assisted transition is observed. The probability of this process in indirect bandgap semiconductors decreases with increasing the number of particles [14]. Therefore, light absorption in indirect bandgap semiconductor materials near the absorption edge occurs less intense compares with direct bandgap semiconductor materials.

From the above discussion, this rise in absorption can be used to determine the energy or bandgap of a semiconductor material using the relation:

$$(3.39) \quad E_G = \frac{hc}{\lambda_{red}}$$

where h is Planck's constant, c is the speed of light, λ_{red} is the red edge of absorption, i.e., the wavelength at which light absorption occurs and E_G is the bandgap. However, this is only a rough estimate of the bandgap as the energy distribution of the electron states differ from that of the density of state for an ideal crystal, see Figure 3.5a. This difference is due to the fact that real semiconductors are not perfect and the presence of inhomogeneities (defects) creates additional fields with respect to the periodic field of the lattice. These additional fields create the potential which depends randomly on the coordinates. The presence of these additional fields introduces the appearance of

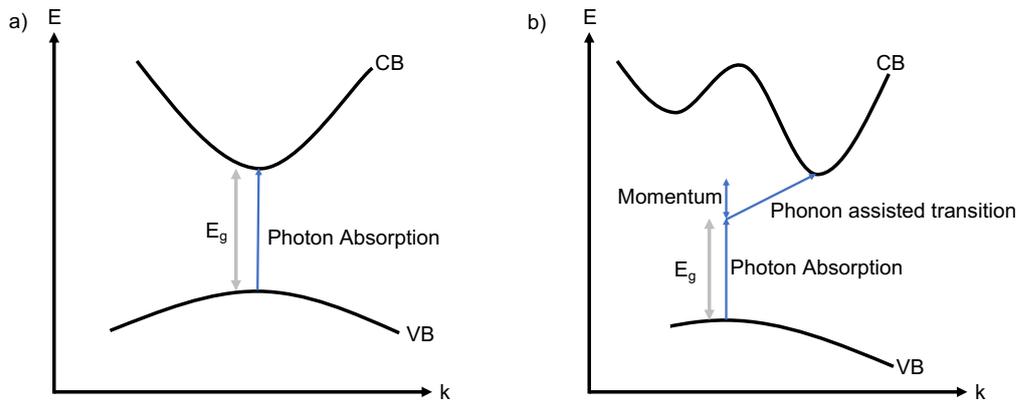


FIGURE 3.4. Transitions from the valence band to the conduction band: direct bandgap (a) and indirect bandgap (b).

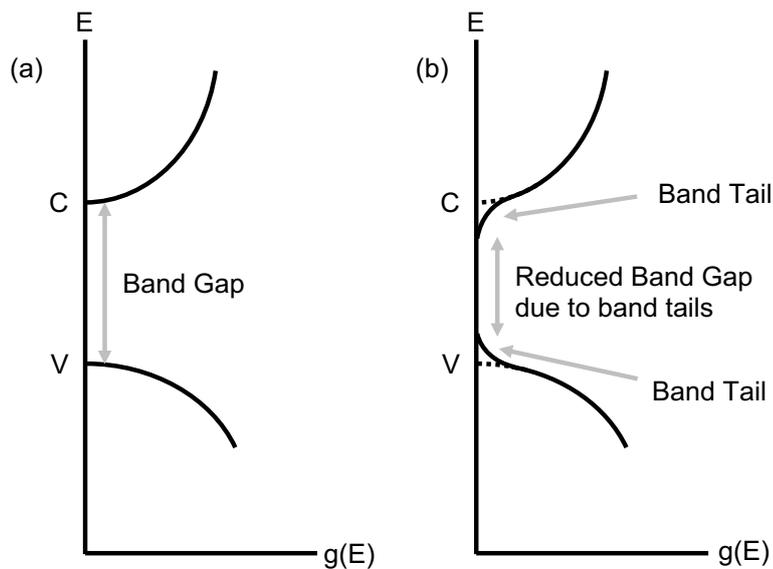


FIGURE 3.5. Density of state for: ideal (a) and real semiconductor (b).

so-called band tails, as detailed in Section 3.6, in the density of the electronic state shown in Figure 3.5(b). The band tails will result in a red shift absorption edge, and so a reduced bandgap of the disordered semiconductor compared to that of an ideal semiconductor material.

To determine the bandgap energy more precisely, one can use the spectral dependence of the absorption coefficient, α , for transitions between the allowed states which can be

described by the following relations:

$$(3.40) \quad \alpha(h\nu) = A(h\nu - E_g)^{1/2}$$

and

$$(3.41) \quad \alpha(h\nu) = B(h\nu - E_g)^2$$

for direct and indirect transitions, respectively. In Equation (3.40) and (3.41), A and B are constants that are independent of the wavelength and $h\nu$ is the photon energy.

Using the absorption coefficient, one can produce a Tauc plot, where certain power of the absorption coefficient can be taken in order to find the bandgap of the semiconductor to form so called Tauc coordinates. Equations 3.40 and 3.41 determine that the plot for a direct bandgap the Tauc coordinates would take a α^2 relation whereas, for an indirect bandgap, the plot would take $\alpha^{1/2}$ relation. These plots allow to extrapolate the energy gap, normally, with a straight line fit to the data and the intersection with the x -axis which then determines the bandgap value as illustrated in Figure 3.6. Note that this does not take into consideration the effects of band tailing.

An example of a complex Tauc plot for a indirect bandgap semiconductor material is shown in Figure 3.7 with three primary regions. First region is high absorption and corresponds to absorption due to electron transitions from one delocalized (band like) state to another delocalized state. Typically, this region is for band-to-band transitions where the absorption coefficient exhibits a power-law decrease. The second region is absorption from band like states to band tail states, or band tail states to other band tail states. The density of states is still quite high. In this region, the absorption coefficient typically falls exponentially. Finally, region three have transitions to/from or among localized states in the mobility gap and the absorption is roughly constant.

3.6 Band Tailing

Here we will discuss the perturbation of the bands with the formation of ‘band tails’ or ‘tail states’ that extend the bands into the energy gap, see Figure 3.5. These band tails can influence the fundamental absorption in so, by reducing the bandgap. This is more likely to be a feature of indirect bandgap due to the phonon process that is seen in conserving energy. This phonon process can be impacted by impurities and or disorder in the semiconductor. Therefore, it is worth taking this into account when extracting the bandgap of indirect bandgap semiconductors from optical spectroscopy.

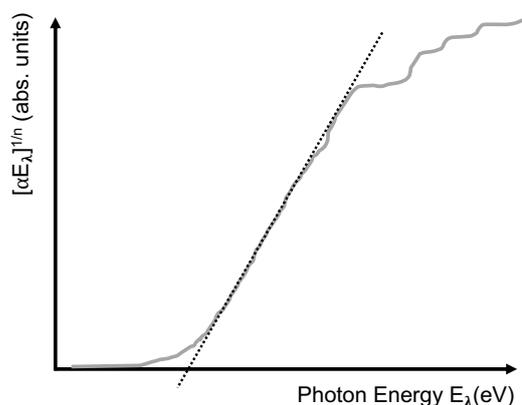


FIGURE 3.6. Theoretical curve shape of a Tauc Plot, showing a linear fit to determine the semiconductor optical bandgap.

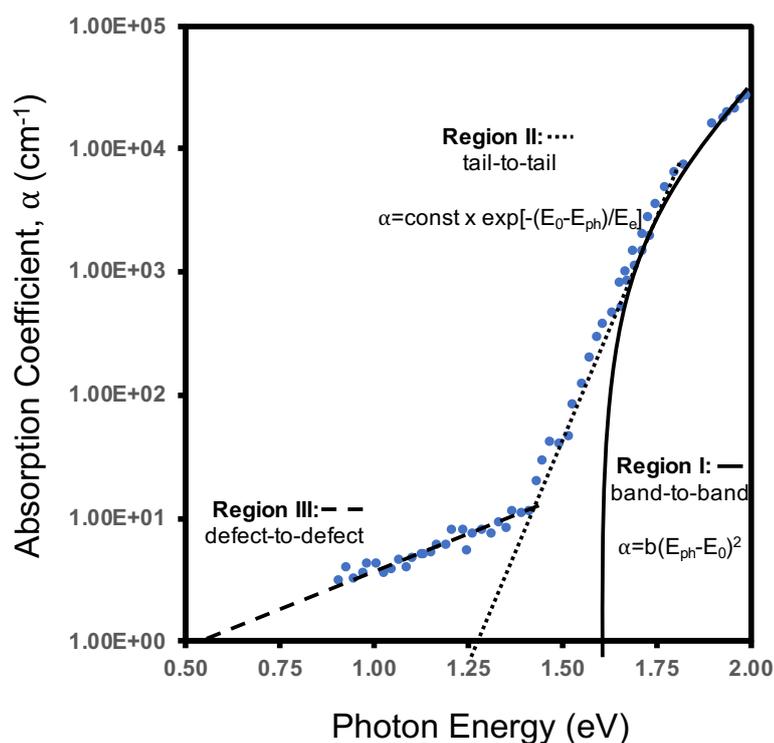


FIGURE 3.7. Complex Tauc plot showing three different regions.

Characterized by the tail parameter, E_0 , and depend on impurity and carrier concentration, temperature and structural disorder [86], band tailing theory is still something of a current problem being investigated. It is however a feature of amorphous semiconductors [75] and heavily doped semiconductors [110].

At the absorption edge, the band density of states just beyond the mobility edge for a free-electron system is normally represented by a power law [20, 90]. Likewise, the same power law expansion can be used as we know that there is a quadratic dependence near the maximum or the minimum of any power-law expansion of any function around an extremum. This power law is seen in Region I of Figure 3.7 where an absorption edge is defined based on fitting this section of the absorption spectrum with the function:

$$(3.42) \quad \alpha = b(E_{ph} - E_0)^2$$

where E_{ph} is the photon energy, E_0 is the absorption edge energy, and b is a constant.

In semiconductor materials, there are states in the energy gap that decrease in density roughly exponentially as one moves into the bandgap [90]. This results in the absorption coefficient decreasing exponentially below the absorption edge energy, E_0 , in Equation (3.42) forming:

$$(3.43) \quad \alpha = \text{const} \times \exp[-(E_0 - E_{ph})/E_e]$$

where E_{ph} is the photon energy, E_0 is the absorption edge energy and E_e is the characteristic width of the dominant band edge.

3.7 Photoelectric Effect

The principle of the photoelectric effect states that, under some circumstances (such as light shining on a metal), electrons known as photoelectrons are emitted from a material. It was first explained by Einstein winning him a Nobel Prize in 1921. These photoelectrons are produced from a single step process whereby electrons that are initially bound to an atom/ion are ejected by a photon. This process involves the transfer of energy from the photon to the electron. If this energy is sufficient, the process will result in the emission of the electron from the atom/ion and, therefore, from the material.

The photoelectron effect can be very useful in the study of material properties by using photons in the X-ray regime to bombard a sample. Such a process is known as X-ray Photoelectron Spectroscopy (XPS) and will be details in Section 3.8.

3.8 X-ray Photons for X-ray Photoelectron Spectroscopy

XPS uses an incident X-ray photon which knocks out an electron that has a binding energy keeping it in its orbit around the atom. The kinetic energy (KE) of this emitted electron can be measured making it a useful tool in surface analyse of a material as the KE is element and environment specific and a function of the binding energy (BE):

$$(3.44) \quad E = E_{ph} - BE - \Phi$$

where E_{ph} is the known photon energy and Φ is the work function of the instrumentation. The KE of the emitted photoelectron allows calculate the binding energy from Equation (3.44) by knowing the work function of the instrumentation and the energy of the incident X-ray photon.

Equation (3.44) does not cover Auger emissions as Auger electron emission is a three-stage process. The first electron represents the photoelectron, E_{ph} , the second and the third are associated with energy of core holes. The second electron drops down from a level which is less than BE in order to fill a core hole. The third electron is used to conserve energy and remove excess energy associated with this transition.

3.9 Resistivity by Four Probe Method

In 1958, Van der Pauw [79] showed a new four-probe technique for measuring electrical properties such as resistivity, that is easier to implement than the linear four-probe approach that has been previously used as shown in Figure 3.8.

Van der Pauw's approach [79] showed that the sheet resistivity of a metallic sample can be obtained from any arrangement of four probe contacts on the edge of a flat homogeneous sample of known thickness. This four-probe method works by passing a current through two probes and measuring the voltage through two separate probes as shown in Figure 3.9. The resistance $R_{ab,dc}$ is defined as $R_{ab,dc} = (V_c - V_d)/j_{ab}$ using a potential difference between probes, c and d when current j_{ab} flows between probes a and b . Likewise, the resistance $R_{bd,ac}$ is defined in a similar way.

The Van der Pauw relationship is given by:

$$(3.45) \quad \exp\left(-\frac{R_{ab,dc}}{\lambda}\right) + \exp\left(-\frac{R_{bd,ac}}{\lambda}\right) = 1$$

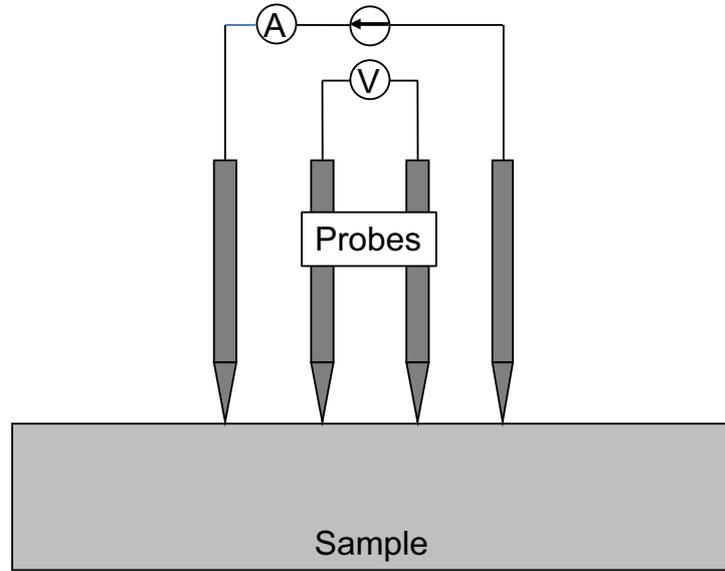


FIGURE 3.8. Schematic of a linear 4-Probe set up.

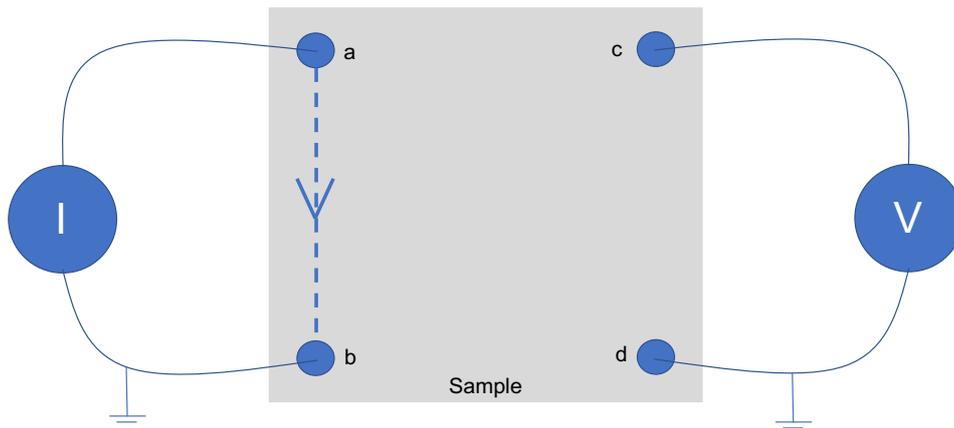


FIGURE 3.9. Schematic of Van der Pauw 4-Probe set up.

where $\lambda = \rho/\pi d$ and ρ is the resistivity of the metallic sample with thickness d . The Van der Pauw relation enables various measurement to be made to find out the resistivity and Hall coefficient of a metallic sample that have arbitrary geometry.

3.10 Device Modelling

Device modelling primarily uses transport models in the simulation of carrier transport in a semiconductor device and can vary in their degree of complexity and computational

cost. These are both usually a sign of how accurate the model is in describing the physical behaviours of a semiconductor device. When a given problem is presented, the approach that is normally taken requires a compromise between accuracy and time it takes. The simplest of transport models is the drift-diffusion model assumes that the carrier temperature is at equilibrium with a lattice temperature. The drift-diffusion model along with some other basic semiconductor equations make up the basic approach to device modelling and will be described in the following sections. In this work, a drift-diffusion model in commercial software Atlas by Silvaco [67] adopts the following models for modeling a heterostructure device: **(1) field-dependent mobility; (2) Shockley-Read-Hall (SRH) recombination; (3) Auger recombination; and (4) Poisson's equation.**

3.10.1 Field-Dependent Mobility

There are two types of electric field-dependent mobility models that are used in Silvaco Atlas: (1) The Standard Mobility Model, and (2) Negative Differential Mobility Model. We will only consider the standard mobility model which takes into account velocity saturation and is defined as [67]:

$$(3.46) \quad \mu_n(E) = \mu_{n0} \left(\frac{1}{1 + \left(\frac{\mu_{n0} E}{V_{SATN}} \right)^{\beta_n}} \right)^{1/\beta_n}$$

$$(3.47) \quad \mu_p(E) = \mu_{p0} \left(\frac{1}{1 + \left(\frac{\mu_{p0} E}{V_{SATP}} \right)^{\beta_p}} \right)^{1/\beta_p}$$

where V_{SATN} and V_{SATP} are the saturation velocities for electrons and holes, β_n and β_p are constants, and μ_{n0} and μ_{p0} are the electron and hole low field mobility.

3.10.2 Shockley-Read-Hall Recombination

Shockley-Read-Hall (SRH) recombination [98] is a two particle process as illustrated in Figure 3.10. The SHR recombination considers carrier generation in space charge regions and recombination in, for example, high injection regions. The SHR recombination is given [77]:

$$(3.48) \quad R^{SRH} = \frac{n \cdot p - n_i^2}{\tau_p \cdot (n + n_1) + \tau_n \cdot (p + p_1)}$$

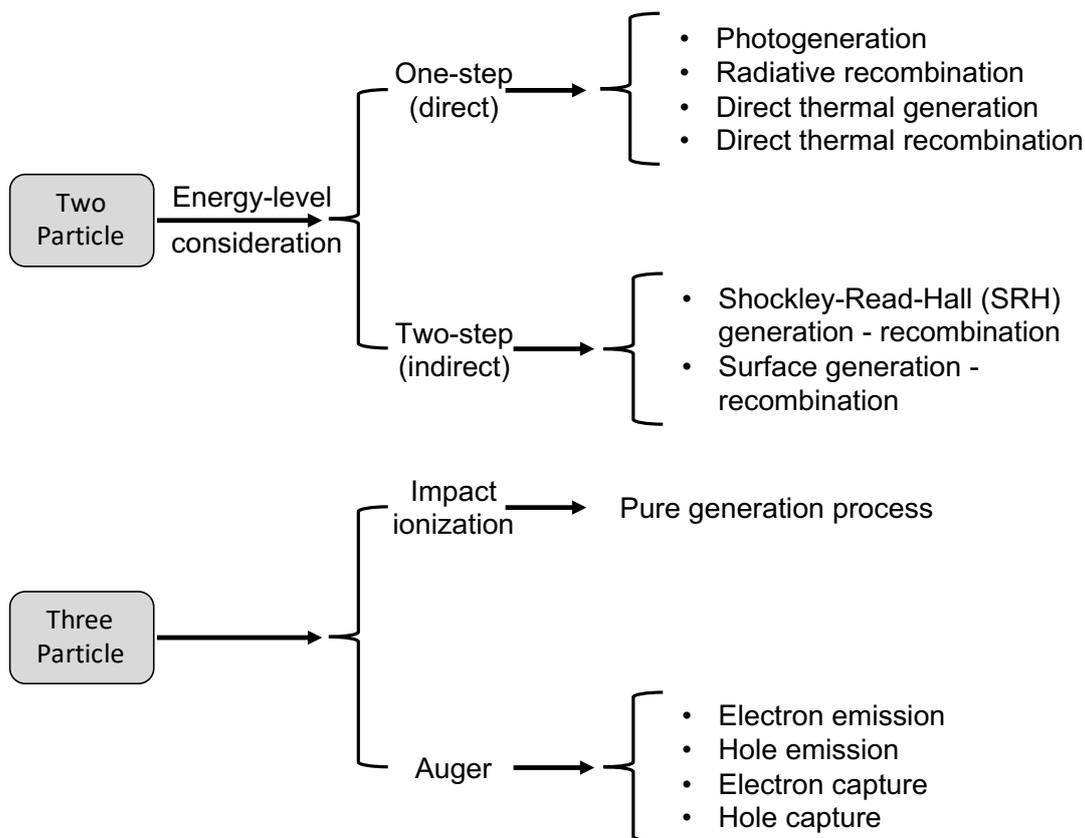


FIGURE 3.10. Groupings for generation - recombination process.

where τ_p and τ_n are the lifetimes of the holes and electrons, respectively, p and n are hole and electron concentration, respectively, and $n_i^2 = n_1 \cdot p_1$ and n_i is the intrinsic concentration. The variables n_1 and p_1 are defined as follows:

$$(3.49) \quad n_1 = N_C(T_L) \cdot \exp\left(\frac{-E_C + E_T}{k_B \cdot T_L}\right)$$

$$(3.50) \quad p_1 = N_V(T_L) \cdot \exp\left(\frac{-E_T + E_V}{k_B \cdot T_L}\right)$$

where E_T is the trap energy level, N_C and N_V are the carrier effective densities of state, T_L is the lattice temperature, E_C and E_V are the conduction band and valence band energy, respectively, and k_B is the Boltzmann constant.

3.10.3 Auger Recombination

Auger recombination is a three particle process, as shown in Figure 3.10, in which an electron and a hole recombine in a band-to-band transition. However, the resulting

energy is given off to another electron or hole. As Auger recombination involves a third particle, it had to be treated differently from the band-to-band recombination. The standard equation for Auger recombination is given by:

$$(3.51) \quad R_{Auger} = C_n(pn^2 - nn_1^2) + C_p(np^2 - pn_1^2)$$

where C_n and C_p are the Auger coefficients, n and p are electron and hole concentrations, respectively, and n_1 is defined in Equation (3.49).

