Theoretical and experimental study of semiconducting iron disilicide and its applications to thin film solar cells

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**THEORETICAL AND EXPERIMENTAL STUDY OF
SEMICONDUCTING IRON DISILICIDE AND ITS
APPLICATIONS TO THIN FILM SOLAR CELLS**

TAN KHING HONG
SCHOOL OF ELECTRICAL AND ELECTRONIC ENGINEERING
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ABSTRACT

Transition metal silicides have been studied extensively for many years due to their potential technological importance and applications. Recently, the semiconducting phase of iron disilicide (β -FeSi₂) has received considerable attention due to its potential applications in optoelectronic and microelectronic areas. This is attributed to its direct bandgap of 0.86 eV that corresponds to $\sim 1.5 \mu\text{m}$ of the optical fiber communication. In addition, β -FeSi₂ is expected as a promising photovoltaic material with a theoretical conversion efficiency as high as 23% due to its ultrahigh optical absorption coefficient in the order of 10^5 cm^{-1} near the absorption edge. These properties, along with other features such as abundance of constituent elements, nearly lattice-matched to Si, and high thermal stability and oxidation resistance, have made β -FeSi₂ one of the most attractive materials of choice for future generation thin film photovoltaic applications.

In this work, both theoretical and experimental study of β -FeSi₂ was explored. The theoretical study based on the first-principles calculations provides the fundamental understanding of various properties of β -FeSi₂, including equilibrium crystal structure, bandgap properties, effects of native vacancy defects, and impurity doping in β -FeSi₂. The experimental study involves the formation and structural, optical, and electrical characterization of sputtered and processed β -FeSi₂ as well as eventual demonstration of semiconducting β -FeSi₂-based heterojunction thin film solar cells on the Si platform.

First-principles calculations revealed the existence of both direct and indirect transitions in β -FeSi₂ and confirmed its semiconducting property. The presence of Fe or

Si vacancies was found to introduce energy levels in the forbidden gap and affect the electrical conductivity of β -FeSi₂ depending on the types of vacancy defects, with Fe vacancies produce donor-like defect states below the conduction band while Si vacancies produce acceptor-like defect states above the valence band. Boron (B) and Arsenic (As) were shown to be shallow impurities in β -FeSi₂ and therefore could be effective dopants for β -FeSi₂. In particular, *p*-type and *n*-type conductivities were suggested for the B- and As-doped β -FeSi₂, respectively. The impurity doping was found to induce structural relaxation via lattice distortion, with As doping causing elongation of the As-Si bonds and contraction of the As-Fe bonds while B doping resulting in both inward and outward relaxations of the neighboring Si and Fe host atoms.

Structural analysis conducted on the sputter-deposited and rapid thermal annealed FeSi₂ films confirmed the formation of semiconducting β -FeSi₂ at ≥ 500 °C, below which the films remained fully amorphous. Optical absorption study based on the proposed optical absorption model concluded a direct bandgap behavior for both amorphous and polycrystalline semiconducting FeSi₂. A high optical absorption coefficient in the order of 10^5 cm⁻¹ at 1.0 eV and a direct bandgap of 0.86 eV were determined for β -FeSi₂. The observed subgap optical absorption could be attributed to the band tailing and correlated with the residual carrier concentration. Electrical characterization indicated *n*-type conductivity for the FeSi₂ on the *p*-Si, whose electrical junction was found to exhibit good rectifying characteristics at 800 °C.

The effects of B and As doping in β -FeSi₂ formed by ion implantation technique were also studied experimentally. The conductivity modulation for doping control can be achieved, with B and As doping giving rise to the *p*-type and *n*-type films, respectively,

which confirmed the theoretical predictions. A carrier concentration in a tunable range of 10^{17} cm^{-3} and a mobility in the order of $100 \text{ cm}^2/\text{Vs}$ were consistently obtained. Using this knowledge, *p*-type B-doped $\beta\text{-FeSi}_2/n\text{-Si}$ heterojunction thin film solar cells were fabricated. The effects of various physical parameters on the output characteristics of the cells were investigated and found to have a direct influence on the cell performance.

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LIST OF ABBREVIATIONS

2D	two-dimensional
AFM	atomic force microscopy
AM	air mass
AR	antireflection
ASW	augmented spherical wave
BFGS	Broyden-Fletcher-Goldfarb-Shanno
BZ	Brillouin zone
CASTEP	Cambridge serial total energy package
CBM	conduction band minimum
CMOS	complementary metal-oxide-semiconductor
CVD	chemical vapor deposition
DC	direct current
DFT	density-functional theory
DOS	density of states
DUV	deep ultraviolet
EDS	energy dispersive X-ray spectroscopy
EHP	electron-hole pair
FA	furnace annealing
FESEM	field-emission scanning electron microscopy
<i>FF</i>	fill factor

FGA	forming gas annealing
FLAPW	full-potential linearized augmented plane wave
FTS	facing-target sputtering
GADDS	general area detector diffraction system
GGA	generalized gradient approximation
HF	hydrofluoric acid
HRTEM	high resolution transmission electron microscopy
IBS	ion beam synthesis
IC	integrated circuit
IR	infrared
ITO	indium tin oxide
I - V	current-voltage
JCPDS	joint committee on powder diffraction standards
LDA	local density approximation
LMTO	linear muffin-tin orbital
MBE	molecular beam epitaxy
MIS	metal-insulator-semiconductor
MOSFET	metal-oxide-semiconductor field-effect transistor
MP	Monkhorst-Pack
PBE	Perdew-Burke-Ernzerhof
PDOS	partial density of states
PLD	pulsed laser deposition
PV	photovoltaic

PVD	physical vapor deposition
RCA	Radio Corporation of America
RDE	reactive deposition epitaxy
RF	radio frequency
RMS	root mean square
RT	room temperature
RTA	rapid thermal annealing
RTP	rapid thermal processing
SEM	scanning electron microscopy
SIMS	secondary ion mass spectroscopy
SRIM	stopping and range of ions in matter
TEM	transmission electron microscopy
TM	transition metal
TOF-SIMS	time-of-flight secondary ion mass spectroscopy
UHV	ultrahigh vacuum
USP	ultrasoft pseudopotential
VBM	valence band maximum
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Background

Transition metal (TM) silicides have been studied extensively for many years due to their potential technological importance and applications. The interest in TM silicides essentially originates from the two important properties that are generally present in these materials, i.e., (1) their low and metal-like electrical resistivity and (2) high thermal stability and oxidation resistance. Refractory metal silicides such as WSi_2 , TaSi_2 , and MoSi_2 were widely used for the gate structures in earlier metal-oxide-semiconductor field-effect transistors (MOSFETs) that contain a non-self-aligned silicide [1]. TiSi_2 and CoSi_2 were promising candidates for the self-aligned silicide (also referred to as the *salicide*) applications [1, 2]. NiSi has lately emerged as the leading candidate in advanced Si-based complementary metal-oxide-semiconductor (CMOS) technology [1, 3, 4].

While metallic silicides have traditionally been the mainstay of research investigations, semiconducting silicides have gained significant interest in recent years. Among the semiconducting TM silicides, beta-phase iron disilicide ($\beta\text{-FeSi}_2$) has received considerable attention due to its potential applications in optoelectronic and microelectronic areas [5, 6]. This is largely attributed to its direct bandgap of 0.86 eV that corresponds to $\sim 1.5\ \mu\text{m}$ of the optical fiber communication [7]. In addition, $\beta\text{-FeSi}_2$ is expected as a promising photovoltaic (PV) material with a theoretical conversion efficiency as high as 23% [8] due to its high optical absorption coefficient in the order of

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10^5 cm^{-1} near the absorption edge [7]. This ultrahigh optical absorption coefficient has made $\beta\text{-FeSi}_2$ a very attractive material of choice for thin film PV applications.

In thin film PV applications, due to the reduced material requirements, numerous viable processing techniques, and hence lower cost, virtually any semiconductor can be used. Some existing thin film PV technologies include III-V (InP, InGaP, GaAs, and AlGaAs), II-VI (CdS and CdTe), and other compound semiconductors such as CdInSe₂, Cd(In,Ga)Se₂, etc. The majority of these chemical elements have limited known reserves to match the future demand of the mass production as low cost solar cells. For future generation PV devices, one of the major considerations comes from the materials availability, which is also the demand issued from the semiconductor industries in the early 21st century that environmentally friendly (nontoxic) and abundant chemical elements should basically be used for the fabrication of various practical energy devices [9].