3.10.4 Poisson's Equation

Poisson's equation gives the relationship between electrostatic potential and the local charge densities. The electric field is defined as a negative gradient and therefore as a negative derivative of the electrostatic potential. This is due to the electric field starting off at a higher potential region and pointing towards a lower potential region. Poisson's equation is given by [93]:

$$(3.52) \quad \frac{d\Psi(x)}{dx} = -E(x)$$

where E is the electric field and Ψ is the electrostatic potential. From Gauss Law, the electric field is related to the local charge density, $\rho(x)$, by the following relation [93]:

$$(3.53) \quad \frac{d\Psi(x)}{dx} = \frac{\rho(x)}{\epsilon}$$

where ϵ is the permittivity of free space. Substituting the expression of the electric field from Equation (3.52) into Equation (3.53) gives the relationship of the charge density against the potential as:

$$(3.54) \quad \frac{d^2\Psi(x)}{dx^2} = -\frac{\rho(x)}{\epsilon}$$

Equation (3.54) is commonly used, for example, to determine the potential and field distribution caused by a charge density, ρ , within the depletion layer.

3.10.5 Continuity Equation

Derived from the first Maxwell Equation [97], the continuity equation (3.60) can be obtain with the following modifications. First the divergence operator 'div' is applied to the first Maxwell Equation:

$$(3.55) \quad \text{div rot } \vec{H} = \text{div } \vec{J} + \frac{\partial \rho}{\partial t} = 0$$

where \vec{J} is the total electric current density, t is time, ρ is the electric charge density and $\text{rot } \vec{H}$ is given by:

$$(3.56) \quad \text{rot } \vec{H} = \vec{J} + \frac{\partial \vec{D}}{\partial t}$$

Then we need to split the total conduction current density \vec{J} into individual components for holes \vec{J}_p and electrons \vec{J}_n as:

$$(3.57) \quad \vec{J} = \vec{J}_p + \vec{J}_n$$

The space charge density is also needed to be taken into account when deriving the continuity equation. This is simply given by:

$$(3.58) \quad \rho = q \cdot (p - n + C)$$

where n and p are electron and hole concentrations, respectively, C is the net ionized impurity concentration, and q is the elementary charge.

We will assume that all charges in the semiconductor (not including the mobile carrier electrons and holes) are invariant. Therefore, we can neglect the influence of charged defects giving:

$$(3.59) \quad \frac{\partial C}{\partial t} = 0$$

If we combine Equations (3.55), (3.57), and (3.58), while making use of Equation (3.59), we obtain the following continuity equation:

$$(3.60) \quad \text{div}(\vec{J}_p + \vec{J}_n) + \frac{\partial}{\partial t}(p - n) = 0$$

3.10.6 Drift-Diffusion Transport Model

In this thesis, the drift-diffusion transport model have been primarily used in our device modeling. The drift-diffusion transport model assumes that carrier are in thermal equilibrium, and that the velocity of carriers will respond to changes in the electric field instantaneously. With these simple assumptions, the drift-diffusion transport model gives a simple computational effective tool for simulating semiconductor devices.

The drift-diffusion model is made up of the following set of equations: **(1) Current-Density Equations;** **(2) Continuity Equations;** and **(3) Poisson's Equation** as follows:

(1) Current-Density Equations [105]. The most common current conduction consists of the drift component, usually caused by an electric field, and the diffusion component, caused by the carrier-concentration gradient. These two components can be written for both the electrons (e) and the holes (h) in a device using equations:

$$(3.61) \quad J_n = qn\mu_n E + qD_n \Delta n$$

$$(3.62) \quad J_p = qp\mu_p E + qD_p \Delta p$$

$$(3.63) \quad J_{cond} = J_n + J_p$$

where J_n and J_p are the electron and hole current densities, respectively, μ_n and μ_p are the electron and hole mobility, respectively, E is the electric field, and D_n and D_p are the diffusion coefficients of the electrons and holes, respectively.

(2) Continuity Equations include time-dependent phenomena such as low-level injections, generation, and recombination. The continuity equations for the electrons and holes can be written as:

$$(3.64) \quad \frac{\partial n}{\partial t} = G_n - U_n + \frac{1}{q} \Delta \cdot J_n$$

$$(3.65) \quad \frac{\partial p}{\partial t} = G_p - U_p + \frac{1}{q} \Delta \cdot J_p$$

where G_n and G_p are the electron and hole generation rate, respectively, and U_n and U_p are the the electron and hole recombination rates, respectively.

(3) Poisson's Equation for drift-diffusion which takes into account ionised donor and acceptor impurity densities.

$$(3.66) \quad \Delta \cdot \epsilon \Delta V = -(p - n + N_D^+ - N_A^-)$$

where V is the electrostatic potential, E is the applied electric field, n and p are the density of electrons and holes, respectively, and N_D^+ and N_A^- are the density of ionised donor (D^+) and acceptor (A^-) impurities, respectively.

METHODOLOGY

The chapter is organized as follows: Section 4.1 starts with an introduction into the MC simulator used and the material properties of Al_4SiC_4 that are of interest to the computational model. The chapter also outlines the scattering mechanisms relevant to carrier transport in Al_4SiC_4 . Also, due to the positioning of the valleys in Al_4SiC_4 a new valley transformation is derived for two of the three M valley, that is the M_2 and M_3 valleys, see Figure 2.1, because of their respective positions from the principle M valley. Section 4.2 looks at the experimental method for spectrophotometry, X-ray photoelectron spectroscopy and two and four probe measurements. The final section, Section 4.3, details the methodology for the device simulations which uses commercial Technology Computer Aided Design (TCAD) software and mentions material models and specifies methods used in the simulations.

4.1 Ensemble Monte Carlo Simulator

The ensemble MC technique detailed in Chapter 3 is well suited to forecast electron transport properties of semiconductors [107]. Therefore, this technique is used to assess electron transport properties of ternary carbide Al_4SiC_4 by adopting our in-house developed ensemble bulk MC code [48]. The bulk MC method assumes that carriers move in infinite real space and, therefore, the particle position is sufficient to track only in

momentum/ \mathbf{k} -space. In the momentum space, Equation 3.5 simplifies to:

$$(4.1) \quad \frac{\partial f}{\partial t} = -\mathbf{F} \cdot \Delta_{\mathbf{k}} f + \left(\frac{\partial f}{\partial t} \right)_{collision}$$

The in-house ensemble bulk MC code uses analytical non-parabolic ellipsoid band structure with the $E - \mathbf{k}$ relation given by:

$$(4.2) \quad E(\mathbf{k}) = \frac{\hbar^2}{2m^*} (k_x^2 + k_y^2 + k_z^2)$$

The simulation moves the particles individually at a set time step for a set amount of time with scattering events occurring assuming free flights under constant electric field. This process requires calculation of free flight time for each particle, which intern depends on the total scattering rate. The free flight time is determined stochastically by generating a uniform random number r into the analytical form in Equation 3.16. After the free flight has been determined, the scattering can take place using a pre-calculated scattering probability followed by determination of the electron state after the scattering. The electron scattering probability is calculated using Fermi Golden Rule which is first-order time-dependent perturbation theory assuming a weak perturbation [106], see Section 3.3.5. Physical quantities of interest for carriers such as average velocity, total and kinetic energy, diffusion constant, relaxation time, or valley occupation can be monitored during the simulation run at any time step and outputted, typically, at the end of the whole simulation run. Further information on the MC code can be found in Section 3.3.

4.1.1 Monte Carlo Implementation

The in-house developed ensemble bulk MC simulation code has been adapted to investigate the electron transport in bulk Al_4SiC_4 with full details of the model outlined in Section 3.3. The simulations predict bulk properties of Al_4SiC_4 when electron transport can be considered to be free in the 3D \mathbf{k} -space. We have employed a two-valley model for the conduction band of Al_4SiC_4 based on the band-structure obtained by Pedesseau et. al. [82] as seen in Figure 4.1. The two arrows in this figure indicate the two valleys that we are considering in the simulation model. The first valley, the M valley, is situated 2.78 eV above the valence band maximum of the Γ valley and provides an indirect bandgap. The second valley, the K valley, is situated 0.52 eV above the M valley, see Figure 4.2, and provides also an indirect bandgap. We have chosen to use the value of 2.78 eV for the bandgap as this has been obtained in our experimental work [31].

Figure 4.2 includes the number of equivalent bands that have been identified for the two valleys of interest for MC simulations. The number of equivalent valleys in

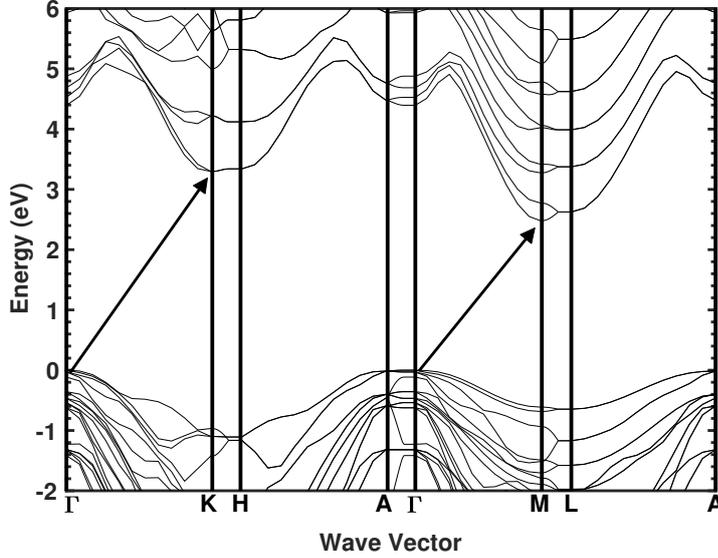


Figure 4.1: Re-scaled Al₄SiC₄ bandstructure obtained from Pedesseau et. al. [82] DFT calculations, with two black arrows indicate the two valleys that we are considered in the MC simulations.

each of the two valleys is based on the hexagonal lattice that Al₄SiC₄ is known to have [6, 43, 81, 82, 95, 101, 118]. Figure 5.1(a) shows that the *K* valley is present in six locations, each of which contribute one third to the first Brillouin zone leading way to a total of two equivalent bands. The *M* valley is present in six locations similar to the *K* valleys. However, due to their positions between the *K* valleys, each of these six *M* valleys contribute one half to the first Brillouin zone leading way to a total of three equivalent bands. The band-structure model of Al₄SiC₄ is analytical non-parabolic anisotropic band-structure [27]. We have considered the following electron scattering mechanisms in the MC simulations which will play a decisive role in the electron transport (see Table 4.1): electron interactions with acoustic phonons, with polar and non-polar optical phonons, and with ionised impurities when simulating electron transport properties in a *n*-type doped Al₄SiC₄.

The MC simulations assume a crystal temperature at 300 K and the orientation of applied electric field along $\langle 0001 \rangle$ crystallographic direction of hexagonal lattice structure [6, 43, 81, 82, 95, 101, 118]. The material parameters, including parameters for electron-phonon interactions, are collected in Table 4.2. In the case of acoustic deformation potential, we have opted for the value reported for 4H-SiC [49] as the closest semiconductor material to Al₄SiC₄ with a well-known electron-phonon deformation

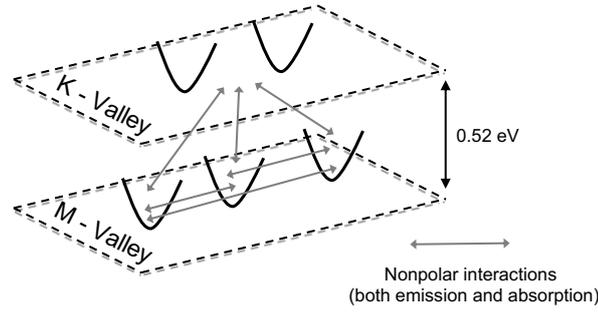


Figure 4.2: Schematic of conduction band minimum valleys in Al_4SiC_4 showing the number of equivalent bands in each valley and the separation between the two considered valleys.

potential because an acoustic deformation potential is currently unknown in Al_4SiC_4 . The critical electric field of Al_4SiC_4 is calculated, to ensure that we only simulate below this value, using [41]:

$$(4.3) \quad \epsilon_c = a(E_G)^n$$

where $a = 2.3818 \times 10^5$ and $n = 1.995$ for an indirect bandgap semiconductor, and E_G is the bandgap of the semiconductor. Assuming the bandgap of 2.78 eV, we obtain a critical electric field of 1831 kV cm^{-1} for Al_4SiC_4 . This critical electric field is well below our maximum electric field of 1400 kV cm^{-1} we have simulated to.

The optical phonon energies that have been used in these simulations have been extracted from IR/Raman spectroscopy from the works of Zevgitis et al. [118]. Here, we have taken the three highest peaks in the $Z(\text{XX})Z$ polarisation configuration, where one would expect to see only A_1 and E_2 modes. The first peak we have taken is at a wave-number of 690 cm^{-1} , which relates to an energy of 85.55 meV, is an E_2 , non-polar mode, longitudinal optical phonon. The second peak is at a wave-number of 543 cm^{-1} , which relates to an energy of 67.32 meV, and is an A_1 , polar mode, transverse optical phonon. Finally, the third peak is at a wave-number of 865 cm^{-1} , which relates to an energy of 107.25 meV, and is an A_1 , polar mode, longitudinal optical phonon.

At the moment, a specific relationship between vibrational states and electrons is not clear as to which vibrational states directly contribute or hinder the electron mobility. The electron effective masses in Table 4.2 have been extracted from DFT calculations by Pedesseau et al. [82]. Here, we have assumed that the minima of conduction band have a parabolic energy dispersion, see 3.1. The relative effective mass, m^* , can be then

Valley	Scattering Between	Polar / Non Polar	Inter / Intra - Valley
M_1	$M_1 \rightarrow M_1$	Polar	Intra
	$M_1 \rightarrow M_1$	Polar	Intra
	$M_1 \rightarrow M_2$	Non Polar	Inter
	$M_1 \rightarrow M_3$	Non Polar	Inter
	$M_1 \rightarrow K$	Non Polar	Inter
M_2	$M_2 \rightarrow M_2$	Polar	Intra
	$M_2 \rightarrow M_2$	Polar	Intra
	$M_2 \rightarrow M_1$	Non Polar	Inter
	$M_2 \rightarrow M_3$	Non Polar	Inter
	$M_2 \rightarrow K$	Non Polar	Inter
M_3	$M_3 \rightarrow M_3$	Polar	Intra
	$M_3 \rightarrow M_3$	Polar	Intra
	$M_3 \rightarrow M_1$	Non Polar	Inter
	$M_3 \rightarrow M_2$	Non Polar	Inter
	$M_3 \rightarrow K$	Non Polar	Inter
K	$K \rightarrow M_1$	Non Polar	Inter
	$K \rightarrow M_2$	Non Polar	Inter
	$K \rightarrow M_3$	Non Polar	Inter

Table 4.1: Electron-phonon scattering transitions considered in the MC model.

extracted from the following relation:

$$(4.4) \quad \frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 E(\vec{k})}{\partial k^2}$$

The dispersion relation is a quadratic polynomial, as illustrated in Figure 3.1, in the form: $y = a + b x + c x^2$. The second order derivative, $2c$, is related to the energy dispersion relation by:

$$(4.5) \quad 2c = \frac{\partial^2 E(\vec{k})}{\partial k^2}$$

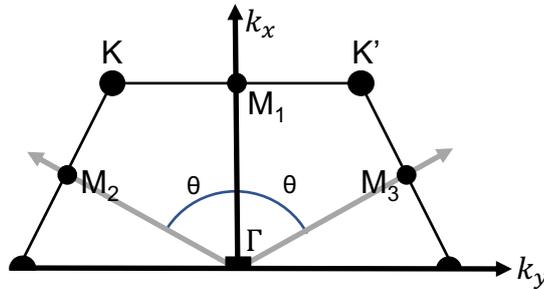
Equation (4.4) is solved for the M and K valleys in both the longitudinal and transverse directions giving values of relative effective masses shown in Table 4.2.

4.1.2 Wave-vector Transformation

The location of the principal electron valley, M , in Brillouin zone requires that components of electron wave-vectors in the band structure anisotropic analytical model of MC simulations are transformed accordingly. Therefore, we have enhanced our MC

Table 4.2: Al_4SiC_4 material parameters.

Parameter (Unit)	Value
Mass Density (g/cm^3)	3.03 ^a
Lattice Constant (\AA)	3.28 ^a
Piezoelectric Constant (C/m^2)	0.47 ^a
Longitudinal Acoustic Velocity (m/s)	10577 ^a
Transverse Acoustic Velocity (m/s)	6431 ^a
Polar Optical Phonon Energies (meV)	67.32 ^b , 107.24 ^b
Non-Polar Optical Phonon Energy (meV)	85.55 ^b
Acoustic Deformation Potential (eV)	11.4 ^a
Indirect BandGap (eV)	$E_G^{(M)} = 2.78$ M-Valley $E_G^{(K)} = 3.30^a$ K-Valley
Electron Effective Mass	$m_l^{*(M)} = 0.5678m_e^c$ $m_t^{*(M)} = 0.6952m_e^c$ $m_l^{*(K)} = 1.0569m_e^c$ $m_t^{*(K)} = 0.9360m_e^c$

^aRef. [82]^bRef. [118]^cExtracted value from DFT calculations [82]FIGURE 4.3. Location of the M valleys within the Al_4SiC_4 hexagonal structure, where $\theta = \pm 60$

code with the wave-vector transformations which include a combination of Herring-Vogt transformation [40] and a rotational transformation of valleys.

The rotational transformation applied to the M valleys looks at transforming from an elliptical space \mathbf{k} -vectors components, k_x , k_y , and k_z , to spherical vector components, k_x^* , k_y^* , and k_z^* , while considering the angular distance that the M_2 and M_3 valleys have in

relation to the M_1 valley, our reference valley, located along the k_x direction as illustrated in Figure 4.3. The angular distance that the M_2 and M_3 valleys have in a relation to the M_1 valley can be defined along the k_x and k_y axes, as these valleys are rotated about the k_z axis (the k_z axis does not need to be transformed). The \mathbf{k} -vector transformations for each of the components are defined as:

$$(4.6) \quad k_x^* = k_x \cos(\theta) - k_y \sin(\theta)$$

$$(4.7) \quad k_y^* = k_y \cos(\theta) + k_x \sin(\theta)$$

$$(4.8) \quad k_z^* = k_z$$

In Eqs. (4.6—4.11), θ represents the angular distance the M_2 or M_3 valley rotates from the M_1 valley. The inverse transformations are given by:

$$(4.9) \quad k_x = k_x^* \cos(\theta) + k_y^* \sin(\theta)$$

$$(4.10) \quad k_y = k_y^* \cos(\theta) - k_x^* \sin(\theta)$$

$$(4.11) \quad k_z = k_z^*$$

Finally, we assume an isotropic valley approximation for the K valleys due to their low electron occupation.

4.2 Experimental Methods

4.2.1 Spectrophotometry

Spectrophotometry, also known as Transmission/Absorption Spectroscopy, is an analytical technique. It is based on measuring the amount of light absorbed, transmitted or reflected by a sample at a given wavelength, through the conservation of energy they are related as:

$$(4.12) \quad T + R + A = 1$$

This technique is useful in characterising the absorption, transmission and reflectivity of a sample to reveal optical or electronic properties of a material.



FIGURE 4.4. Perkin Elmer Lambda 950 spectrophotometer image taken from the Perkin Elmer website.

In this work, a Perkin Elmer Lambda 950, see Figure 4.4, has been used to study the optical absorption of Al_4SiC_4 crystals. This spectrophotometer can measure transmittance and reflectance of light on or through a sample. Two sources of light provide the necessary frequencies of light in order to perform UV/Vis/NIR spectroscopy, first a deuterium arc lamp for UV light and then a tungsten-halogen lamp for visible and IR light. This allows the spectrophotometer to operate between 175-3300 nm of which we performed our experiments in the range of 250-1000 nm. Two detectors were used to cover this range. First, a photo-multiplier (PM) for the UV and visible wavelength and, second, an InGaAs sensor for the NIR wavelength. The two detectors switch over at 860.8 nm which is visible on the output data by a small blip. A custom aperture was made in order to mount the Al_4SiC_4 samples in order to cope with the small size of the crystals with diameters of 0.5, 1 and 2 mm. The acquisition of the optical signal was done in a cylindrical chamber with a geometric configuration to allow for a total transmittance acquisition, as shown in Figure 4.5.

The energy range of this spectrometer is adequate to excite inter-band excitation of outer electrons but over the threshold for vibrational states as this would require infrared energy levels. Figure 4.5 shows that the light is orthogonal to the sample. This allows for optical absorption to be calculated from the total transmittance using Beer-Lambert Law given by Equation (3.36) in Section 3.4.

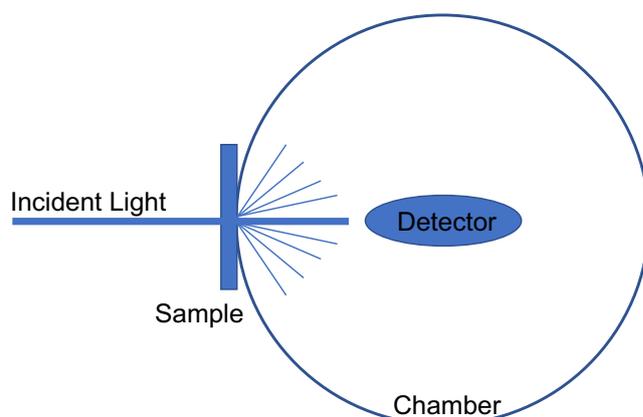


FIGURE 4.5. Geometric set up of the UV/Vis/NIR Spectroscopy chamber.

4.2.2 X-Ray Photoelectron Spectroscopy

A X-ray Photoelectron Spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique. It is based upon the photoelectric effect, see Section 3.7, where emission of electrons is seen following the excitation of core level electrons by photons. It is useful for characterising the chemical composition and surface properties of materials as well as details regarding the valence band and work function of a material.

In this work, two different XPS set ups have been used. First, DAISY Fun (Darmstadter Integrated System for Fundamental Research) that incorporates PHOIBOS 150, Focus 500 with XR50M (SPECS) Al $K\alpha$ at 1486.74 eV and, second, Kratos Supra XPS with Ocean optics USB 2000+ spectrometer. The operating principle for both set-ups remains the same.