It was reported that a number of unconventional solar cell candidates, including FeS₂, possess low material extraction cost and sufficient capacity to meet global demands [10]. Semiconducting $\beta\text{-FeSi}_2$, being rationally defined as a “Kankyo (environmentally friendly) Semiconductor” [11], is composed of two most abundant and nontoxic chemical elements (i.e., Fe and Si) and expected to be capable of meeting future energy demands. Besides the aforementioned high optical absorption coefficient and theoretical conversion efficiency as well as direct bandgap behavior, $\beta\text{-FeSi}_2$ is nearly lattice-matched to Si and also highly resistant to oxidation and chemically stable at temperatures as high as 937 °C [12]. These features are of great importance and make $\beta\text{-FeSi}_2$ potentially one of the most promising materials for future generation thin film PV applications.

1.2 Objectives

The project aims to study the structural, optical, and electrical properties of sputtered and processed β -FeSi₂ and to demonstrate the application potential of β -FeSi₂ to thin film solar cells on the Si platform. This will be achieved in four phases as follows:

1. To study theoretically the equilibrium crystal structures of β -FeSi₂, the effects of vacancy defects on the electrical conductivity, and the effects of B and As doping in β -FeSi₂. The theoretical study was performed by first-principles calculations based on the density-functional theory (DFT).
2. To study the structural, optical, and electrical properties of unintentionally doped β -FeSi₂ formed by direct sputter deposition from a stoichiometric iron disilicide target via rapid thermal annealing (RTA) and their evolution with annealing temperature.
3. To study the doping effects of B and As in β -FeSi₂ formed by ion implantation into the silicide thin films and subsequently RTA and to characterize the electrical properties of B- and As-doped β -FeSi₂ thin films.
4. To demonstrate semiconducting β -FeSi₂-based heterojunction thin film solar cells on the Si platform. To study the output characteristics and performance of the β -FeSi₂/Si heterojunction solar cells and to investigate the effects of key physical parameters on the cell performance.

1.3 Scope of the Project

This project involves both theoretical and experimental study of β -FeSi₂. The theoretical study provides the fundamental understanding of various properties pertinent

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to β -FeSi₂, such as equilibrium lattice parameters, bandgap properties, effects of vacancy defects and impurity doping in β -FeSi₂, which support and complement the experimental results. The project involves the formation and characterization of sputter-deposited and RTA-annealed FeSi₂ thin films. The structural, optical, and electrical properties of the silicide films as well as their evolution with annealing temperature were investigated. The project also studies the effects of B and As doping on the electronic and structural properties of β -FeSi₂. The effectiveness of B and As as the p -type and n -type dopants in β -FeSi₂ for doping control, respectively, were explored. Using this knowledge, various p -type B-doped β -FeSi₂/ n -Si heterojunction thin film solar cells were fabricated. Electrical characterization was performed to study the output characteristics and performance of these PV devices.

This project covers numerous materials and device characterization techniques. The main characterization techniques used include X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), secondary ion mass spectroscopy (SIMS), photo-absorption measurements, four-point probe measurement, Hall effect measurements, and current-voltage (I - V) measurements.

1.4 Organization of the Thesis

The organization and outline of various chapters of this thesis are provided as follows.

Chapter 1 provides an introductory overview related to the TM silicides, in particular, the semiconducting β -FeSi₂ and its potential capabilities for future generation thin film PV applications. It also describes the objectives and scope of this project.

Chapter 2 gives a detailed review on the key findings in the earlier work on β -FeSi₂. The material properties and formation of β -FeSi₂ as well as its applications to thin film solar cells are presented. It covers the fundamental physics and operation of solar cells. In addition, theoretical studies on β -FeSi₂ are reviewed.

Chapter 3 describes the experimental methodology that includes thin film silicide formation and materials as well as device characterization techniques used in this project.

Chapter 4 presents the first-principles study of β -FeSi₂ based on the DFT. It describes the basic principles and simulation approaches used in the calculations. The crystal properties of β -FeSi₂ are studied. The effects of Fe and Si vacancies are also investigated. In addition, the effects of B and As doping in β -FeSi₂ are discussed.