Once the sample has been prepared and inserted into the apparatus, the sample is illuminated with a monochromatic light of energy $E_{ph} = h\nu$ where ν is the frequency of the light and h is Planck's constant. The energy range of E_{ph} will determine if the process is known as X-ray photoelectron spectroscopy (XPS) for $E_{ph} \approx 10^3$ eV or ultraviolet photoelectron spectroscopy (UPS) for $E_{ph} \approx 10^1$ eV. Energy transference for this process has been detailed in Section 3.8. The electron core levels for an element are displayed by a low energy distribution and their positions are characteristic for the emitting element and have a range of a few eV for different oxidation states. However, when it comes to the valence band, this is less well defined and exhibits a broad spectrum, with shifts large enough to make a clear assignment of elements difficult.

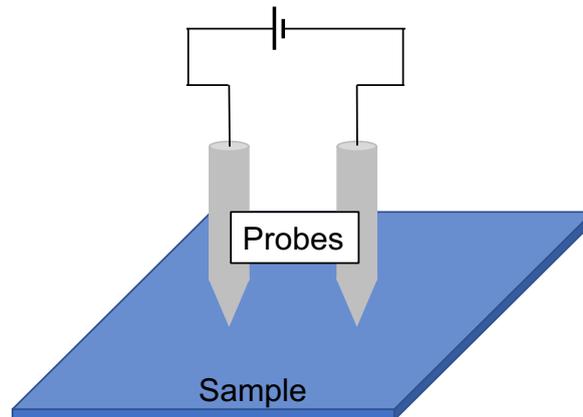


FIGURE 4.6. Two-probe set up.

4.2.3 Two and Four Probe Measurements

Two- and four-probe based instrumentation are techniques used to measure the I-V characteristics of a material and thus extract a sheet resistance of the material. The two-probe set up is simply passing a voltage through a sample and measuring the current output, see Figure 4.6. A four-probe set up is slightly more complicated as it employs a constant current through two of the probes and measures the voltage output across another set of probe and works by the Van der Pauw method described in Section 3.9 (see Figure 3.9).

In this work, both two- and four-probe set ups by a Ametek ModuLab XM Material Test System are used where the data are collected using the XM-studio Software in Grenoble, see Figure 4.7 and 4.8. In Swansea, the measurements has been taken by using Ossila software.

4.3 Technology Computer Aided Design

Technology Computer Aided Design (TCAD) is an electronic program design to automate the models of integrated circuit (IC) fabrication and device operation. Based on their application, there are two main categories: (1) **Process CAD** and (2) **Device CAD**.

(1) **Process CAD** is related to the simulations at the front-end of processing ICs and the steps required to fabricate a devices up to metallization. It is used to simulate such steps as oxidation and diffusion and deposition and etching to name a few. The process CAD is not used in this thesis and so will not be covered in any further depth.

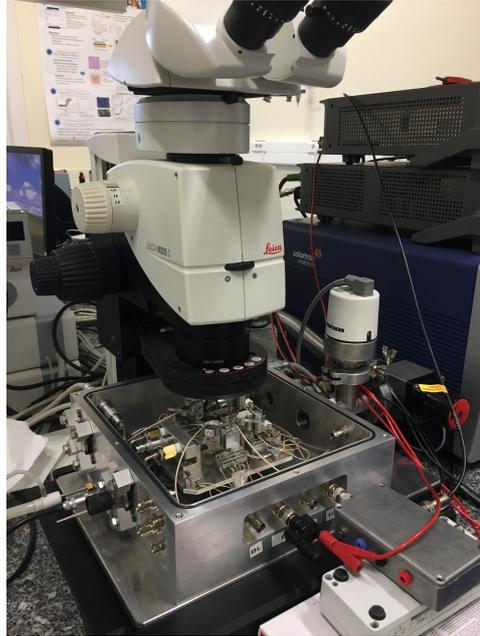


FIGURE 4.7. Probing station set up in Grenoble at Neel Institute.



FIGURE 4.8. Probing station set up in Grenoble at Neel Institute.

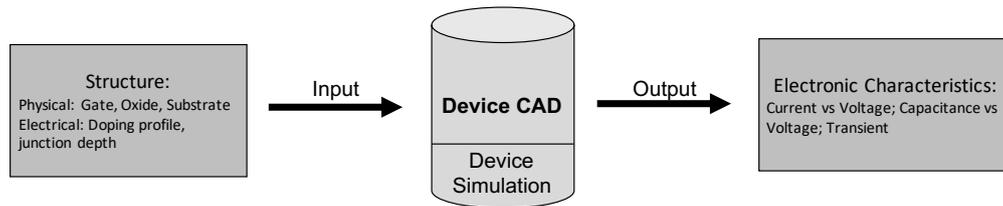


FIGURE 4.9. Flow diagram showing the process device CAD takes in order to run a simulation.

(2) **Device CAD** simulates IC device operations based on a suite of physical models that describe carrier transport in a material (see Figure 4.9). Device CAD ranges from simple drift-diffusion where it solves Poisson’s Equation, Equation 3.66, and the continuity equations, Equations 3.64 and 3.65, to more complex and thus computationally challenging models such as the energy balance transport model, which solves a simplification of the BTE, or ensemble MC technique.

With TCAD, one is able to study a particular technology and explore it over a wide range of scenarios. This means that there is a fast and cost efficient way for device optimisation and technology development as well feasibility and reliability studies of a device.

In this thesis, the TCAD software of choice is the Silvaco package, which has the ability for both Process CAD (Silvaco Athena) and Device CAD (Silvaco Atlas). Here, Silvaco Atlas is used to model a SiC/Al₄SiC₄ heterostructure device. The methodology used in Silvaco Atlas is comprised in the following way [67]: (1) **structure specification**; (2) **material models specification**; (3) **numerical method selection**; (4) **solution specification**; and (5) **result analysis**, each of which are described in detail in the following sections.

4.3.1 Structure Specification

Apart from specifying the device structure to the required dimensions, it is important to specify an adequate mesh in order to define the geometry of the structure to be simulated, see Figure 4.10.

The mesh is used to define the points in the structure at which the physical parameters are calculated, i.e. electron or hole density. Silvaco Atlas uses the finite element method where the simulation domains are subdivided into small triangular regions and solved for the dependent variable in the sub-regions using a polynomial approximation [97]. This approach is easy to manipulate computationally and resulting smooth func-

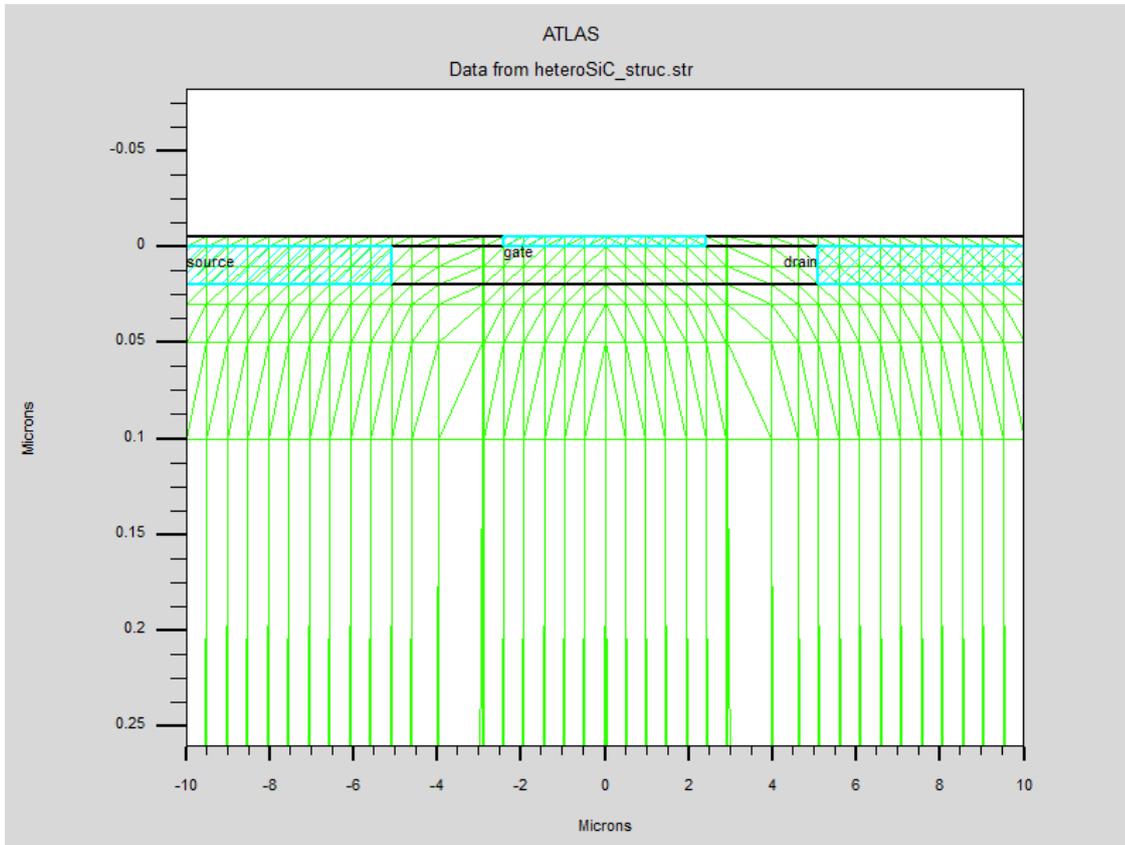


FIGURE 4.10. Mesh design for a heterostructure device.

tions can be accurately approximated. It therefore comes at no surprise that if one has a dense mesh or a large number of nodes, the accuracy of the model improves, but at the cost of computational time. Therefore, one has to create a balance between accuracy and computational time.

The approach that is therefore taken is to have a dense mesh in the area where there is high electric field, interfaces, or regions of abrupt changes in the doping profile or concentration. If required, there are guidelines on how to create an effective mesh within the Silvaco Atlas manual [67].

4.3.2 Material Models and Method Specification

The semiconductor materials that make up the heterostructure device have their material properties defined using energy bandgap, permittivity, effective density of states, etc.. Additionally, a workfunction of the metal gate, that is associated with Schottky barrier height, is specified. The simulation of electron transport needs a model describing the

dependence on the following: electric field, carrier concentration, and lattice temperature.

The Silvaco software provides a choice of numerical techniques that are used in solving the coupled, non-linear partial differential equations, that can describe semiconductor device operation. These numerical techniques are iterative and include: (1) Newton, (2) Gummel, (3) Block, and (4) Newton-Gummel method. The iterations begin with an initial guess of the solution. This initial guess is subsequently updated with a new estimate of the solution and the iterations continue with continuous refinement until the solution convergence criteria is met.

Doping has to be also specified in the relevant areas of the device. The drain and the source contacts in a semiconductor device will have the interface made of a heavily doped region of n -type doping in order to mimic a good Ohmic contact at the metal-semiconductor interface [25].

COMPUTATIONAL RESULTS

The chapter starts with an details of the ensemble MC simulation code used to obtain the results on electron transport in the ternary carbide. The chapter then reports on the modeling by Atlas of a heterostructure device designed using the ternary carbide. Details on transport models employed in the simulator are outlined before reporting on the device performance ending by drawing a conclusion on the device modeling results.

5.1 Monte Carlo Simulations

In this work, we have employed an in-house bulk ensemble MC simulation code to foresee electron transport properties of Al_4SiC_4 . The MC simulation uses a combination of known material properties from reported experimental data and theoretical calculations using the DFT. Al_4SiC_4 has a hexagonal lattice [6, 43, 81, 82, 95, 101, 118] comprising of multiple valleys, Γ , A , L , H , M , and K , as shown in Figure 5.1(a) and 5.1(b). We will demonstrate that only the two lowest valleys, the M and K valleys, are of interest for electron transport as the occupation of all other upper valleys is negligible.

5.1.1 Electron Transport Results

This section details the results from the ensemble MC simulator starting with Figure 5.2 which illustrates the electron drift velocity as a function of the applied electric field. The

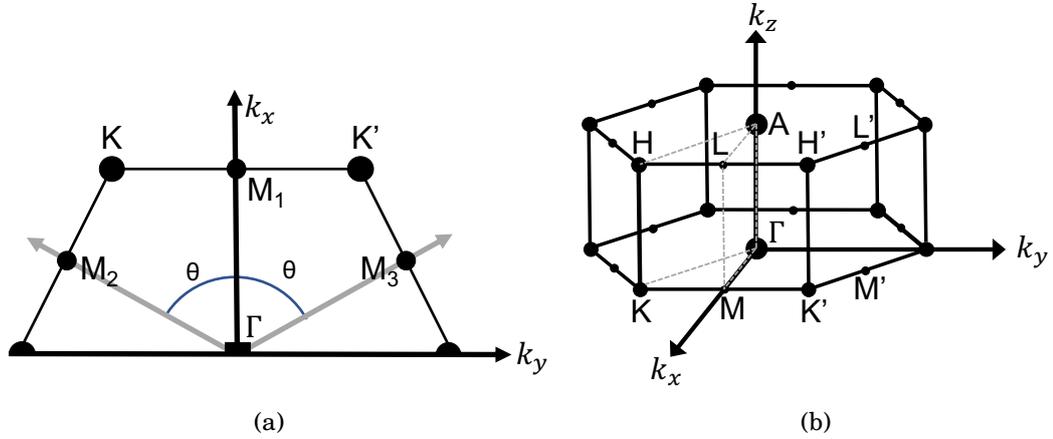


Figure 5.1: (a) 2D hexagonal (0001) plane and showing the location of the M valleys within the Al_4SiC_4 hexagonal structure, where $\theta = \pm 60^\circ$. (b) 3D hexagonal structure showing location of principal valleys.

figure shows the applied electric field in a range from 0.01 to 1400 kVcm^{-1} . The electron velocity increases with increasing electric field quickly at a relatively low electric field and starts to saturate at about electric field of 200 kVcm^{-1} . At an applied electric field of 1400 kVcm^{-1} , the maximum drift velocity is approximately $1.35 \times 10^7 \text{ cms}^{-1}$ at which point the electron velocity is very well saturated. This saturation is caused by a strong emission of two polar optical phonons at energies of 67 meV and 107 meV (see Table 4.2). The average kinetic energy as a function of applied electric field is plotted in Figure 5.3. The kinetic energy has approximately a linear increase as the electric field increases considering that electric field is plotted on a logarithmic scale.

We have monitored electron kinetic energy that is larger than the band gap of Al_4SiC_4 in the simulations. At the largest electric field of 1400 kVcm^{-1} occurring in the simulations in Figures 5.2 and 5.3, the amounts of electrons over this energy amounts to 0.119% of the total number of electrons simulated. This indicates that electron transport in the material is close to a breakdown due to excessive impact ionisation at electric field of 1400 kVcm^{-1} . This result indicating onset of impact ionisation supports our calculated critical electric field of 1831 kVcm^{-1} . Figures 5.3 and 5.2 show electron mobility and electron diffusion as a function of applied electric field, respectively. The electron mobility and the electron diffusion have an exponential decay as electric field increases. The electron mobility and electron diffusion at a low electric field are $82.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $2.1 \text{ cm}^2 \text{ s}^{-1}$, which are at their respective maxima, while they are $9.63 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $0.25 \text{ cm}^2 \text{ s}^{-1}$ at a high electric field of 1400 kVcm^{-1} , respectively.

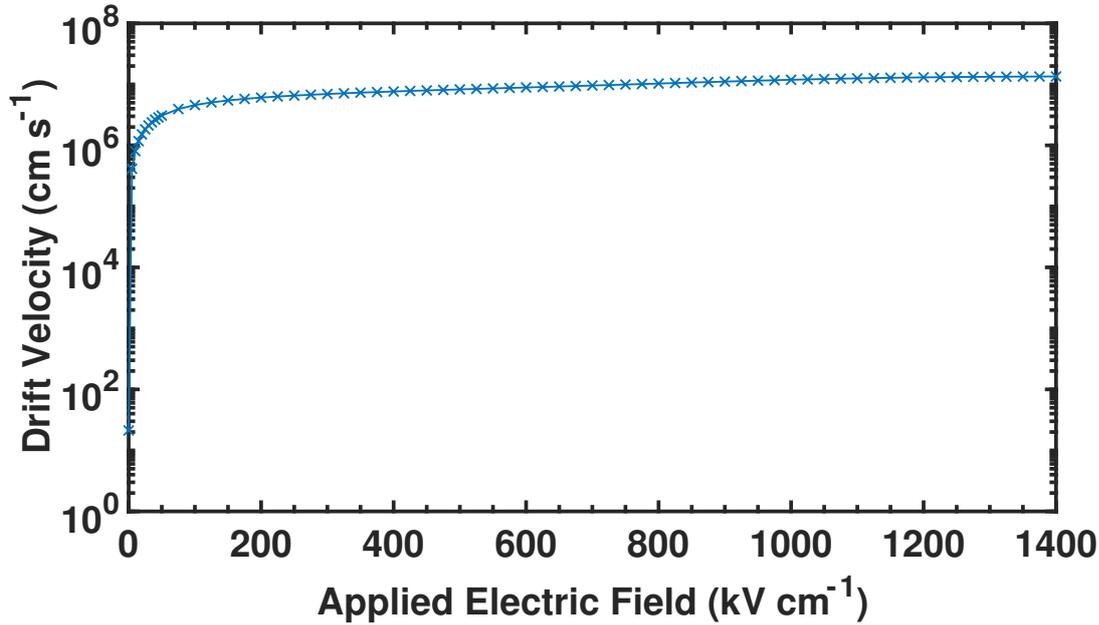


Figure 5.2: Electron drift velocity as a function of applied electric field in bulk Al_4SiC_4 .

Figure 5.6 is using a stacked plot to illustrate a population of electrons occupying each valley (M and K valleys) obtained from the MC simulations. The M valley gets populated evenly at the start of the simulation as expected until the electrons have enough energy to make a transition into the K valley. The K valley does not start to get populated until approximately 450 kVcm^{-1} but remains populated less than 20% even at the largest electric field which justifies our approximation of isotropic K -valley.

Finally, we examine the relationship between electron mobility and ionized impurity concentration in Figure 5.7. The electron mobility of Al_4SiC_4 has a typical dependency on the ionized impurity concentration when the mobility remains approximately constant until an ionized impurity concentration of $2 \times 10^{16} \text{ cm}^{-3}$. When the ionized impurity concentration increases further, the electron mobility start to decline down to about $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ as seen in many semiconductor materials [48].

5.1.2 Conclusions

The MC simulations of the electron transport in Al_4SiC_4 which has a hexagonal crystal structure have been adapted to include a rotational transformation in the lowest conduction band, the M valley, to account for a strong anisotropy of electron effective mass. The strong anisotropy of the electron effective mass in the M valley has profound impact

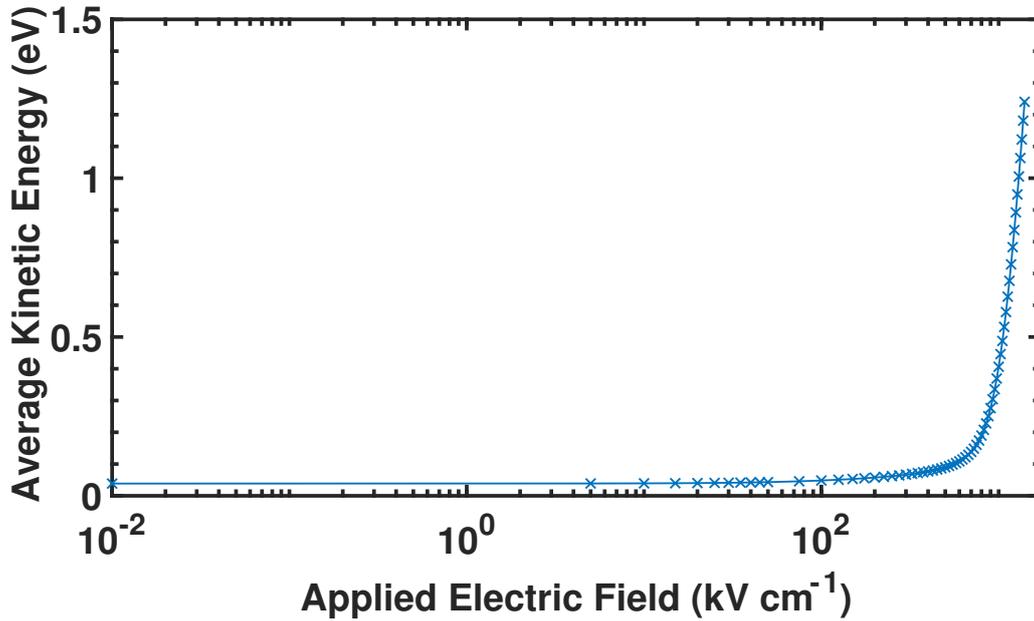


Figure 5.3: Average electron kinetic energy as a function of applied electric field in bulk Al_4SiC_4 .

on electron drift velocity and mobility. The electron effective mass extracted from DFT calculations have shown that there is a large effective mass in both the longitudinal and transverse directions for the K valley of $1.0569 m_e$ and $0.9360 m_e$, respectively, compared with those for the M valley of $0.5678 m_e$ and $0.6952 m_e$, respectively.

The MC simulations allows to predict material transport properties in Al_4SiC_4 . We have predicted dependence of electron drift velocity, electron mobility, average kinetic energy of electrons, and electron population against the applied electric field, all of which can serve as crucial indicators to assess the electronic and opto-electronic performance of devices. We have shown that the electron drift velocity increases with increasing electric field reaching $1.35 \times 10^7 \text{ cms}^{-1}$ at approximately 1400 kVcm^{-1} . The electron kinetic energy has a linear increase as expected and reaches 1.24 eV at 1400 kVcm^{-1} . The threshold energy barrier when electron start to transfer from the M valley to the K valley occurs at electric field of approximately 450 kVcm^{-1} . We predict that as the electrons with higher energy, that is greater than the band gap of the material, will start to increase rapidly as the electric field draws closer to the critical field of 1831 kVcm^{-1} causing a breakdown to occur.

The electron mobility decreases with an increase of the electric field from approximately $82.9 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ to $9.6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and the diffusion decreases from approximately

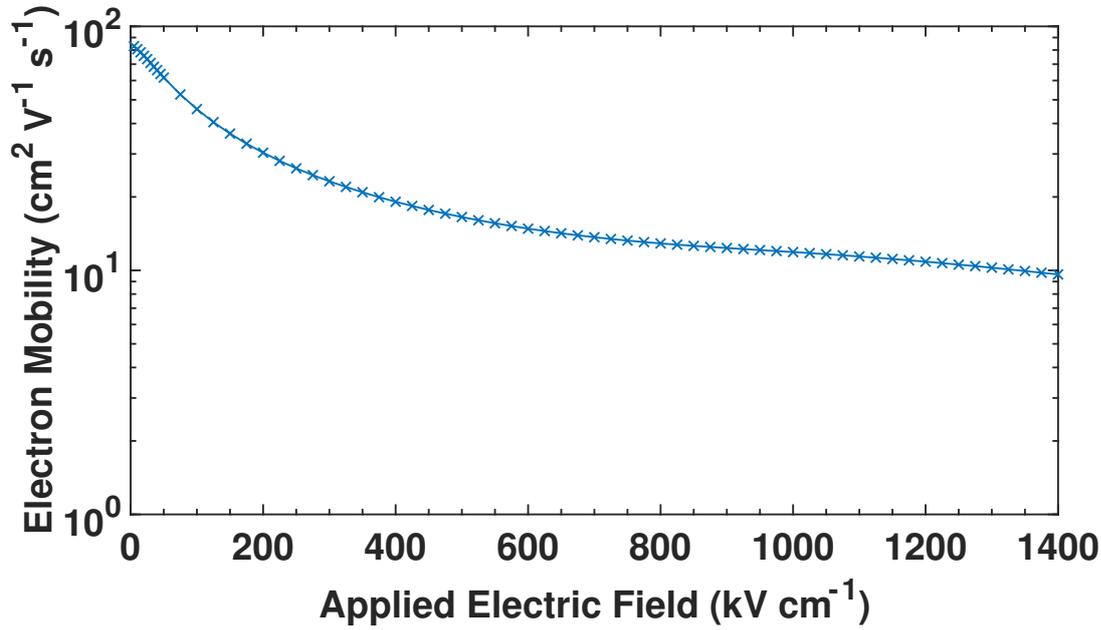


Figure 5.4: Electron Mobility as a function of applied electric field in bulk Al_4SiC_4 .

2.14 to $0.25 \text{ cm}^2\text{s}^{-1}$, both over a range of very low electric field to 1400 kVcm^{-1} . Finally, we have shown that the electron mobility dependent on the ionized impurity concentration declines from its maximum value of $82.9 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at low doping concentrations up to $2 \times 10^{16} \text{ cm}^{-3}$ to about $10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at a very high doping concentration of 10^{21} cm^{-3} . These predicted material properties show a limited usage of the Al_4SiC_4 in a channel of potential metal-oxide-semiconductor field effect transistors (MOSFETs) due to a maximum drift velocity and electron mobility of $1.35 \times 10^7 \text{ cms}^{-1}$ and $83 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ respectively. When comparing these two material properties of Al_4SiC_4 with properties of know semiconductor materials, a maximum drift velocity of Al_4SiC_4 is only 61.4 % of the maximum drift velocity of GaN ($2.2 \times 10^7 \text{ cms}^{-1}$) and electron mobility of Al_4SiC_4 is 6.7 % of the GaN electron mobility ($1250 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) [76]. Compared to 6H-SiC, Al_4SiC_4 is only 67.5 % of the maximum drift velocity of 6H-SiC ($2 \times 10^7 \text{ cms}^{-1}$) and only 16.6 % of the 6H-SiC electron mobility ($500 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) [76]. Finally comparing to silicon, Al_4SiC_4 is 135 % of the maximum drift velocity of silicon ($1 \times 10^7 \text{ cms}^{-1}$) and only 5.5 % of the silicon electron mobility ($1500 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) [76].

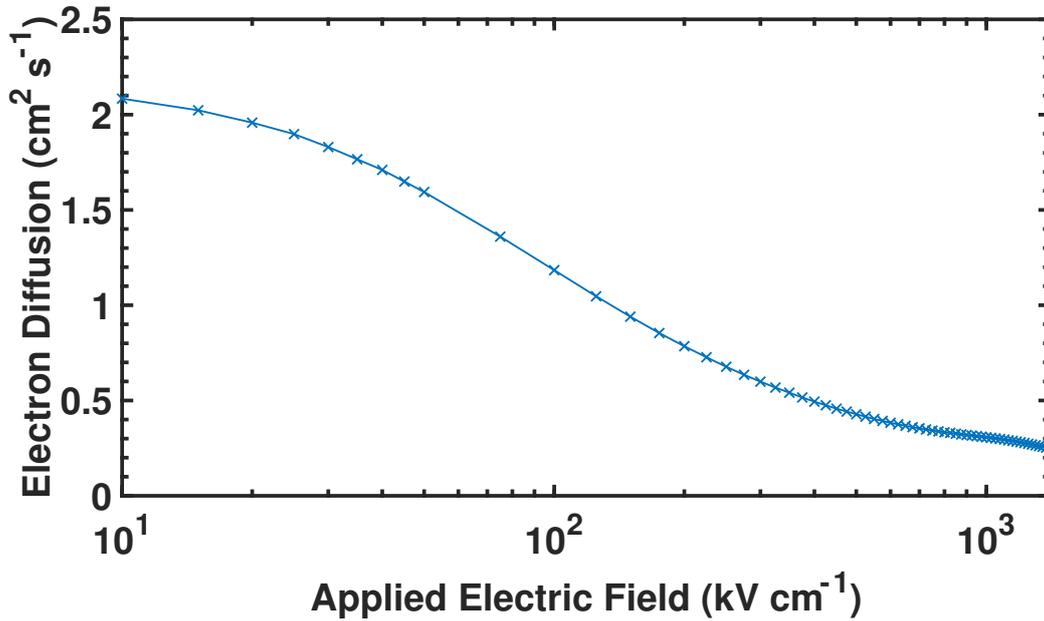


Figure 5.5: Electron diffusion as a function of applied electric field in bulk Al_4SiC_4

5.2 Device Simulations

In this work, we have employed a commercial TCAD Silvaco software by using two-dimensional (2-D) ATLAS simulations to foresee device characteristics of a $\text{SiC}/\text{Al}_4\text{SiC}_4$ based heterostructure transistor for the first time. The device simulations use a combination of material properties of Al_4SiC_4 [31, 32] along with other published material properties [60]. Where material properties are unknown, we have used the material properties of 4H-SiC which are well known [39]. The device architecture is designed with a gate length of $5 \mu\text{m}$ to meet requirements of power applications. This initial $5 \mu\text{m}$ gate length transistor architecture is then scaled down to explore improvement in device characteristics. The characteristics that are investigated are DC current-voltage (I-V) characteristics, transconductance, device breakdown, and a comparison between three devices scaled laterally.

5.2.1 Transistor Simulations

Figures 5.8 to 5.10 show the conduction and valence band profiles with overlap of the electron concentrations in off and on conditions. When the device is in the off state, that is when zero bias is applied, the Fermi level is located between the conduction band and the valence band. When in the on state, that is when an bias of $V_D=5 \text{ V}$ and $V_G=1 \text{ V}$ is

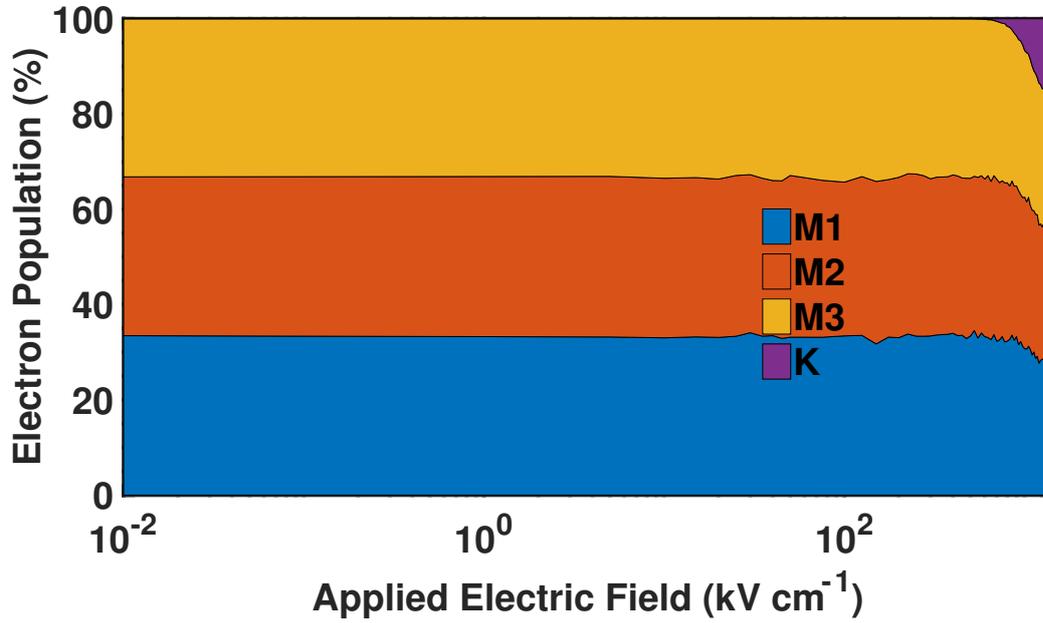


Figure 5.6: Stacked plot of the calculated valley occupancy of electrons in the three M and K valleys as a function of applied electric field in bulk Al_4SiC_4 .

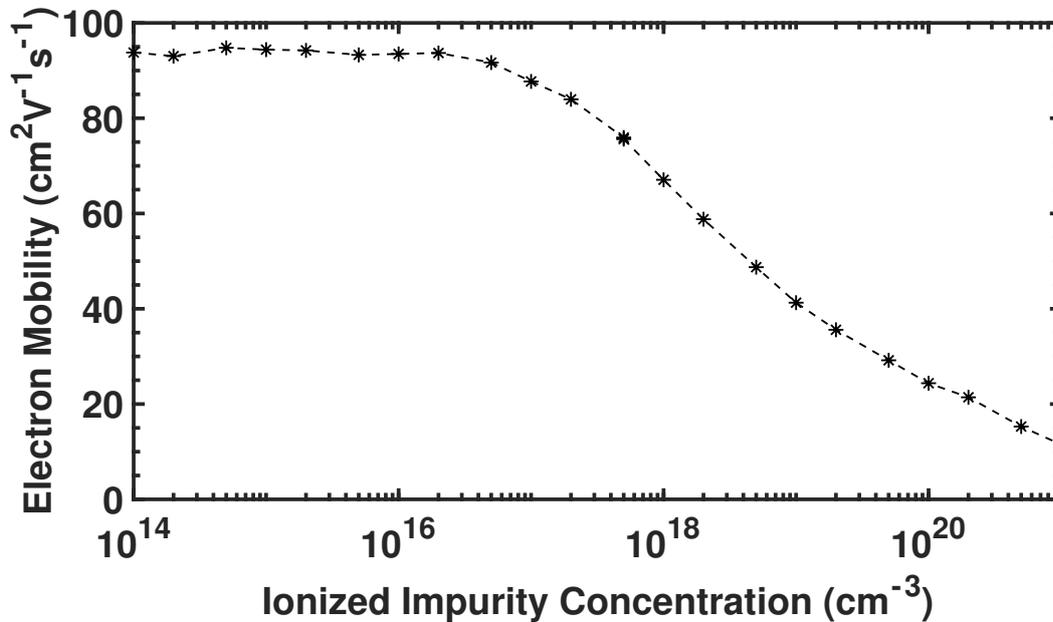


Figure 5.7: Electron mobility as a function of ionized impurity concentration in bulk Al_4SiC_4 .

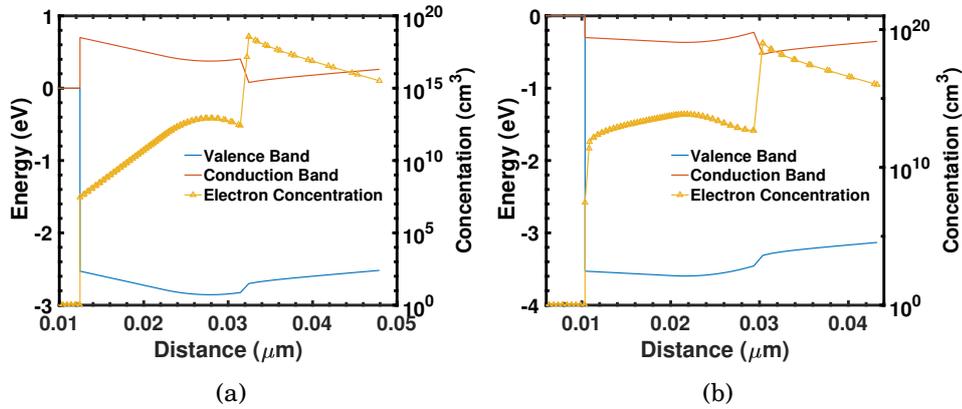


Figure 5.8: Conduction and valence band profiles (left) overlapped with electron density (right) across the middle of the 5 μm gate length device in an off state with zero bias applied (a), and in an on state at $V_D=5$ V and $V_G=1$ V (b).

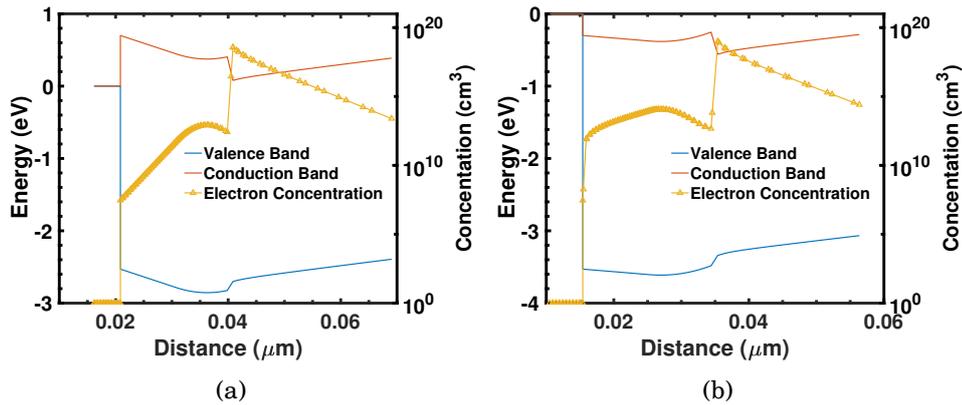


Figure 5.9: Conduction and valence band profile (left) overlapped with electron density (right) across the middle of the 2 μm gate length device in an off state with zero bias applied (a), and in an on state at $V_D=5$ V and $V_G=1$ V (b).

applied, the Fermi level shifts up so that the level is located within the conduction band of the device and the electron concentration increases by a factor of six.

5.2.2 Device Structure

The 2-D device simulator Atlas by Silvaco is used here to investigate a designed heterostructure transistor for power applications as see in Figure 5.11. The device heterostructure, which has been optimised for a large channel electron density, comprises of a thin layer of n -type doped 4H-SiC with a concentration of $2.5 \times 10^{18} \text{cm}^{-3}$ on a top of

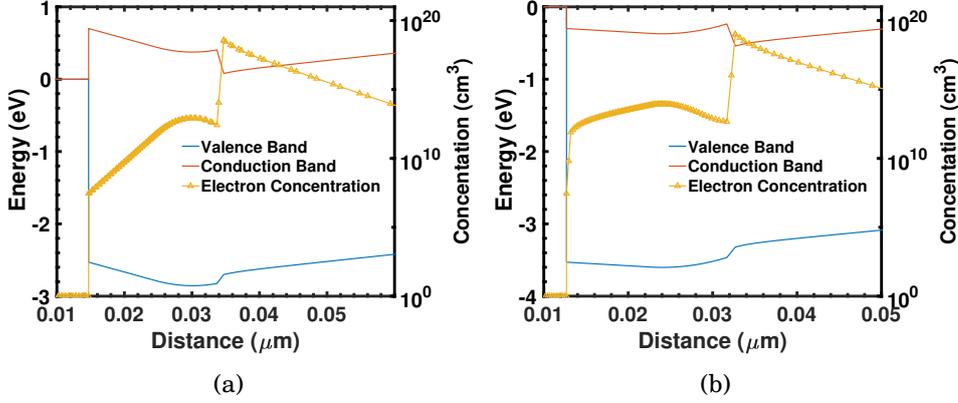


Figure 5.10: Conduction and valence band profile (left) overlapped with electron density (right) across the middle of the $1 \mu\text{m}$ gate length device in an off state with zero bias applied (a), and in an on state at $V_D=5 \text{ V}$ and $V_G=1 \text{ V}$ (b).

large layer of p -type doped Al_4SiC_4 with a concentration of $1 \times 10^{16} \text{ cm}^{-3}$. The purpose of the thin layer of n -type doped SiC is to provide supply of carriers into the device channel which occurs at the interface between the SiC and the Al_4SiC_4 because of the offset in their conduction bands. The SiC/ Al_4SiC_4 heterostructure device has a gate length of $5 \mu\text{m}$, a channel length from source-to-drain of $10 \mu\text{m}$, a source-to-gate distance of $2.5 \mu\text{m}$ and a gate-to-drain distance of $2.5 \mu\text{m}$. The thickness of the layers is fixed to 20 nm for SiC and to $3 \mu\text{m}$ for Al_4SiC_4 .

Thickness (nm)	Gate length (nm)		
	5000	2000	1000
Source-to-gate spacer (L_{SG})	2500	1000	500
Gate-to-drain spacer (L_{GD})	2500	1000	500
Source thickness (T_S)	25	25	25
SiC as barrier (T_C)	20	20	20
SiC n -type layer (T_{C1})	10	10	10
Al_4SiC_4 as buffer (T_B)	3000	3000	3000
Gate thickness (T_G)	5	5	5
Drain thickness (T_D)	25	25	25

Table 5.1: Corresponding dimensions of the scaled heterostructure transistors shown in Figure 5.11. Note that L_S and L_D dimensions in Figure 5.11 are assumed to be large enough to make good Ohmic contacts.

The initial $5 \mu\text{m}$ gate length SiC/ Al_4SiC_4 heterostructure transistor is laterally scaled

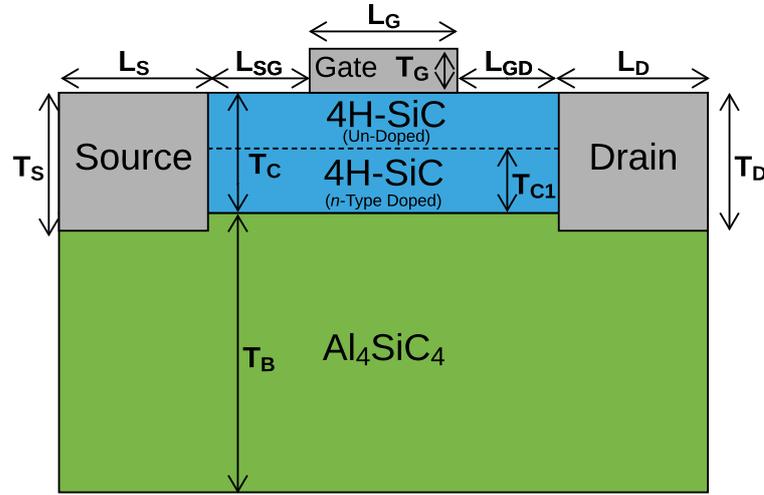


Figure 5.11: Cross-section of the heterostructure SiC/Al₄SiC₄ transistor designed for power applications, see Table 5.1 for dimensions. The concentration of *n*-type doped 4H-SiC layer is $2.5 \times 10^{18} \text{ cm}^{-3}$.

to gate lengths of $2 \mu\text{m}$ ($4 \mu\text{m}$ channel length from the source to the drain) and $1 \mu\text{m}$ ($2 \mu\text{m}$ channel length from the source to the drain). The source-to-gate and the gate-to-drain dimensions are scaled to $1 \mu\text{m}$ for the $2 \mu\text{m}$ gate length device and to $0.5 \mu\text{m}$ for the $1 \mu\text{m}$ gate length (see Table 5.1).

5.2.3 Device Model

All simulations were done in SILVACO ATLAS 2D V5.26.1.R using a 2D drift-diffusion transport model with field dependent mobility [67] and Auger recombination [67] simulating both holes and electrons. The solution technique that is used by the simulations is the combined Gummel-Newton algorithm. The material parameters for Al₄SiC₄ are summarized in Table 5.2.

5.2.4 Scaled SiC/Al₄SiC₄ Heterostructure Transistors

The $I - V$ characteristics of each heterostructure transistor are simulated for a gate bias (V_G) from 0 V to 20 V, and for the drain bias (V_D) from 1 V to 40 V as depicted in Figures 5.12-5.14. When V_D is increased, the drain current starts to saturate due to a limitation of the maximum electron density in the channel which is determined by the conduction band offset as seen in Figures 1–3. The drain current saturation

Parameter (unit)	Value
Electron mobility (cm^2/Vs)	242.5 ^a
Electron saturation velocity (cm/s)	8×10^6 ^a
Bang gap at 300°C (eV)	2.78 ^a
Permittivity	8.32 ^b
Affinity (eV)	3.546 ^a
Conduction band density at 300°C (cm^{-3})	7.887×10^{19} ^a
Valence band density at 300°C (cm^{-3})	1.2×10^{19} ^a
Electron recombination coefficient	5×10^{-31} ^c
Hole recombination coefficient	2×10^{-31} ^c

^aCalculated from previous works [32]^bRef. [60]^cRef. [2]

Table 5.2: Al_4SiC_4 material parameters considered in the simulations of heterostructure transistors.

exhibits itself as inability to substantially increase saturation current at higher V_D (between 15 V to 40 V). The $I_D - V_G$ characteristics show a linear region, an on-set of the saturation, and a saturation region. At $V_D = 40$ V, the complete drain current saturation occurs determining the maximum drain current which a scaled transistor can deliver at approximately 1.68×10^{-4} A/ μm , 2.44×10^{-4} A/ μm , and 3.50×10^{-4} A/ μm for gate lengths of 5 μm , 2 μm , and 1 μm , respectively.

The metal-gate workfunction that is used in the simulations is taken to be 3.9 eV. The threshold voltage is determined from the $I_D - V_G$ characteristics where a linear fit is taken against the linear region of the data. The threshold voltage is found to be 71.0 mV, 28.3 mV, and 28.3 mV for a 5 μm , 2 μm , and 1 μm gate length transistors, respectively. The sub-threshold slope has been extracted from the $I_D - V_G$ characteristics on a semi-logarithmic scale by fitting a linear line at a low drain bias of $V_D = 5$ V. The sub-threshold slope is 197.3 mV/dec, 97.6 mV/dec, and 96.1 mV/dec for devices with gate lengths of 5 μm , 2 μm , and 1 μm , respectively, all of which are much larger than the ideal sub-threshold slope of 60 mV/dec [13, 116].