Chapter 5 studies the structural, optical, and electrical properties of FeSi₂ thin films and their evolution as a function of RTA temperature. The phase evolution and microstructures of silicide thin films are examined. The optical absorption and bandgap properties are studied. The carrier transport properties and diode characteristics are also discussed.

Chapter 6 presents the electrical study on the impurity-doped β -FeSi₂ thin films formed by ion implantation technique. The distribution profiles of implanted dopant ions are studied. The effects of B and As doping on the electrical properties of B- and As-doped β -FeSi₂ are investigated. In addition, the effects of Si doping in β -FeSi₂ are discussed.

Chapter 7 studies the PV characteristics of p -type B-doped β -FeSi₂/ n -type Si heterojunction thin film solar cells. The fabrication process and characterization of solar cells are described. The transmittance spectra and photocurrent generation of silicide are

studied. The photocurrent enhancement and the impact of area effect on the performance parameters are also discussed. In addition, the output characteristics and the effects of various physical parameters are investigated.

Chapter 8 summarizes the major results and findings in this project. It also offers future research direction based on the results of this project.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter gives reviews of some related work which described the material properties and formation of β -FeSi₂ as well as its applications to thin film solar cells. Relevant fundamental theories and operating principles of solar cells are elucidated with the case of conventional *pn* junction. In addition, theoretical studies on β -FeSi₂ by first-principles calculations are summarized and presented.

2.2 Semiconducting Silicides

2.2.1 General properties

Silicon forms many stable compounds with metals and such compounds are termed *silicides*. The majority of silicides are metallic while only a few of them are reported to be semiconducting. Metallic silicides are an essential part of the Si-based CMOS technology. They have been extensively used as ohmic contacts, gate structures, local interconnects, or even Schottky barriers and are often characterized by their low and metal-like resistivity at room temperature (RT) (typically between 15 and 150 $\mu\Omega$ -cm) and high thermal stability. Their resistivity decreases as the temperature decreases.

In contrast to metallic silicides, semiconducting silicides have resistivity between that of a conductor and an insulator (typically ranging from m Ω -cm to hundreds of Ω -cm at RT) and their resistivity generally increases as the temperature decreases. Moreover,

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they exhibit other general properties of semiconductors such as the existence of energy gaps. Some examples of the semiconducting TM silicides include chromium disilicide (CrSi_2) [13], manganese silicide (MnSi_{2-x}) [14], rhenium disilicide (ReSi_2) [15], β - FeSi_2 [16], ruthenium silicide (Ru_2Si_3) [17], osmium silicide (Os_2Si_3) [17], and iridium silicide (Ir_3Si_5) [18]. Their bandgaps range from 0.12 eV (ReSi_2) [19] to 2.3 eV (Os_2Si_3) [20]. Of all semiconducting TM silicides, β - FeSi_2 has held most attention and investigations due to its attractive physical properties.

2.2.2 Material properties of semiconducting β - FeSi_2

2.2.2.1 Phase diagram and Fe-Si compounds

Figure 2.1 shows the phase diagram of Fe-Si system [21]. It can be seen that some of the transformation temperatures and melting points are not entirely established due to the complexity of the system. However, four basic compounds are thought to form in the system, which are the metal-rich silicide Fe_3Si , the intermediate phase Fe_5Si_3 , the monosilicide FeSi , and the disilicide FeSi_2 . The melting points of these compounds are summarized in Table 2.1.

Table 2.1. Melting point of common compounds found in the Fe-Si system.

Compound	Melting point ($^{\circ}\text{C}$)
Fe	1538
Fe_3Si	1240
Fe_5Si_3	1203
FeSi	1410
FeSi_2	1212

There are two main stable phases for FeSi₂: the semiconducting β phase at low temperature and the metallic α phase at high temperature. β -FeSi₂ is the only disilicide phase exhibiting semiconducting properties and it belongs to orthorhombic crystal system with *Cmca* space group [16]. Thermodynamically, it is stable in contact with Si up to the phase transition temperature of about 937 °C, beyond which the transformation to the high temperature metallic α phase takes place [12].

Figure 2.1. Phase diagram of Fe-Si system [21].

2.2.2.2 Electronic structure and bandgap

The electronic structure and bandgap properties of β -FeSi₂ have been studied both theoretically [22, 23] and experimentally [24, 25]. The theoretical calculation of the electronic band structure of β -FeSi₂ by Christensen [22] revealed the existence of both

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indirect and direct bandgaps. The same conclusion was obtained theoretically by Filonov *et al.* [23], where they also pointed out that the nature of the gap is very sensitive to structural variations in β -FeSi₂.