Breakdown of the devices is determined from simulated $I_D - V_D$ characteristics seen in Figures 5.15-5.16 when the transistors are off. The bias at which the device breaks down becomes smaller as the gate length decreases, 59.0 V, 31.0 V, and 18.0 V for gate lengths of 5 μm , 2 μm , and 1 μm , respectively. The 5 μm gate length heterostructure transistor exhibits a non-equilibrium stage between holes and electrons in a form of a kink in its $I_D - V_D$ characteristics at approximately 35 V followed by the device breakdown at 59.0 V. The kink and the device breakdown voltage, when the drain current sharply rises, is seen

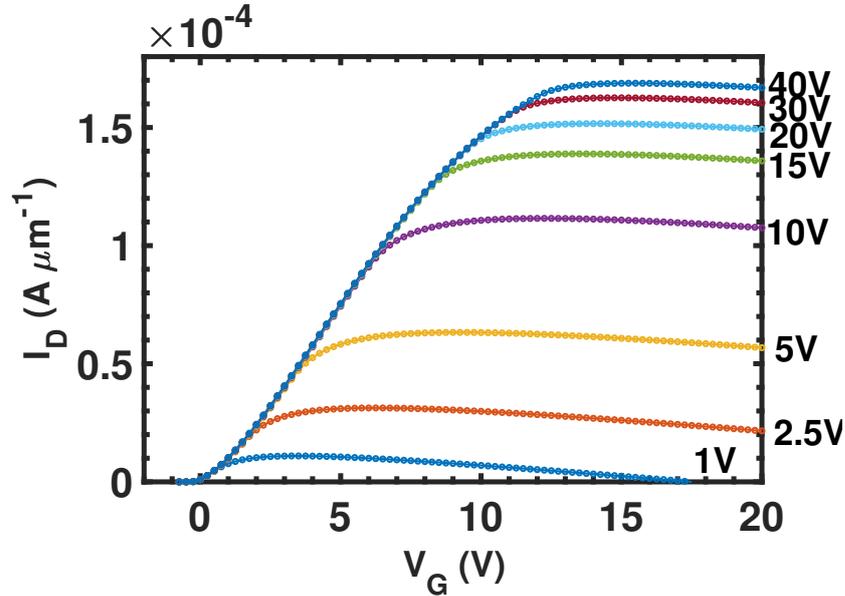


Figure 5.12: $I_D - V_G$ characteristics at indicated drain biases (V_D) for the 5 μm gate length SiC/Al₄SiC₄ heterostructure transistor.

in Figure 5.15. A similar kink is seen in the 2 μm gate length heterostructure transistor where a sharp rise occurs at approximately 25 V followed by the device breakdown at 31.0 V (see Figure 5.16). No kinks appear in the smallest gate length device where the breakdown voltage occurs at 18.0 V (see Figures 5.17).

Finally, we extract transconductance at a low drain bias of 2.5 V and a high drain bias of 30 V in order to ascertain how well the device will be performing in a switching operation. As the device gate length decreases, the transconductance increases from 1.25 mS/mm (1.69 mS/mm) to 31.90 mS/mm (36.5 mS/mm) and 59.3 mS/mm (65.1 mS/mm) at a low drain bias of 2.5 V (at a high drain bias of 30 V) as summarized in Table 5.3 and, in turn, the switching speed of the device will improve. The decline of the transconductance in the 1 μm gate length transistor at the high drain bias of 30 V is caused by a kink at around 13 V at a drain bias of 30 V detectable in the $I_D - V_G$ characteristics shown in Figure 5.14. The kink separates two transport regimes in the transistor operation. The first transport regime is a standard electron accumulation in the channel giving linear regime of the $I_D - V_G$ characteristics. The second transport regime occurs when additional channel is created by electrons spilling into a conduction band minimum in the SiC layer (see the conduction band in the SiC layer in Figure 5.10(b)).

On top of proportional lateral scaling of the device, we also performed asymmetric scaling on the 2.0 μm gate length heterostructure, where we increased the gate-to-

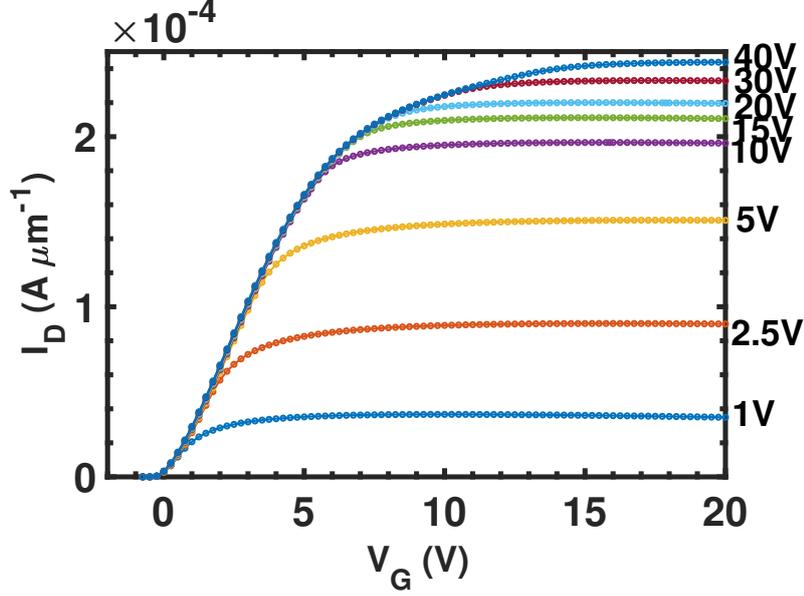


Figure 5.13: $I_D - V_G$ characteristics at indicated drain biases (V_D) for the scaled SiC/Al₄SiC₄ heterostructure transistor with a 2 μm gate length.

drain spacer to 2.5 μm in order to re-distribute high electric field occurring between the gate and the drain along the longer distance and thus lower the field when transistor architecture is scaled laterally from a gate length of 5 μm gate to 2 μm and 1 μm . The rest of device sizes stayed the same as per Table 5.1. This asymmetric heterostructure transistor design delivers a breakdown voltage increased by 17.25 V, that is from 31.0 V to 48.25 V. We also look at increasing the breakdown voltage of the 1 μm gate length heterostructure transistor by creating an asymmetric design of the device where the source-to-gate spacer is fixed to 0.5 μm but the gate-to-drain spacer is increased to 1.0 μm and to 2.5 μm . The 1 μm gate length asymmetric heterostructure with a 1.0 μm gate-to-drain spacer exhibits an increase in the breakdown voltage of 4.75 V, that is from 18.0 V to 22.75 V. The 1 μm gate length asymmetric heterostructure with a 2.5 μm gate-to-drain spacer exhibits an increase in the breakdown voltage of 11.25 V, that is from 18.0 V to 29.25 V. Therefore, lateral scaling of the SiC/Al₄SiC₄ heterostructure transistor can deliver increase in the device transconductance and decrease in the breakdown can

Drain Bias (V)	5 μm	2 μm	1 μm
2.5	$1.25 \times 10^{-6} \text{ S}/\mu\text{m}$	$3.19 \times 10^{-5} \text{ S}/\mu\text{m}$	$5.93 \times 10^{-5} \text{ S}/\mu\text{m}$
30	$1.69 \times 10^{-6} \text{ S}/\mu\text{m}$	$3.65 \times 10^{-5} \text{ S}/\mu\text{m}$	$6.51 \times 10^{-5} \text{ S}/\mu\text{m}$

Table 5.3: Maximum transconductance of the scaled heterostructure transistors.

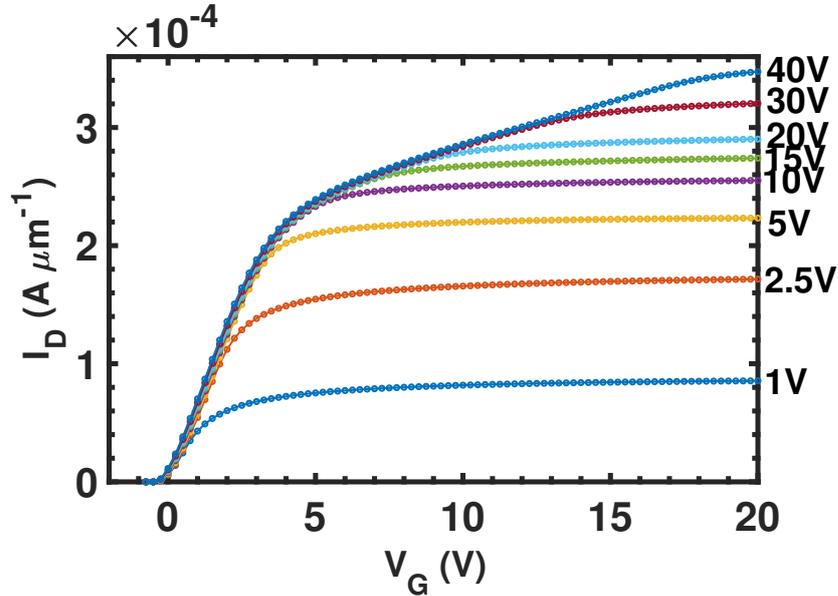


Figure 5.14: $I_D - V_G$ characteristics at indicated drain biases (V_D) for the scaled SiC/Al₄SiC₄ heterostructure transistor with a 1 μm gate length.

be mitigated by using asymmetric device structure where the distance between the gate and the drain is increased.

5.2.5 Conclusions

A performance of heterostructure transistor made of SiC/Al₄SiC₄ material system with a novel ternary carbide of Al₄SiC₄ has been simulated in Silvaco Atlas using known experimental [31] and theoretical data [32]. The heterostructure transistor with a gate length of 5 μm and two heterostructure transistors laterally scaled to gate lengths of 2 μm and 1 μm with respective lateral scaling of source-to-gate distance, channel length, and gate-to-drain distance have been simulated using drift-diffusion transport model in commercial simulator Atlas by Silvaco. The variants of asymmetric scaled heterostructure transistors with the increased gate-to-drain distance to achieve a larger breakdown voltage have been also studied.

The threshold voltage, at which the device turns on, is positive in each of the devices with a metal-gate work function of 3.9 eV. Therefore, the device remains off unless a gate bias is applied and all the scaled SiC/Al₄SiC₄ heterostructure transistors provide a n -channel enhancement-mode, normally-off device operation. The threshold voltage reduces as the gate length is reduced from 71.0 mV to 28.3 mV, and to 28.3 mV for

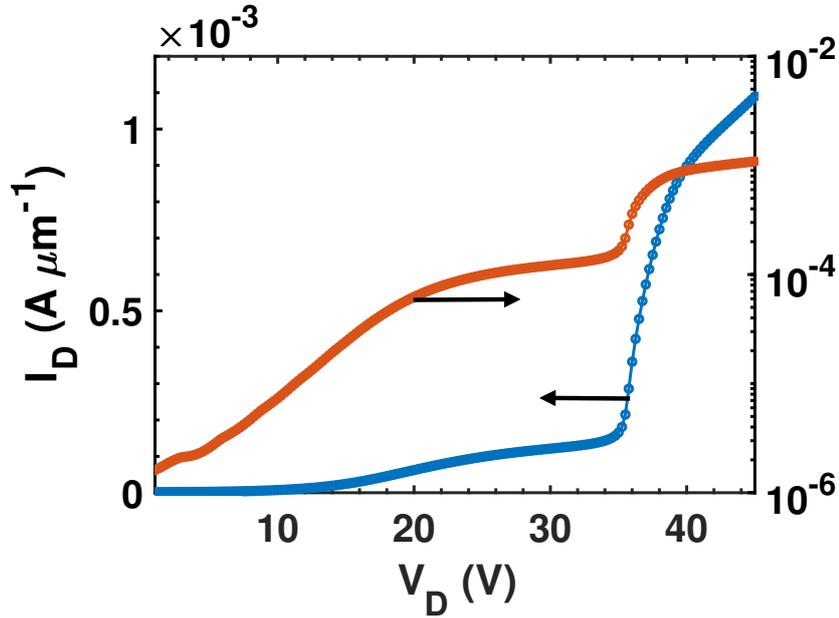


Figure 5.15: Breakdown of 59.0 V for a heterostructure device with a 5 μm gate length on a linear scale (left) on a log scale (right).

5 μm , 2 μm , and 1 μm gate length transistors, respectively. Sub-threshold voltages of 197.3 mV/dec, 97.6 mV/dec, and 96.1 mV/dec for gate lengths of 5 μm , 2 μm , and 1 μm , respectively, are observed which are, in all cases, much larger than the ideal value of 60 mV/dec at 300 K. The bias point at which the device breakdown occurs reduces from 59.0 V, to 31.0 V, and to 18.0 V as the gate length reduces from 5 μm to 2 μm and to 1 μm , respectively. We also saw that the breakdown voltage can be increased to 48.25 V when we increase the gate-to-drain spacer to 2.5 μm in the 2 μm gate device, and to 22.75 V and to 29.25 V in the 1 μm gate device when the gate-to-drain spacer is increased to 1.0 μm and to 2.5 μm . The drain current saturation point increases with the reduction of the gate length and increase of the drain voltage. At a large drain voltage of 40 V, a drain current saturation appears at $1.68 \times 10^{-4} \text{ A}/\mu\text{m}$, $2.44 \times 10^{-4} \text{ A}/\mu\text{m}$, and $3.50 \times 10^{-4} \text{ A}/\mu\text{m}$ for gate lengths of 5 μm , 2 μm , and 1 μm , respectively.

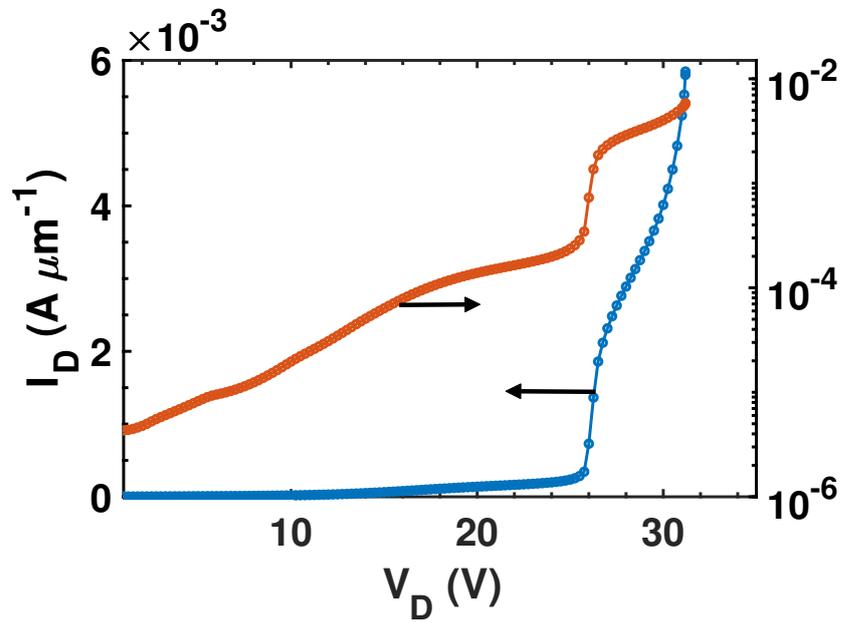


Figure 5.16: Breakdown of 31.0 V for a heterostructure device with a $2 \mu\text{m}$ gate length on a linear scale (left) on a log scale (right).

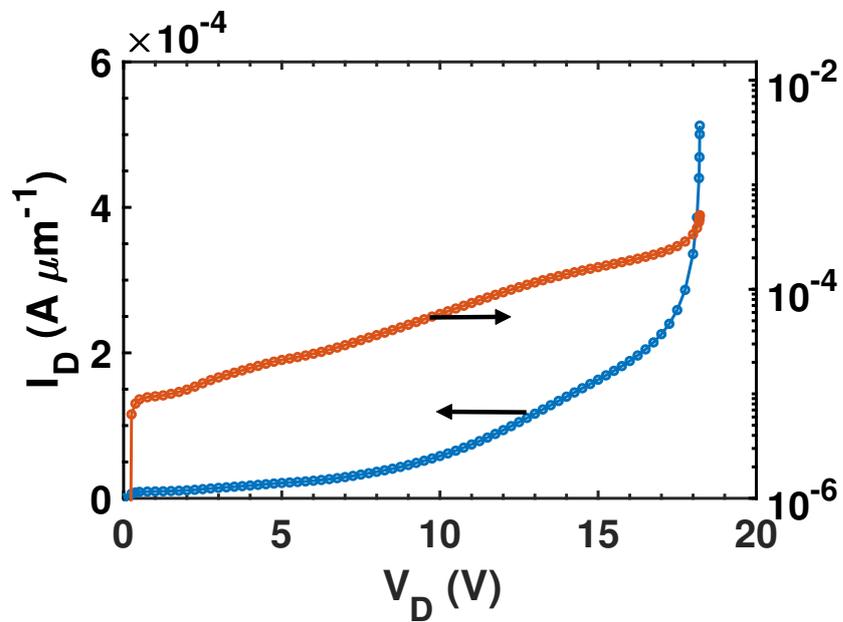


Figure 5.17: Breakdown of 18.0 V for a heterostructure device with a $1 \mu\text{m}$ gate length on a linear scale (left) on a log scale (right).

EXPERIMENTAL RESULTS

This chapter is organised as follows. It starts with an introduction into the various experimental methods that were used to characterise Al_4SiC_4 . Section 6.2 introduces the UV/Vis/NIR spectroscopy experiments and details the results. Section 6.3 looks at the XPS experiments that were carried out, detailing the results obtained from them. Section 6.4 looks at the final group of experiments that were performed, these being two- and four-probe DC current voltage measurements and again details the results obtained. Finally, Section 6.5 draws a conclusion from all the experiments.

6.1 Introduction

In this work, a multitude of experiments have been carried out in order to characterise Al_4SiC_4 , these being UV/Vis/NIR Spectroscopy, X-Ray Photoelectron Spectroscopy (XPS) and two- and four-probe DC current voltage characterisation. Each of these techniques work off different physical principles of which have been detailed in Chapters 3 and 4. Two sets of samples have been used in these experiments. One fabrication method has been solution grown crystals of Al_4SiC_4 [118] and second fabrication method has grown crucible melt crystals of Al_4SiC_4 [108], both of which have been provided by Grenoble University for use in this joint research thesis.

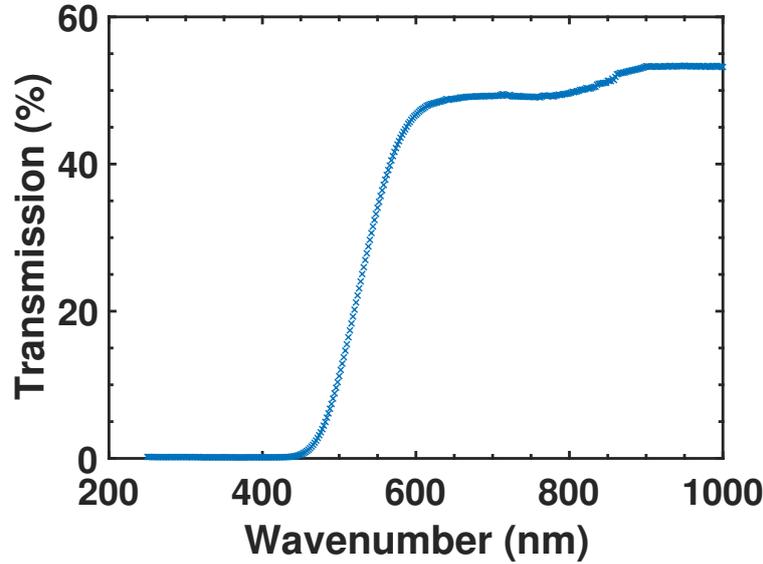


FIGURE 6.1. Wave-number as a function of the light transmission through the solution grown sample of Al_4SiC_4 obtained from the UV/Vis/NIR spectroscopy.

6.2 UV/Vis/NIR spectroscopy

Solution grown samples [118] are used in the UV/Vis/NIR spectroscopy due to the requirements of the spectroscopy system needing to be able to transmit light through a sample. This experiment was performed on the Perkin Elmer Lambda 950 spectrophotometer at LMGP, Grenoble University. These sample were prepared by cleaning them in isopropanol and acetone for 5 minutes each in a sonic bath. The samples are then attached individually to an aperture on the spectrophotometer. The light of wavelengths ranging from a 250 nm to 1000 nm is shone at them and the transmitted light is measured. The measured transmitted light is plotted as a function of wave-number in Figure 6.1. Figure 6.1 shows around 50% transmission over a wavelength of 600 nm before a rapid decrease in transmission down to 0% at 450 nm. Therefore, the sample starts to absorb the transmitted light at 600 nm before total absorption is seen from 450 nm down to 250 nm.

The data in Figure 6.1 is then converted to optical absorption ($ah\nu$), using the Beer-Lambert's Law details in Section 3.4, and incident photon energy using $E = h\nu$ to form a Tauc plot. The plot can be used to extract a bandgap as illustrated in Figure 6.2. The linear region in the plot often referred to as Urbach tailing serves to ascertain a bandgap for the material. However, in our case, the Urbach tailing results in a band gap of only

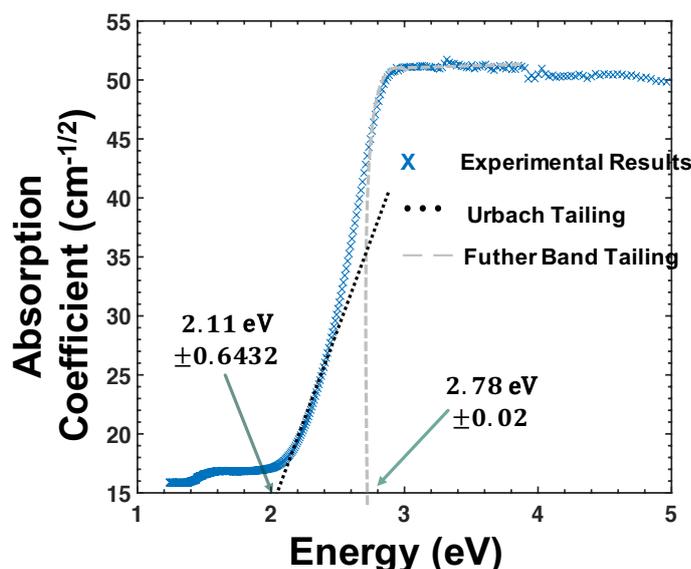


FIGURE 6.2. Tauc plot showing photon energy as a function of absorption coefficient, showing a best fit to the Urbach tail giving a bandgap of 2.11 eV, as well as further band tailing giving a bandgap of 2.78 eV.