Figure 2.2 shows the electronic band structure of β -FeSi₂ calculated by the linear muffin-tin orbital (LMTO) method within the local density approximation (LDA) scheme by Filonov *et al.* The band structure is characterized by a direct bandgap of 0.742 eV at the Λ point located in the middle of the Γ -Z distance in the Brillouin zone (BZ), and the second larger direct bandgap of 0.825 eV at the Y point. The conduction band minimum (CBM) at the Y point is only 8 meV higher than that at the Λ point. Due to such a small difference between the energy values of CBM, it is difficult to define the nature of the gap unambiguously and therefore one can speak in terms of a quasi-direct gap.

Figure 2.2. Electronic band structure of β -FeSi₂ calculated by the LMTO method [23].

In most experimental studies, a direct bandgap for β -FeSi₂ has been frequently reported. This can be ascribed to the defect-induced absorption tail extending into the forbidden gap of β -FeSi₂ which might shield the indirect optical transitions. However, there have been discrepancies about the bandgap value, which generally falls in the range of 0.84-0.89 eV as shown in Table 2.2. Such discrepancy in the experimental data can be attributed to a number of possible factors such as different growth techniques and processing conditions as well as the method of bandgap extraction being employed.

Table 2.2. Reported bandgap data of semiconducting β -FeSi₂.

Direct bandgap (eV)	Reference
0.87	[5]
0.85-0.87	[12]
0.87	[25]
0.85	[26]
0.847	[27]
0.89	[28]
0.87	[29]
0.85	[30]

2.2.2.3 Optical properties

The optical properties of β -FeSi₂ have been widely investigated and measured on the nanocrystalline, polycrystalline, and epitaxial thin films [5, 26, 28, 31]. Figure 2.3 shows the optical absorption coefficient of β -FeSi₂ as a function of photon energy [32]. The *absorption coefficient* α is defined as the relative number of photons absorbed per

unit distance, given in units of cm^{-1} . The values of the refractive index n and extinction coefficient k for FeSi_2 over a wide energy range up to 5 eV are tabulated in Ref. [33], which are plotted by the author and presented in Figure 2.4. These accepted values of n and k were obtained from the transmittance and reflectance measurements on the epitaxial films grown by molecular beam epitaxy (MBE).

Figure 2.3. Optical absorption coefficient as a function of photon energy for $\beta\text{-FeSi}_2$ [32].

Figure 2.4. Refractive index and extinction coefficient as a function of energy for FeSi_2 .

2.2.2.4 Impurity doping

There have been many attempts to introduce impurity atoms into β -FeSi₂ to tailor its semiconducting properties. Currently, most theoretical and experimental studies focused primarily on the investigations of TMs as suitable dopants for β -FeSi₂ as shown in Table 2.3. It was found experimentally [34-36] that doping with V, Cr, and Mn results in *p*-type conductivity whereas doping with Co, Ni, Pd, and Pt gives *n*-type conductivity. Such conductivity modulation with doping is strongly dependent on the doping species and the host lattice site in which the impurity atoms reside.

Table 2.3. Doping effects of various impurity elements in semiconducting β -FeSi₂. Preferential substitutional site (Fe or Si) of some impurity elements was obtained theoretically by first-principles calculations from Refs. [37, 38].

Impurity element	Preferential substitutional site	Conductivity type	Reference
Al	Si	<i>p</i>	[37]
V	...	<i>p</i>	[34]
Cr	Fe	<i>p</i>	[34, 38]
Mn	Fe	<i>p</i>	[34, 36, 38]
Co	Fe	<i>n</i>	[34, 35, 37, 38]
Ni	Fe	<i>n</i>	[34, 35, 38]
Pd	...	<i>n</i>	[34]
Pt	...	<i>n</i>	[34]

Group III and V atoms have also been considered as alternative elements for doping. It had been demonstrated experimentally about the doping of β -FeSi₂ films with

B and As by cosputtering [39], where *p*-type and *n*-type conductivities were obtained for the B- and As-doped β -FeSi₂, respectively. Figure 2.5 shows the hole mobility versus net hole concentration and electron mobility versus net electron concentration plots for the B- and As-doped β -FeSi₂ prepared by facing-target sputtering (FTS) method, respectively [11, 39]. In the FTS method, the substrate is placed perpendicular to the two targets that are positioned parallel such that higher plasma density, lower damage and temperature rise on the substrate surface are achieved. It clearly suggests that the carrier concentration and mobility over a wide tunable range can be achieved with doping.