2.108 eV. According to computational works, the bandgap should be at least 2.4 eV and, therefore, another solution had to be applied in order to ascertain the bandgap. By taking further band tailing into account, we reveal a bandgap of 2.778 eV. This further band tailing can be explained through several means such as doped material, defective material. Further details on the further band tailing are in Sections 3.5 and 3.6.

6.3 XPS

The first measurement performed on each sample as part of the XPS analysis was a survey spectrum. This is a sensitive (high pass energy), low-resolution scan over a large binding energy range (0 to 1200 eV). Although this is a low-resolution scan and so precise analysis is impossible, it does give a good overview of the elements in the sample composition leading way to identification of interesting energy ranges to be examined in further details. Figure 6.3 shows a survey spectrum of a crucible melted samples [108] of Al_4SiC_4 with the main peaks labelled as to what their chemical element is. Note that the small peaks within the spectrum are not taken into consideration as of yet, as we are only looking at the main peaks that make up the majority of the sample.

The following chemical elements collected in Table 6.1 can be identified from the XPS

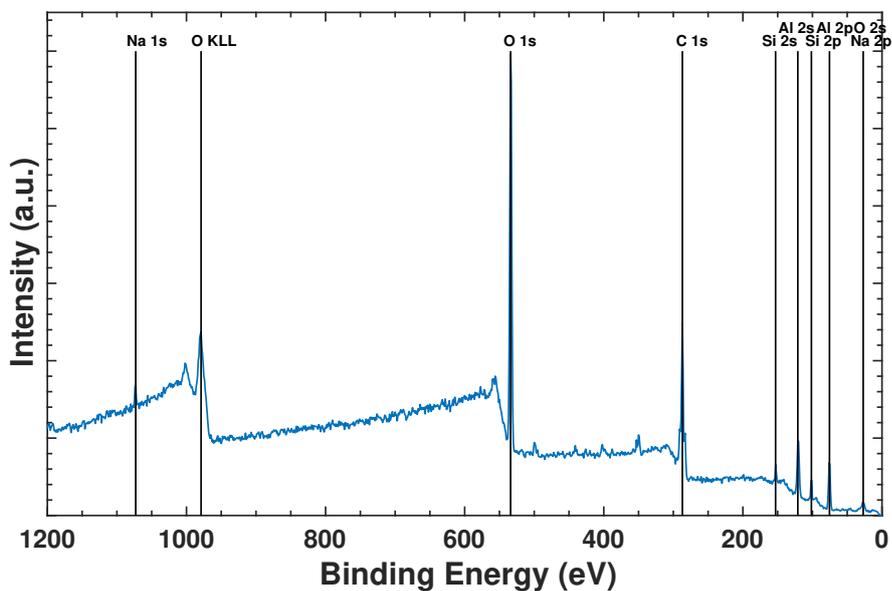


Figure 6.3: XPS survey spectra for a crucible grown sample of Al_4SiC_4 over the range of 0 – 1200 eV measured on the DAISY FUN system at Darmstadt University. Here the peaks detail where certain elements have been found. We have added lines to these peaks to show what the elements are.

survey spectrum in Figure 6.3.

Chemical Element	Binding Energy (eV)
Na 1s	1073
O KLL	979
O 1s	534
C 1s	287
Si 2s	153
Al 2s	121
Si 2p	101.5
Al 2p	75.5
O 2s or Na 2p	27

Table 6.1: Table of the chemical elements picked up in the XPS survey spectrum of Al_4SiC_4 in Figure 6.3 with their corresponding binding energy.

6.3.1 Composition

A low-resolution scan is performed over the sample after various types of surface treatments such as etching and sputtering. In order to be able to perform all of the surface treatments, the sample has to be split into two pieces (A and B). We can then compare the chemical elements make up of each treatment to see what affect it has on the sample. The treatments that were performed as listed below:

- ARXPS on sample A
- Annealed at 600°C for 20 minutes on sample A;
- Argon⁺ sputter at 250V, 10mA for 3 minutes on sample A;
- Argon⁺ sputter at 500V, 10mA for 5 minutes on sample A;
- Wet etched - Sample B was put into a solution of H₂SO₄ to 2 parts H₂O₂ for 9 minutes followed by NH₄F for 4 minutes.

The results of the survey spectra are detailed in the pie charts in Figures 6.4a - 6.4f and reveals the chemical elements that have been picked up.

Figures 6.4a - 6.4f shows the chemical make up of the sample after each of the surface treatments have been performed, except for the case where the sample has been angled at 70° and compared with an unprocessed sample. Here we can see that the material is primarily made up of aluminium, silicon and carbon as we would expect the compound to have. However, there is also a lot of oxygen present in most of the record samples. Table 6.2 details the pie charts in Figures 6.4a - 6.4f, from this we can make the following analysis of sample.

The unprocessed sample, Figure 6.4c, primarily contains aluminium (29.9%), carbon (38.9%), oxygen (24.4%) and silicon (5.52%) with small amounts of nitrogen (1.07%) and sodium (0.217%). It is most likely that the small amounts of nitrogen and sodium are contamination from handling the sample. The oxygen is most likely an oxide layer formed on the surface of the sample and aluminium, carbon and silicon are the elements that make up our Al₄SiC₄ sample.

The ARXPS, which was performed on the sample at 70°, Figure 6.4b and shows the following primary elements, aluminium (23.0%), carbon (52.4%) and oxygen 24.5%) with a small amount of sodium (0.159%). The ARXPS allows one to vary the emission angle at which the electrons are collected, thereby enabling electron detection at different depths, leading one to be able to have a 'bulk angle', 0°, and 'surface angels', > 0°. Here we have

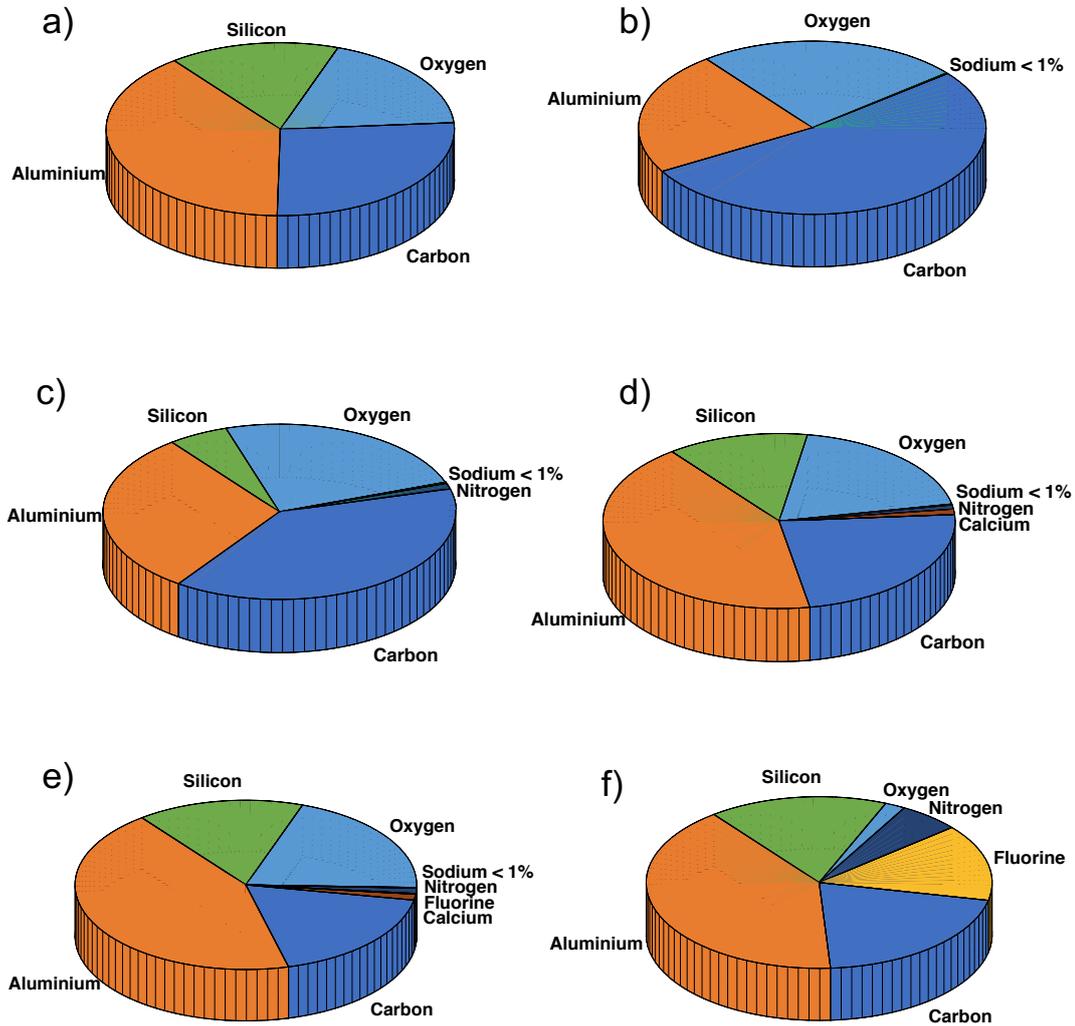


Figure 6.4: Compositions of surface treated or angled samples taken from XPS survey spectrum's that were recorded on the DAISY FUN system at Darmstadt University: annealed sample (a), ARXPS sample (b), unprocessed sample (c), sputter at 250V sample (d), sputtered at 500V sample (e), wet etched sample (f).

performed the ARXPS at 70° in order to ascertain surface details. From the ARXPS analysis we see an absence of silicon and only aluminium, carbon and oxygen present. This is due to detecting the surface layers of the material rather than the bulk material, see Figure 2.2 which shows a molecular model of the material clearly showing the layers of the material, and the ARXPS reveals that the surface is on a carbon layer with linking aluminium atoms. The ARXPS has also detected the sodium contamination but not the nitrogen contamination that was seen on the unprocessed sample Figure 6.4c.

After annealing the sample, Figure 6.4a, shows four elements making up the sample,

Chemical Element	Percentage found (%)					
	Unprocessed	Annealed	ARXPS	Sputtered 250V	Sputtered 500V	Wet Etched
Aluminium	29.9	39.3	23	42.4	43.6	40.6
Carbon	38.9	26.5	52.4	23.4	18.1	20.6
Calcium	0	0	0	0.992	1.1	0
Fluorine	0	0	0	0	0.153	14.4
Nitrogen	1.07	0	0	0.772	1	5.73
Sodium	0.217	0	0.159	0.173	0.136	0
Oxygen	24.4	18.4	24.5	19.3	20.1	1.89
Silicon	5.52	15.8	0	13	15.8	16.7

Table 6.2: Percentage of chemical elements found in each of the XPS survey spectra as shown in the pie charts Figures 6.4a - 6.4f

aluminium (39.3%), carbon (52.4%), oxygen (18.4%) and silicon (15.8%). Comparing this sample to the unprocessed sample, Figure 6.4c, we can see that the nitrogen and sodium contaminants have been removed. Also removed have been 6% of oxygen and 12.4% carbon leading way to higher amounts of silicon, 10.28% increase, and aluminium, 9.4% increase.

After sputtering at 250V and 500V the sample, Figures 6.4d and 6.4e, shows four main elements, aluminium (42.4%, 43.6%), carbon (23.4%, 18.1%), oxygen (19.3%, 20.1%) and silicon (13.0%, 15.8%). We can also see that nitrogen (0.772%, 1.0%) and fluorine (0%, 0.153%) contaminants have been introduced during this surface treatment. Comparing this surface treatment to the unprocessed sample, Figure 6.4c, we see an increase in aluminium, 12.5% and 13.7%, and silicon, 7.48% and 10.28%. We also see a decrease in carbon, 15.5% and 20.8%, and oxygen 5.1% and 4.3%.

Finally, after wet etching, Figure 6.4f, we can still see the four main elements, aluminium (40.6%), carbon (20.6%), oxygen (1.89%) and silicon (16.7%). However, we see an addition of fluorine (14.4%) and nitrogen (5.73%) that have introduced during the etching process. Comparing the etched sample to the unprocessed sample, we can see that there has been an increase of aluminium (10.7%) and silicon (11.18%) and a decrease in carbon (18.36%) and oxygen (22.51%).

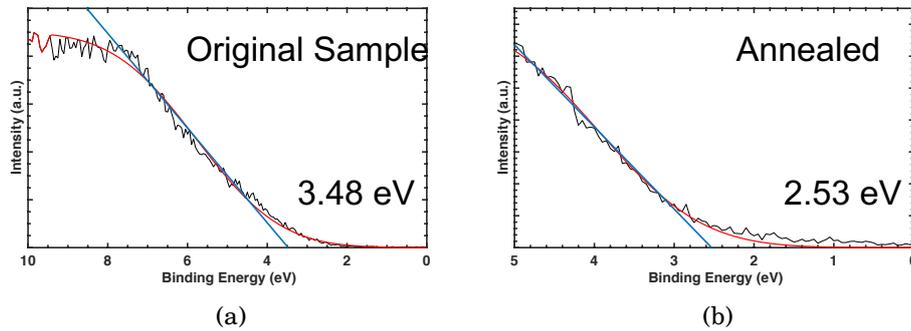


Figure 6.5: XPS valence band profiles obtained with the DAISY FUN system at Darmstadt University for: the unprocessed sample (a), and from the annealed sample (b). A step down function (red line) is fitted to the measured data with a tangent (blue line) to the step down function. The point at which the tangent crossed the axis is noted on each of the figures, this is the amount the Fermi level lies above the valence band.

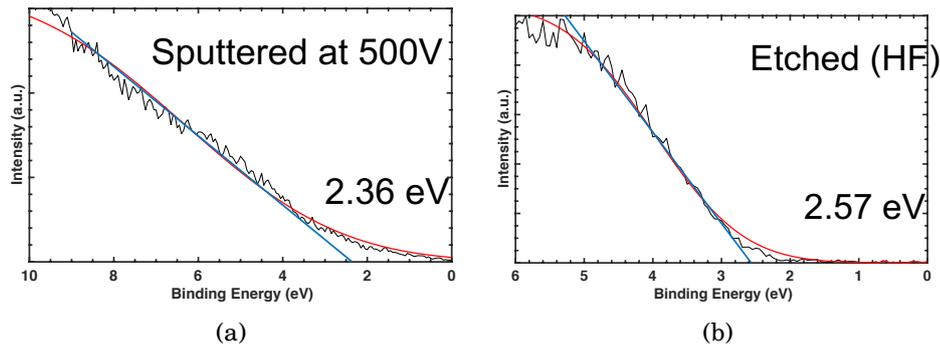


Figure 6.6: XPS valence band profile obtained with the DAISY FUN system at Darmstadt University for: the sputtered sample at 500 V (a), and wet etched sample with HF (b). A fitted step down function (blue line) and its tangent (red line) are also shown. The point at which the tangent crossed the axis is noted on each of the figures, this is the amount the Fermi level lies above the valence band.

6.3.2 Valence Band

A detailed scan was undertaken at the lowest binding energy from 0 to 10 eV in order to get a valence band spectrum for the samples, see Figures 6.5 to 6.7. Each spectrum is fitted with a step-down function along with a tangent to this function. The point at which this tangent crosses the x -axis is the point where the Fermi level, E_F , lies above the valence band.

Figures 6.5 to 6.7 show that the point at which the Fermi level lies shifts lower when the sample are cleaned by various methods. The higher the value for the Fermi level

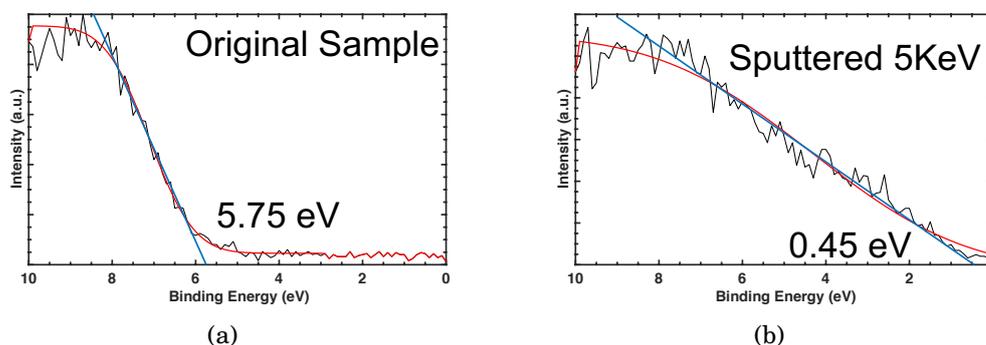


Figure 6.7: XPS valence band profiles obtained on the Kratos Supra XPS spectrometer at Swansea University for: unprocessed sample (a), and sputter sample at 5 keV (b). A fitted step down function (blue line) and a tangent to this (red line) are also shown. The point at which the tangent crossed the axis is noted on each of the figures, this is the amount the Fermi level lies above the valence band.

indicate a thicker oxidation layer on top of the Al_4SiC_4 sample which is clear to see when we look at depth profile in Section 6.3.4. This oxidation layer is marking the material n -type as the Fermi level is sitting above the midpoint between the valence band and the conduction band. As the sample is cleaned and the oxidation layer gets removed, the sample goes from being n -type to p -type as the Fermi level sit below the midpoint between the valence band and the conduction band.

6.3.3 Workfunction

By performing ultraviolet photoelectron spectroscopy (UPS) we can determine the workfunction of the sample by determining the low kinetic energy cut-off point of the material. This was performed on sample after some of the surface treatments was and was done on both the DAISY FUN system at Darmstadt University and on the Kratos Supra XPS spectrometer at Swansea University. The main difference between the two set ups was, the Kratos Supra XPS spectrometer uses a helium 1α gas as a discharge in the determination of the workfunction and the DAISY FUN system did not. This means that calculating the workfunction is slightly different. Equation (6.1) is used when using helium, $\text{He}1 = 21.21$ eV, and Equation (6.2) is used when helium is not used.

$$(6.1) \quad \Phi = \text{He}1 - 2_{\text{cutoff}}^{\text{nd}}$$

$$(6.2) \quad \Phi = 2_{\text{cutoff}}^{\text{nd}} - E_F$$

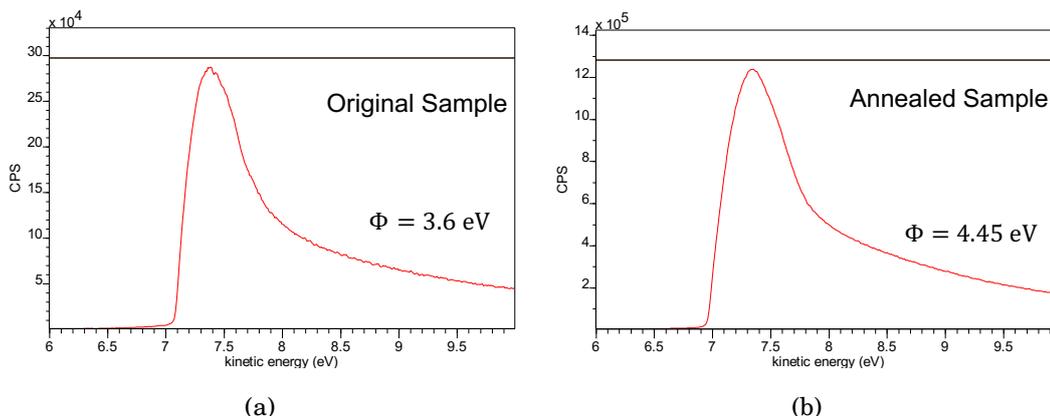


Figure 6.8: UPS spectrum obtained on the DAISY FUN system at Darmstadt University showing the secondary cut-off point and the calculated workfunction for: unprocessed sample (a), and annealed sample (b).

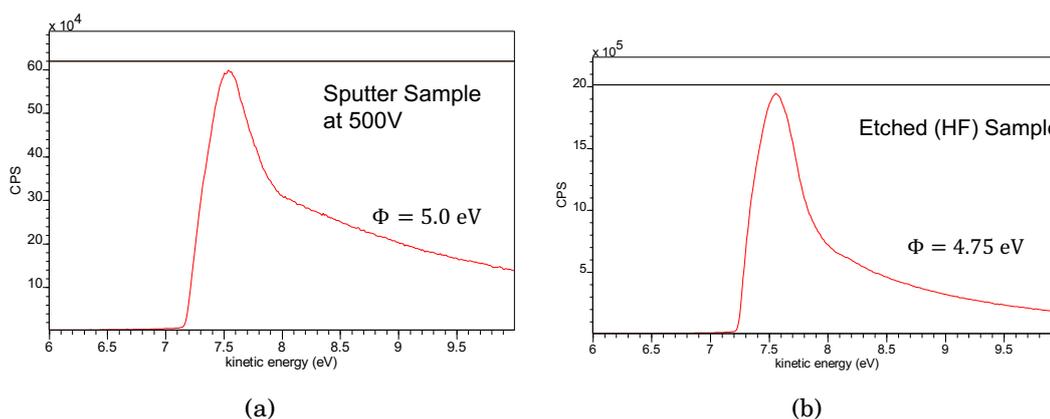


Figure 6.9: UPS spectrum obtained on the DAISY FUN system at Darmstadt University showing the secondary cut-off point and the calculated workfunction for: sputter sample at 500V (a), and wet etched sample with HF (b).

When helium gas discharge is used, the calculation is straightforward as the helium is used as a reference energy and then combined with the secondary cut off point, see Equation 6.1. When the helium is not used we need to know the position of the Fermi level which comes from the XPS valence band data that was measured in Figures 6.5-6.7 and is combined with the secondary cut off point, see Equation 6.2.

Figures 6.8 to 6.10 present a UPS spectra detailing the workfunction for 2 samples which have undergone different surface treatments. A variation in the workfunction can be seen. It can be seen that the workfunction of the Al_4SiC_4 sample increases from 3.6 eV to 5 eV as the cleaning is performed on the sample on the DAISY FUN system at

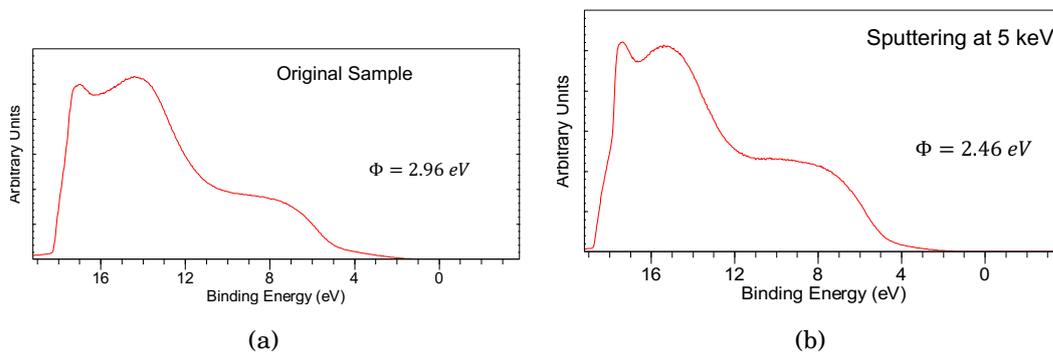


Figure 6.10: UPS spectrum obtained on the Kratos Supra XPS spectrometer at Swansea University showing the secondary cut-off point and the calculated workfunction for: unprocessed sample (a), and sputter sample at 5 keV (b).