Figure 2.5. Plots of (a) hole mobility vs. net hole concentration and (b) electron mobility vs. net electron concentration for the B- and As-doped β -FeSi₂, respectively [11, 39].

2.2.3 Silicide formation

The fabrication of β -FeSi₂ thin films on the Si platform generally exploits the whole variety of techniques developed in microelectronics, including solid-state reaction, ion beam synthesis (IBS), electron beam evaporation, pulsed laser deposition (PLD), sputtering, and MBE [8, 40-44]. Nevertheless, it is possible to classify them into three main groups based on the dominant physical and chemical processes involved. These are (1) solid-state diffusion, (2) IBS, and (3) atomic and molecular deposition.

In the solid-state diffusion synthesis and IBS, the fabrication steps usually involve first the deposition of the silicide forming components and subsequently their thermal processing for silicidation. This is in contrast to atomic and molecular deposition method, where silicidation is realized within one cycle by maintaining substrates at an elevated temperature during the deposition. Both polycrystalline and epitaxial thin film silicides can be formed by these techniques. In the following sections, the basic principles of each approach and its practical applications for β -FeSi₂ thin film formation are discussed.

2.2.3.1 Solid-state diffusion

Two types of structures are used for the formation of thin film silicides by this technique: (1) pure metal films on a Si substrate and (2) films composed of intermixed metal and Si atoms. The films are deposited at RT by sputtering or evaporation. In the former, silicidation starts at the metal/Si interface during the subsequent thermal annealing. The growing silicide consumes Si from the substrate during the process of silicidation. In the latter, both silicide forming components are simultaneously deposited onto the substrate in amounts usually close to or corresponding to the stoichiometric

ratio. Subsequent thermal annealing results in diffusion intermixing of the components and promotes their chemical interactions to form the desired silicide.

The formation of silicides in metal-on-Si structures is always accompanied by a net volumetric change related to the Si consumption from the substrate. It is possible to calculate the thickness of the Si consumed (d_{Si}) and silicide formed (d_{silicide}) for a given thickness of metal deposited based on the atomic density of the respective elements in the silicide phases [33]. Table 2.4 shows the result of the calculation for FeSi₂, assuming the volume change is completely accommodated by a change in the thickness.

Table 2.4. Volumetric change during FeSi₂ formation.

Disilicide formed	$d_{\text{Si}}/d_{\text{Fe}}$	$d_{\text{silicide}}/d_{\text{Fe}}$
β -FeSi ₂	3.39	3.20
α -FeSi ₂	3.64	3.36

The silicidation process is critically dependent on the ambient and temperature-time regimes of post-deposition thermal processing. This is because most metals do chemically react with O₂ and N₂, and such reactions can compete with the silicide formation or even suppress it when high temperature processing is being employed. RTA can potentially reduce the contamination and oxidation-related problems due to its short duration of anneals.

Both polycrystalline and epitaxial β -FeSi₂ thin films have been synthesized by this approach [40, 45-50]. It was observed that an annealing temperature of 900 °C appears to be the upper limit for β -FeSi₂ formation, beyond which it may transform into

the metallic α phase. This observation agrees with the implication from the phase diagram of the Fe-Si system (see Figure 2.1). Annealing at 600-700 °C for 1-2 h is sufficient to transform 20-50 nm Fe into the disilicide, below which FeSi will remain in the silicide film [48, 49]. Higher annealing temperature of 750-850 °C is required for Fe films thicker than 100 nm [50].

For the mixed metal-and-Si structures, both silicide forming components (i.e., Fe and Si) are simultaneously deposited onto the substrate by cosputtering or coevaporation with the atomic ratio of Fe to Si typically close to the desired phase composition (i.e., Fe/Si=1/2 for disilicide). The as-deposited film is usually amorphous because it is only a mixture of the components at the atomic scale. Post-deposition thermal annealing is required to initiate diffusion intermixing of the Fe and Si atoms and promote chemical reactions for the silicide formation. An example of forming β -FeSi₂ thin films by this method can be found in Refs. [8, 51].