Darmstadt University. However, this workfunction increase is not seen with the sample done on the Kratos Supra XPS spectrometer at Swansea University as the workfunction is reduced from 2.96 eV to 2.46 eV after sputtering at 5 keV.

6.3.4 Depth Profiling

Depth profiling is a very useful way to examine a sample. A high resolution scan of selected areas of interest around the carbon, oxygen and aluminum positions is performed after sputtering a sample at 5 keV for 1 minute. Then, another sputtering is performed at the same energy and time length. We repeated this process 35 times cutting into the Al_4SiC_4 sample as seen by the dark square patch in Figure 6.11.

Figure 6.12 shows multiple detailed spectra in the range of 525-543 eV where is the location of the oxygen 1s peak. The spectrum is made up of 35 individual spectra take before each of the 5 eV sputterings. Figure 6.12 therefore details the oxygen 1s peak over the course of the sputterings. The sputtering removes the oxygen from the sample which is evident from the decreasing oxygen 1s peak, but does not vanish all together and, therefore, does not completely remove all of the oxygen from the sample. Note; the first recorded spectra in the 3D plot, Figure 6.12 is at the back of the 3D plot and the last recorded spectra after all 35 sputterings have taken place, is at the front of the 3D plot.

Figure 6.13 shows multiple detailed spectra in the range of 275-295 eV, this is the location of the carbon 1s peak. The spectrum is made up of 35 individual spectra take before each of the 5 eV sputterings. Figure 6.13 therefore details the carbon 1s peak over the course of the sputterings showing that as sputtering is taking place, there is a rise

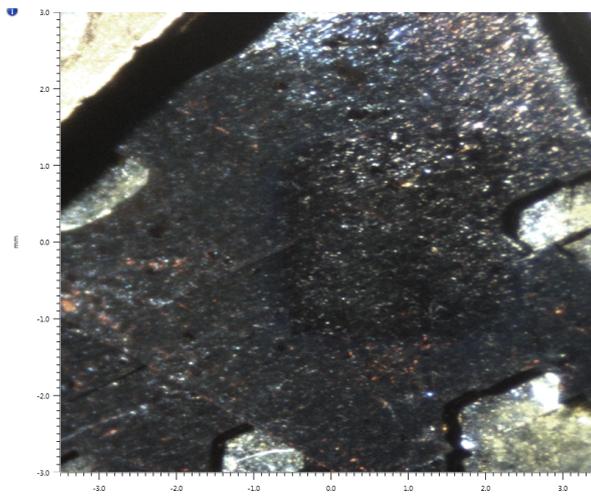


Figure 6.11: Microscope image of the Al_4SiC_4 sample under the Kratos Supra XPS spectrometer showing the area that has been sputtered, by the slightly darker square area.

in the amount of carbon detected. This carbon increase can be detected by a rise in the peak at low binding energy, 282 eV. There is also a peak at high binding energy, 289 eV, which reduces as the sputtering continues. We can analyse these peaks further by taking a cross-section through Figure 6.13, see Figures 6.14 and 6.15. Note; the first recorded spectra is at the front of the 3D plot and the last recorded spectra is at the back of the 3D plot.

Figure 6.14 is taken half way through Figure 6.13 in order to details the diminishing peaks and the rising peaks. The cross-section details three main bonds: C-C, Al-O-C and C-Al. During the sputtering, the C-C bond is decreasing along with the Al-O-C bond and the primary bond, C-Al, is most dominate. This is due to the molecular make-up of Al_4SiC_4 , as shown in Figure 2.2, where the top layer of our sample is showing C-Al and C-C bonds.

Multiple detailed spectra in the range of 66-86 eV, which is the location of the aluminium 2p peak is shown in Figure 6.16. Figure 6.16 is made up of 35 individual spectra taken before each of the 5 eV sputterings and so details the aluminium 2p over the course of the sputtering. Here it can be seen that there is a change in the aluminium bond by a rise in the peak at the lowest energy level and a decrease in the peak at highest energy level. The peaks can be analysed further but taking two cross-section through Figure 6.16, see Figures 6.17 and 6.18.

The first cross-section Figure 6.17 details four main bonds: Al-C, Al-O, Al-O-C, Al-Al

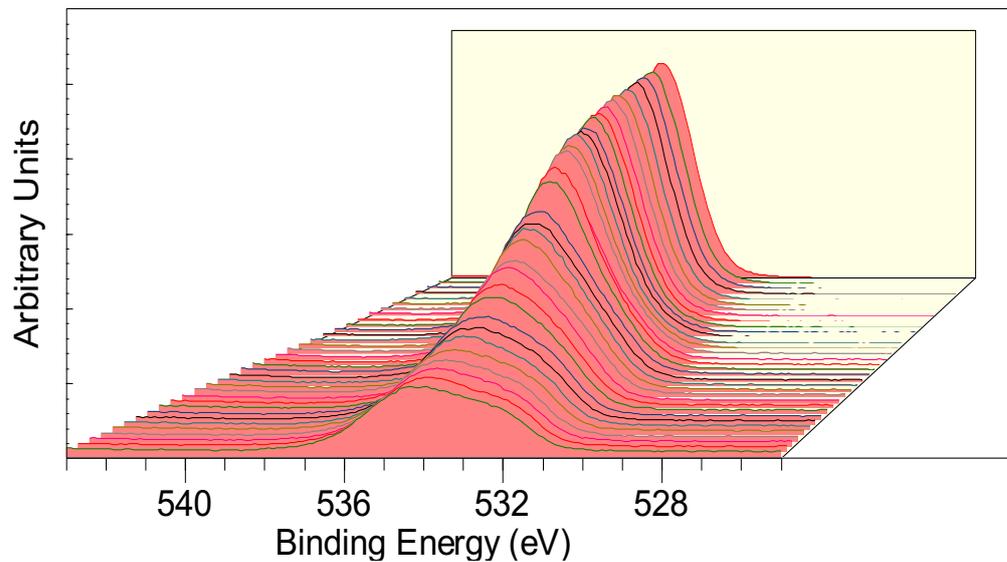


Figure 6.12: Depth profile made up of XPS spectra in the O1s region during the 35 sputterings. The first spectra is at the further point along the z -axis and the last spectra is at the front of the z -axis in order to show the reduction of the O1s peak as the sputters take place

and Al-O. During the 35 sputterings, the Al-O-C and the Al-O bonds are decreasing and the primary bonds, Al-C and Al-Al, come through as most dominant. This is most likely due to the molecular make up of Al_4SiC_4 as illustrated in Figure 2.2 where the top layer of the molecule is made up of Al-C and Al-Al bonds.

6.4 I-V Measurements

Solution grown samples [118] are probed with two separate methods, one a standard two probe method and a four probe Van der Pauw method, as explained in Section 3.9. These samples were prepared by washing them in isopropanol and acetone for 5 minutes each in a sonic bath. The samples are then attached to a sapphire crystal as illustrated in Figure 6.19. Each sample is then probed by moving two sharp titanium tips on to the surface of the samples before current was applied and measurements taken. The results of these measurements are presented in Figures 6.20, 6.21 and 6.22.

An I-V linear region is identified by a straight line (red line on the figure) on Figures 6.20 and 6.21. This is taken in order to calculate the resistivity, resistance, and conductivity of the Al_4SiC_4 sample. The sample was probed on two different system, the Ametek ModuLab XM Material Test System in Grenoble (Neel Institute) and the Ossila

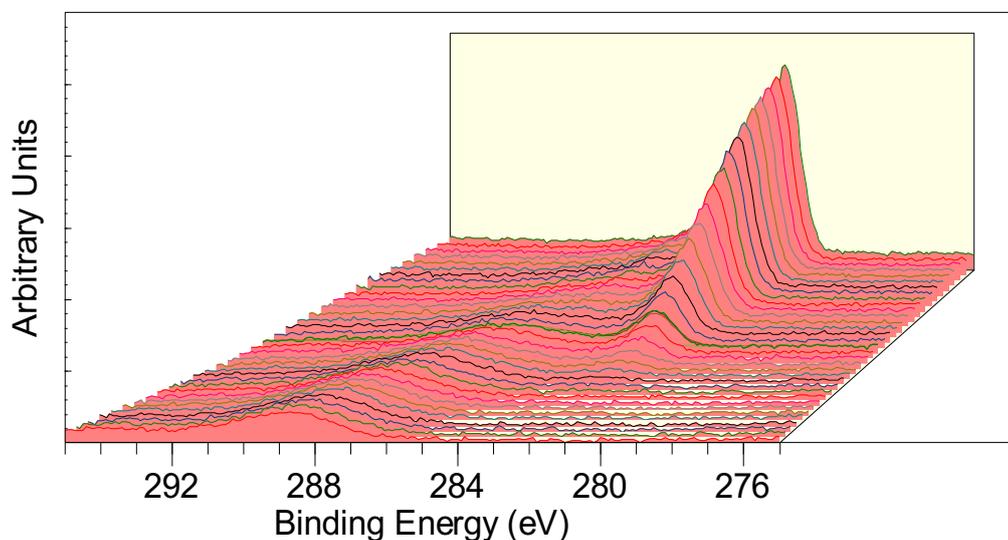


Figure 6.13: Depth profile made up of XPS spectra in the C1s region during the 35 sputterings. The first spectra is at the front of the z -axis and the last spectra is at the further point along the z -axis.

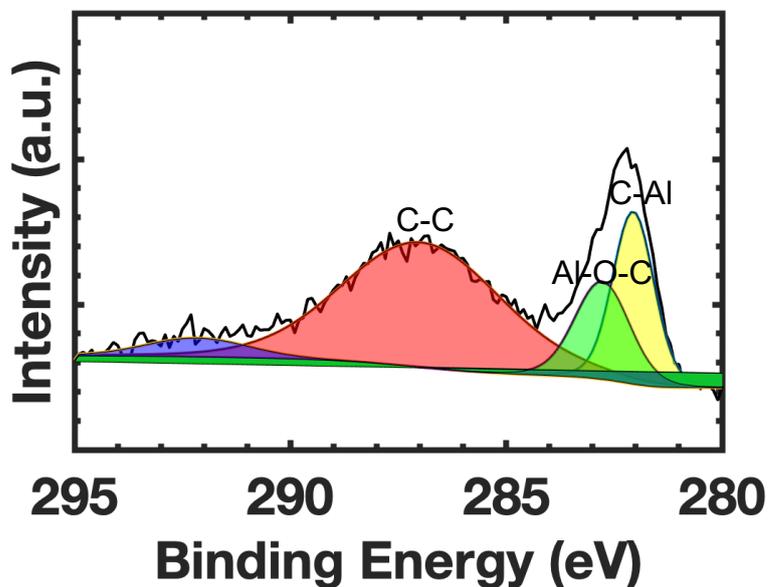


Figure 6.14: XPS spectra taken from the middle of the C1s depth profile, see Figure 6.13, showing the chemical bonds that are present.

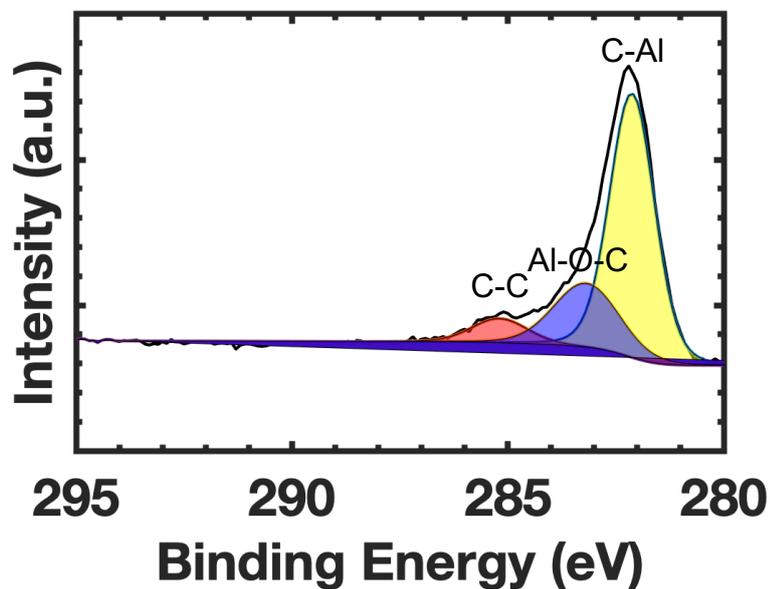


Figure 6.15: Final XPS spectrum of the C1s region after all the 35 sputterings have taken place and showing the chemical bonds that are present.

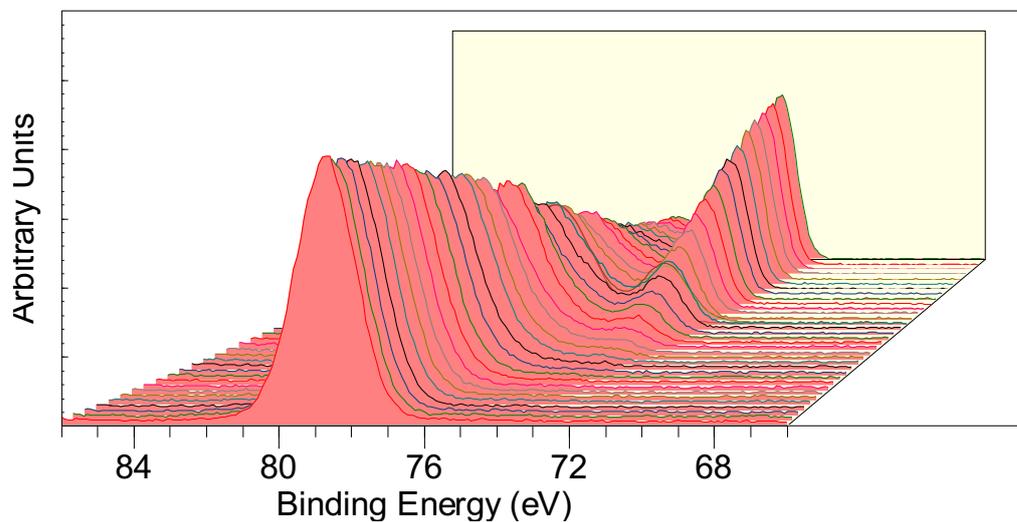


Figure 6.16: Depth profile made up of XPS spectra in the Al 2p region during 35 sputterings. First sputter is at the front of the z -axis and the last sputter is at the back of the z -axis

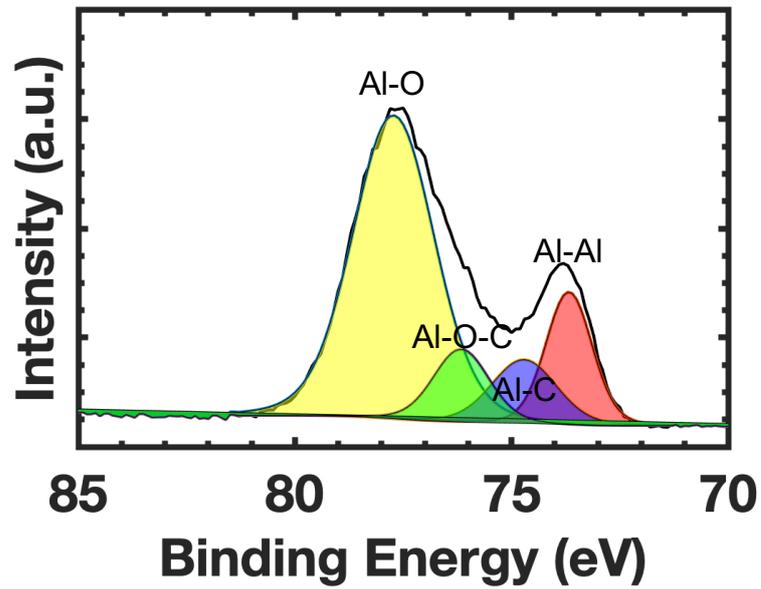


Figure 6.17: XPS spectra taken from the middle of the Al 2p depth profile, see Figure 6.16, showing the chemical bonds that are present.

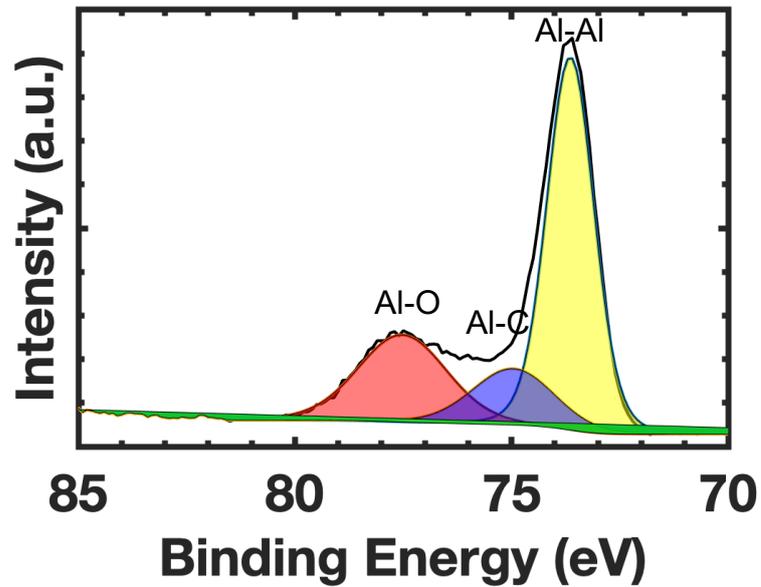


Figure 6.18: Final XPS spectra of the Al 2p region after all the 35 sputterings have taken place and showing the chemical bonds that are present.



FIGURE 6.19. Photographic image of four samples prepared and attached to a sapphire crystal.

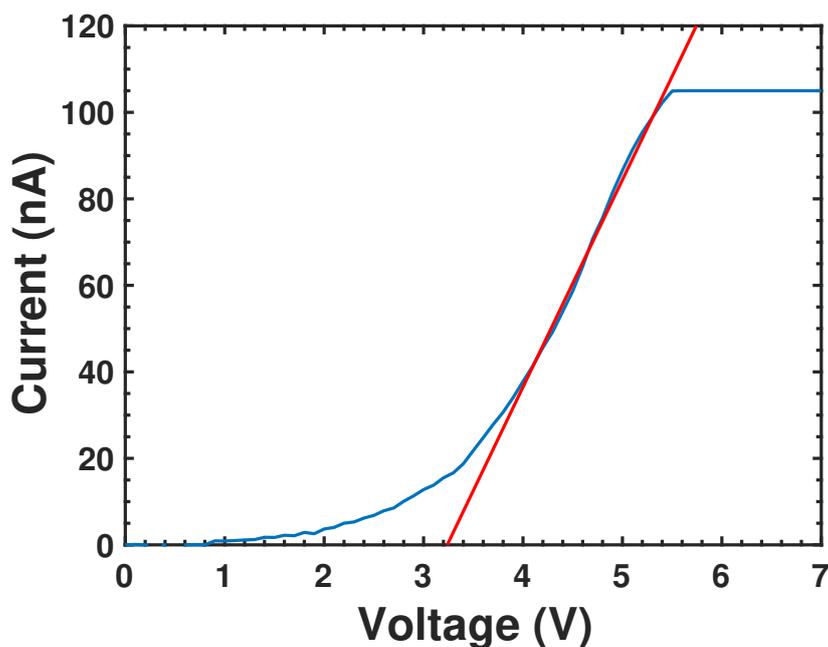


FIGURE 6.20. I-V characteristics obtained from two probe measurements Ossila four-probe system at Swansea University. Blue line shows the data collect and the red line is a linear fit against the slope.

four-probe system in Swansea (Swansea University). There is a lot of noise in the results obtained from on the Ametek ModuLab XM Material Test System compared to the Ossila four-probe system. We also see that the Al_4SiC_4 sample is saturating at around 5.3 V on the Ossila four-probe system, at a lower voltage when compared to 9.8 V on the Ametek

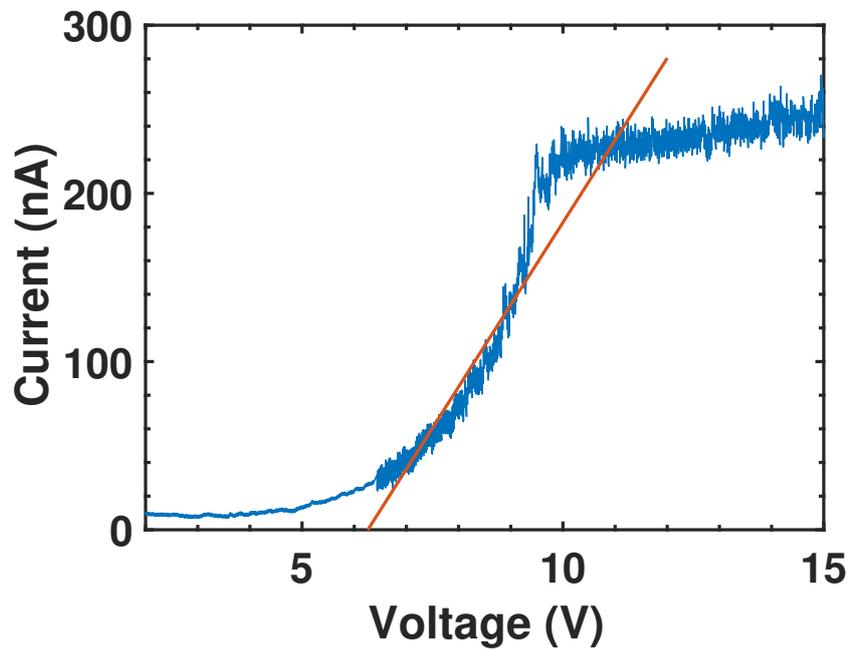


FIGURE 6.21. I-V characteristics obtained from two probe measurements on the Ametek ModuLab XM Material Test System at Neel Institute. Blue line shows the data collect and the red line is a linear fit against the slope.

ModuLab XM Material Test System.

From the probing done in Swansea we have:

$$(6.3) \quad \rho = \frac{I}{V} = 4.79 \times 10^{-8} \Omega m$$

$$(6.4) \quad R = \rho \frac{L}{A} = 4.79 \times 10^{-8} \Omega m \frac{338.71 \times 10^{-6} m}{3.19 \times 10^{-8} m^2} = 5.086 \times 10^{-4} \Omega$$

$$(6.5) \quad \sigma = \frac{1}{R} = \frac{1}{5.086 \times 10^{-4} \Omega} = 1.97 \times 10^3 S m^{-1}$$

Parameters:

L (Distance between probes) = $338.71 \times 10^{-6} m$

W (Width of the sample) = $1276.1 \times 10^{-6} m$

T (Thickness of the sample) = $25 \times 10^{-6} m$

A (Cross-section area) = $W \times T = 3.19 \times 10^{-8}$

Figure 6.22 shows the type of contact that has been made with the probe and the sample which has been identified as a Schottky contact due to the rectifying properties

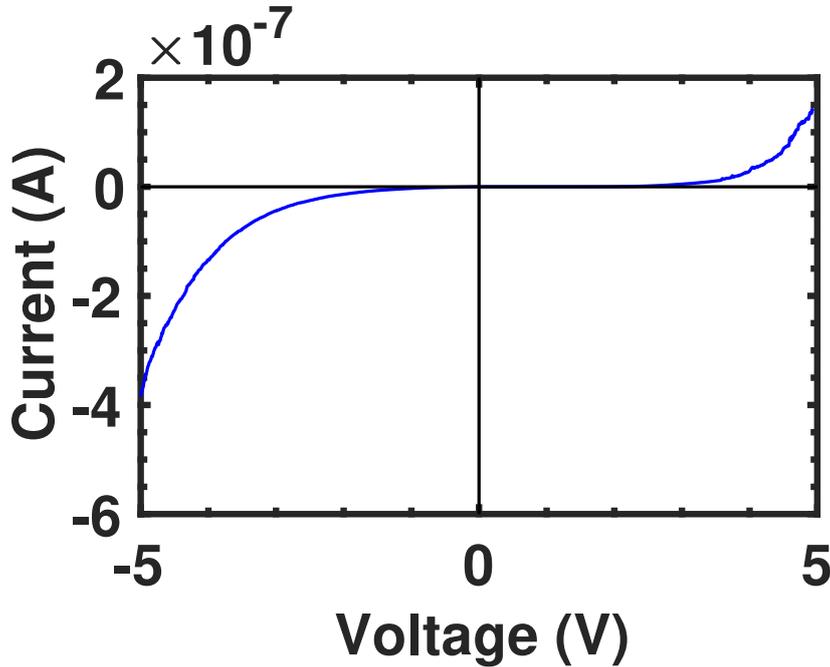


FIGURE 6.22. I-V characteristics obtained from two probe measurements for a sample with silver epoxy contacts showing the type of contact that is being made with the probes and the sample.

Compound	Resistivity (Ωm)	Conductivity ($S m^{-1}$)
Al_4SiC_4 (Swansea)	4.7901×10^{-8}	1.9663×10^3
Al_4SiC_4 (Grenoble)	4.8871×10^{-8}	1.9273×10^3
GaN	10^{-1} [84]	9×10^{-2} [65]
4H-SiC	1.99×10^{11} [63]	10^{-24} [104]

TABLE 6.3. Comparison of resistivity, conductivity for Al_4SiC_4 , un-doped GaN and un-doped 4H-SiC. Note: The the doping has a large impact on the resistivity and conductivity and so these values might vary considerably.

shown on the figure where there the voltage grows exponentially at approximately 3 V and decays exponentially at approximately -2 V.

The resistivity and conductivity of the two samples of Al_4SiC_4 were measured to be almost the same on the two different probing systems, see Table 6.3. Comparing the results of the two-probe measurements with other well known WBG semiconductors we can see that the measured resistivity of the Al_4SiC_4 samples is very small, 7 orders of magnitude, compared to GaN and 19 orders or magnitude smaller than 4H-SiC. As for the conductivity, this is several orders of magnitude higher than GaN and 4H-SiC, 5

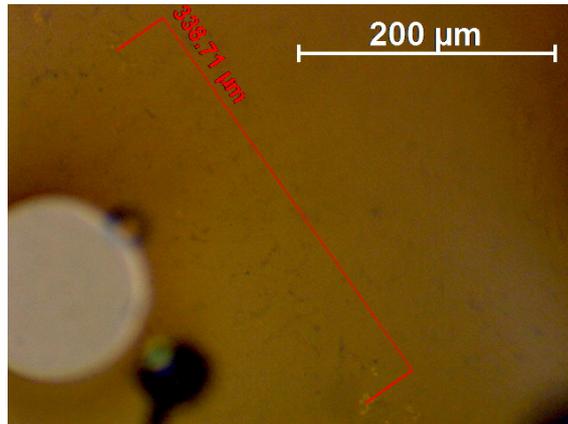


FIGURE 6.23. Microscope image of the Al_4SiC_4 sample showing the measured distance between the two probes.

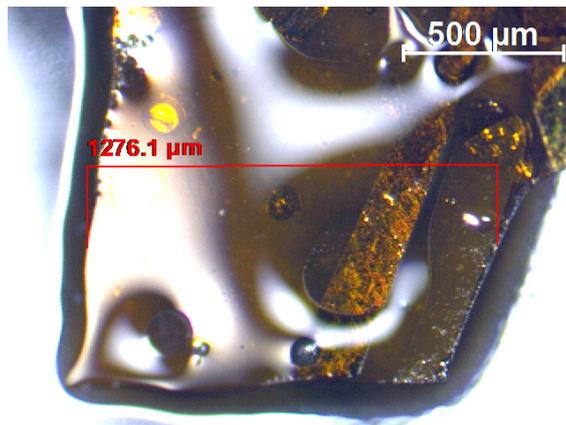


FIGURE 6.24. Microscope image of the Al_4SiC_4 sample showing the measured width of the sample.

order of magnitude and 27 order of magnitude respectively. These results make Al_4SiC_4 a viable semiconductor for use in the electronics industry due to its low resistivity, $4.79 \times 10^{-8} \Omega m$, and high conductivity, $1.97 \times 10^3 S m^{-1}$. However we believe these results to be measuring the contact resistance of probes rather than the sample itself, and so further investigation would be needed to confirm this.

The four-probe measurements are performed in a similar way to the two-probe measurements. Four-probes measurements seen in Figure 6.25 have a voltage applied across two of the probes and a current measured across the other two.

Issues with gaining a good contact with the sample and the probe are found. Therefore, the probing is performed on Al_4SiC_4 samples after the addition of contacts to the surface

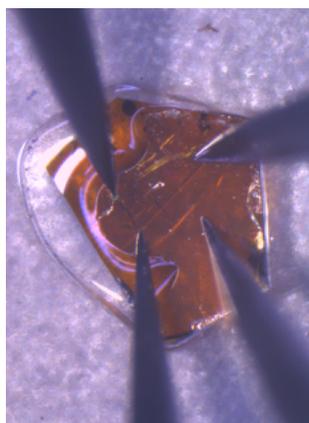


FIGURE 6.25. Microscope image on the Ametek ModuLab XM Material Test System showing the Al_4SiC_4 sample with four probes attached.

of the sample. This is done in order to reduce the contact resistance between the sample and the probes. Two different contact are used: silver epoxy and deposited titanium. The silver epoxy is a silvery/white paste that is applied to the Al_4SiC_4 in four locations using a needle in order to get four small contacts for the titanium probes to be located on. The titanium contact are deposited by using a mask and a deposition process, six titanium contact are deposited in total, where only four are used in the probing process. The titanium contacts can be seen in Figure 6.26.

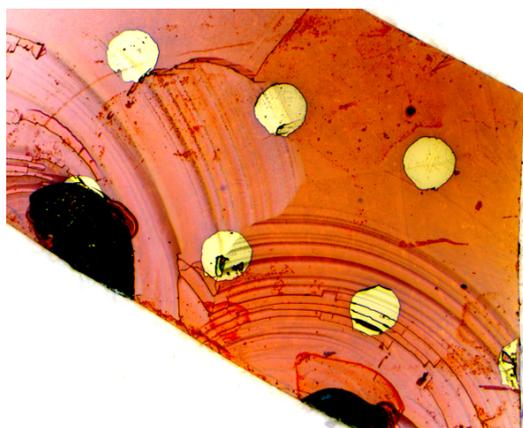


FIGURE 6.26. Microscope image of a Al_4SiC_4 sample with six titanium contacts grown on top.

The best results obtained from the four-probe measurements of Al_4SiC_4 samples shows a small current (-10×10^{-4} to 2.5×10^{-4}) is seen when a negative bias is applied across the voltage probes. Additionally, we had a sample showing only a small positive

current ($0 - 6 \times 10^{-5}$) at a small negative bias of -9×10^{-4} to -5×10^{-4} . Due to the magnitude of both the current and the voltage for these samples it would appear that we have not measured the I-V characteristics of the sample, but instead measured noise on the apparatus.

6.5 Conclusion

Solution grown crystals [118] of Al_4SiC_4 have been examined by use of UV/Vis/NIR spectroscopy in order to ascertain their bandgap. By taking further band tailing into account, the technique has revealed a bandgap of 2.778 ± 0.02 eV which is inline with reported Valence Electron Energy-Loss Spectroscopy (VEELS) experiment [31]. The VEELS experiment was carried out at the University of Cadiz in Spain on a transmission electron microscope (TEM) Field Electron and Ion Company (FEI) Titan Themis system which revealed a bandgap of $2.8 \text{ eV} \pm 0.2 \text{ eV}$.

Crucible grown sample were examined by XPS on two different set ups, the Darmstadter Integrated System for Fundamental Research (DAISY FUN) system at Darmstadt University and on a Kratos Supra XPS spectrometer at Swansea University. The workfunction, valence band and chemical composition were all studied. The data on the workfunction varied from giving a workfunction of $5.0 - 2.46$ eV between the two systems and varied depending on the surface treatment that was performed on the Al_4SiC_4 samples. This variability in workfunction data has made it difficult to make any correlation with the data and the samples and, therefore, further studies of this would be needed in order to ascertain any correlation.

The sample used at Swansea University seems to have bigger oxidation layer than the sample used at Darmstadt University. This oxidation layer seems to have a direct impact on the position of the valence band and thus the location of the Fermi level. The thicker this oxidation layer the higher the valence band sits at, 5.75 eV was the measured position of the valence band on the Kratos Supra XPS spectrometer system, and therefore a higher Fermi level is in the material, thus making it an *n*-type material. As this oxidation layer is removed by surface treatment, the material changes its intrinsic doping characteristic from *n*-type to *p*-type, this was seen after the harshest treatment of 5keV where a valence band position drops from 5.75 eV to 0.45eV . Through the XPS, we have been able to show that contamination from the samples of Al_4SiC_4 can be removed through various surface treatments. The oxygen contamination is the hardest to remove and need a high energy treatment in order to remove it.

The I-V characteristic measurements taken from electrical probing with two probes seems to have only revealed the contact resistance as this must be higher than the sample resistance. We had been able to show that a Schottky contact is present on the sample. In order to mitigate the issue of large contact resistance, we have measured the I-V characteristics by four-probe and with the introduction of contacts on the sample both by silver epoxy and deposited titanium. The magnitude of the current obtained by the four-probe measurements is so small that the measured current contains large amount of noise from the apparatus rather than observable I-V characteristics. This could be an issue with the apparatus set-up or the thick oxidation layer that has been seen on the surface of Al_4SiC_4 sample during XPS.

SUMMARY AND CONCLUSION

This chapter will give a short summary of the obtained results from both the computation and the experimental works. It will then discuss the consequences in a broader context and, finally, it will give an outlook on possible future works.

7.1 Summary

The goal of this work was to evaluate a novel wide bandgap semiconductor material based on ternary carbides, that being Al_4SiC_4 , for applications in the electronics industry, primarily power electronics. Both computational and experimental approaches were used in various applications to ascertain the opto-electronic properties of Al_4SiC_4 . The computational approach looked at two different areas: (1) bulk electrical properties of Al_4SiC_4 and was simulated based on an ensemble Monte Carlo code; and (2) device modelling based on a $\text{SiC}/\text{Al}_4\text{SiC}_4$ heterostructure transistor modelled through Silvaco Atlas [67]. The experimental approach saw three experiments undertaken: (1) UV/Vis/NIR Spectroscopy looked at defining the bandgap of Al_4SiC_4 , (2) XPS looked at the workfunction, a position of the valence band and the overall composition of Al_4SiC_4 , and (3) two- and four-probe DC current voltage characteristics which looked the resistivity of Al_4SiC_4 . The experiments used samples of Al_4SiC_4 that were grown at Grenoble University [108, 118].

Experimental and computational data on material properties of Al_4SiC_4 are rare and often inaccurate also because Al_4SiC_4 is difficult to model computationally. Therefore, scattering potentials for electron-phonon interaction as well as [WHAT ELSE] to be

chosen from material properties of much better know materials. We opted for material properties for 4H-SiC as the semiconductor closest to the material properties of Al_4SiC_4 .

In this work, we have employed an in-house bulk ensemble MC simulation code to foresee electron transport properties of Al_4SiC_4 . The bulk MC simulations assume a two-valley model for the conduction band of Al_4SiC_4 because the M and K valleys are principal valley in the conduction band as illustrated in Fig. 2.1, within an analytical non-parabolic anisotropic band structure. The simulation code was enhanced by including a rotational transformation for the lowest conduction band, the M valley. The MC code incorporates electron effective masses extracted from DFT calculations. The DFT calculations have shown that there is a large effective mass in both the longitudinal and transverse directions for the K valley of $1.0569 m_e$ and $0.9360 m_e$, respectively, compared with those for the M valley of $0.6952 m_e$ and $0.5678 m_e$, respectively, where m_e is the electron mass in vacuum. The large effective masses in the M valley have profound impact on the electron drift and mobility.

The MC simulations allows to predict material transport properties in Al_4SiC_4 . We have predicted dependence of electron drift velocity, electron mobility, average kinetic energy of electrons, and electron population against the applied electric field, all of which can serve as crucial indicators to assess the electronic and opto-electronic performance of devices. We have shown that the electron drift velocity increases with increasing electric field reaching $1.35 \times 10^7 \text{ cms}^{-1}$ at approximately 1400 kVcm^{-1} . The average electron kinetic energy has a linear increase as expected and reaches 1.24 eV at 1400 kVcm^{-1} . The threshold energy barrier, when electron start to transfer from the M valley to the K valley, occurs at electric field of approximately 450 kVcm^{-1} . When the electric field approaches the critical field of 1831 kVcm^{-1} , the number of electrons with higher energy that is larger than the band gap of the material will start to increase rapidly causing a breakdown of the material.

The bulk transport properties of Al_4SiC_4 predicted by the ensemble Monte Carlo modelling has been compared with properties of know semiconductor materials including drift velocity and electron mobility. A maximum drift velocity of Al_4SiC_4 is only 61.4 % of the maximum drift velocity of GaN ($2.2 \times 10^7 \text{ cms}^{-1}$) and electron mobility of Al_4SiC_4 is 6.7 % of the GaN electron mobility ($1250 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) [76]. When the transport properties of Al_4SiC_4 are compared to 6H-SiC, Al_4SiC_4 is only 67.5 % of the maximum drift velocity of 6H-SiC ($2 \times 10^7 \text{ cms}^{-1}$) and only 16.6 % of the 6H-SiC electron mobility ($500 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) [76]. Finally, when the transport properties are compared to silicon, Al_4SiC_4 is 135 % of the maximum drift velocity of silicon ($1 \times 10^7 \text{ cms}^{-1}$) and only 5.5 % of the silicon electron

mobility ($1500 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) [76].

A performance of heterostructure transistor made of SiC/Al₄SiC₄ material system with a novel ternary carbide of Al₄SiC₄ has been simulated in commercial simulator Atlas by Silvaco using known experimental [31] and theoretical data [32]. The heterostructure transistor with a gate length of $5 \mu\text{m}$ and two heterostructure transistors scaled to gate lengths of $2 \mu\text{m}$ and $1 \mu\text{m}$, with respective lateral scaling of source-to-gate distance, channel length, and gate-to-drain distance, have been studied using a drift-diffusion transport model. The variants of asymmetric scaled heterostructure transistors with the increased gate-to-drain distance to achieve a larger breakdown voltage have been also studied. The device modelling through Silvaco Atlas consider a 2D drift-diffusion transport model with field dependent mobility and Auger recombination simulating both holes and electrons.

The device modeling predicted that all of the devices remained off when assuming a metal gate workfunction of 3.9 eV unless a gate bias was applied. Therefore, the SiC/Al₄SiC₄ heterostructure transistor provides a *n*-channel enhancement-mode, normally-off device operation. I_D - V_G (drain current-gate voltage) characteristics in a range of drain biases were obtained for the heterostructure device. The I_D - V_G characteristics exhibit well defined linear and saturation regions but the increase in the saturation current in the I_D - V_G characteristics start to reduce with the drain bias increase. This reduction in the increase in the saturation current is due to a limitation in the increase in electron density at the heterostructure interface creating the device channel which is determined by the conduction band off-set. Additionally, other characteristics that were investigated are transconductance, device breakdown, and a comparison between three devices scaled laterally.

The threshold voltage reduces as the gate length is reduced from 71.0 mV to 28.3 mV, and to 28.3 mV for $5 \mu\text{m}$, $2 \mu\text{m}$, and $1 \mu\text{m}$ gate length transistors, respectively. Sub-threshold voltages of 197.3 mV/dec, 97.6 mV/dec, and 96.1 mV/dec for gate lengths of $5 \mu\text{m}$, $2 \mu\text{m}$, and $1 \mu\text{m}$, respectively, are observed which are, in all cases, much larger than the ideal value of 60 mV/dec at 300 K. The bias point at which the device breakdown occurs reduces from 59.0 V to 31.0 V and to 18.0 V as the gate length reduces from $5 \mu\text{m}$ to $2 \mu\text{m}$ and to $1 \mu\text{m}$, respectively. The breakdown voltage can be increased to 48.25 V when we increase the gate-to-drain spacer to $2.5 \mu\text{m}$ in the $2 \mu\text{m}$ gate device, and to 22.75 V and to 29.25 V in the $1 \mu\text{m}$ gate device when the gate-to-drain spacer is increased to $1.0 \mu\text{m}$ and to $2.5 \mu\text{m}$. The drain current saturation region occurs at smaller gate bias with the reduction of the gate length. At a large drain voltage of 40 V, a drain current

saturation appears at $1.68 \times 10^{-4} \text{ A}/\mu\text{m}$, $2.44 \times 10^{-4} \text{ A}/\mu\text{m}$, and $3.50 \times 10^{-4} \text{ A}/\mu\text{m}$ for gate lengths of $5 \mu\text{m}$, $2 \mu\text{m}$, and $1 \mu\text{m}$, respectively.

Experimental characterisation was carried out with samples of Al_4SiC_4 employing: (1) UV/Vis/NIR Spectroscopy, (2) XPS, and (3) two- and four-probe DC current voltage measurements. UV/Vis/NIR Spectroscopy was performed on solution grown samples of Al_4SiC_4 [118] in order to ascertain the bandgap of Al_4SiC_4 . Due to the small size of the Al_4SiC_4 samples, the default apertures for the spectrophotometer were too large for the samples to be attached and so we had to create smaller apertures in order to accommodate the samples of Al_4SiC_4 that were being used. Once this had been implemented with the spectrophotometer, a bandgap of $2.78 \pm 0.02 \text{ eV}$ was ascertained. This bandgap was inline with our reports of VEELS experiments [31] that found a bandgap of $2.8 \pm 0.2 \text{ eV}$. Once we had this bandgap, we fed it back into the Monte Carlo simulator and device simulator in order to get a more accurate prediction of the electron transport properties of Al_4SiC_4 .

The XPS was performed on crucible melted samples of Al_4SiC_4 [108] in order to look at the workfunction, valence band and chemical make-up of Al_4SiC_4 . The XPS revealed a thick layer of oxide on the sample which was hard to remove and, therefore, affected our results. The affect of this oxide layer is an indeterminate workfunction as the measurements varied from $5.0 - 2.46 \text{ eV}$ between the two systems and varied depending on the surface treatments. The oxide layer also gave a variation in the position of the valence band and the location of the Fermi level. The position of the Fermi level seems to be directly linked to the thickness of the oxide layer. The thicker the oxidation layer is the larger n -type doping occurred in the material indicated by the valence band sitting at 5.75 eV . As this oxidation layer was reduced through surface treatment, the valence band position reduced to 0.45 eV and the material became lightly p -type doped. The XPS also showed that various surface treatments can remove surface contamination where the oxide was hardest to remove.

The two- and four-probe experiments were carried out to ascertain the resistivity of Al_4SiC_4 . However, this proved to be futile as we were unable to overcome the contact resistance despite trying different contacts on the samples. The obtained results either showed the contact resistance or did not show any reliable results because only noise was recorded. This was most likely due to a thick layer of oxide residing on the surface of the Al_4SiC_4 samples.

7.2 Conclusion

Al_4SiC_4 is a robust material suitable for use in harsh environments, primarily due to its wide bandgap of 2.78 ± 0.02 eV which was measured by UV/Vis/NIR Spectroscopy in this work. The predicted material properties from our ensemble MC bulk code show a limited usage of the Al_4SiC_4 as a channel material of potential metal-oxide-semiconductor field effect transistors (MOSFETs) due to a maximum electron drift velocity and electron mobility of 1.35×10^7 cm s^{-1} and $83 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively. Al_4SiC_4 has a lower electron drift velocity compared to GaN. However, the drift velocity gives better continuity at high electric field which could be of some benefit to the power electronic industry. The low electron drift velocity and electron mobility is primarily due to the high electron effective masses that were extracted from band-structure data obtained by DFT calculations. Future works would need to look at the values for the electron effective mass to see if experimental works can confirm the predicted electron mobility and electron drift velocity.

It is therefore the opinion of the author that Al_4SiC_4 would be a weak material for use in power electronics unless further studies reveal better material properties such as a high electron drift velocity and electron mobility. Al_4SiC_4 would also need to be grown in larger crystal sizes than what was used in this work as it was very difficult at times to use the $< 5\text{mm}^2$ samples.

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