2.2.3.2 Ion beam synthesis

Ion implantation has been widely used in microelectronics since the progress in generation of intense metal ion beams in the late 1980s. IBS by metal ion implantation is now commonly employed for the formation of silicides. The process involves direct implantation of metal ions at very high doses (typically in the range of 10^{17} - 10^{18} ions/cm²) into the Si substrates with energies sufficient to produce buried layers, followed by subsequent thermal processing to remove the implantation damage and form a continuous silicide layer [52]. Both polycrystalline and epitaxial β -FeSi₂ thin films have been produced by IBS [53-55].

In Naito *et al.*'s work [53, 54], implantation of Fe^+ ions into the Si substrates with a dose of 4×10^{17} ions/cm² at energy of 120 keV at cryogenic temperature (120 K) produces an amorphous layer with a bilayered structure consisting of amorphous Fe-Si and amorphous Si on the Si substrate. An annealing temperature of 500 °C for 2 h transforms the amorphous Fe-Si layer in the as-implanted sample into polycrystalline ϵ -FeSi and β -FeSi₂ layers, where the transformation from ϵ -FeSi to β -FeSi₂ was observed with increasing annealing temperature [54]. A continuous polycrystalline β -FeSi₂ thin film was obtained after annealing at 750-800 °C for 2 h.

2.2.3.3 Atomic and molecular deposition

This group of methods is primarily based on individual deposition of atoms or molecules of silicide forming components on the substrates that are maintained at an elevated temperature to initiate diffusion intermixing of the components on the surface and trigger chemical reactions yielding silicide formation. These film growth techniques include reactive atomic deposition, chemical vapor deposition (CVD), PLD, and MBE. Each of them is briefly described below.

Reactive atomic deposition involves the deposition of metal atoms onto a hot Si surface. The intermixing and compound formation takes place readily during the deposition because of the well activated atomic diffusion. This allows the formation of silicides without post-deposition thermal annealing. An example of forming β -FeSi₂ thin films by reactive deposition epitaxy (RDE) is shown in Ref. [40]. In this work by Miquita *et al.*, pure Fe was deposited on the Si(111) substrate at temperatures of 400-800 °C. The

transition to β phase occurred between 600 and 700 °C, but single phase β -FeSi₂ was obtained only after annealing at 700 °C for 2 h.

In CVD, both metal and Si atoms are produced simultaneously from the gaseous compounds. The two important factors controlling the process are (1) gas pressure in the reaction chamber and (2) substrate temperature. At the elevated temperature, the gaseous compounds containing silicide forming species decompose and release the metal and Si atoms onto the heated substrate resulting in silicide formation. Chlorinated Fe compounds and iron pentacarbonyl [Fe(CO)₅] are the common precursor gases and vaporizing compounds used for releasing Fe, while silane (SiH₄) or disilane (Si₂H₆) are often used for releasing Si in the CVD process. The growth of β -FeSi₂ thin films by CVD can be found in Refs. [56, 57].

PLD is a thin film deposition technique where a high power pulsed laser beam is focused inside a vacuum chamber to strike a target of the desired composition. Material is then vaporized from the target and deposited as a thin film on the substrate in the form of atomic or molecular clusters. The process can occur in ultrahigh vacuum (UHV) such as during the deposition of FeSi₂, or in the presence of a background gas such as O₂ when depositing oxides and high- k dielectrics. The experimental applications of PLD to form β -FeSi₂ thin films are described in Refs. [42, 58, 59].

MBE has been widely used for the growth of epitaxial silicide films. In MBE, both metal and Si atoms from the separate sources are simultaneously deposited at a stoichiometric ratio onto a heated Si substrate. It is performed under UHV conditions at an extremely low pressure in the order of 10⁻¹⁰ Torr to provide an atomically clean surface for condensation of silicide forming components. Long range surface diffusion of

the atoms results in the compound formation and epitaxial growth on the crystalline Si substrate. Some examples of growing epitaxial β -FeSi₂ thin films on Si substrate by MBE are given in Refs. [44, 60, 61].

2.2.3.4 Additional comments

Among the silicide formation techniques as reviewed, solid-state diffusion is most frequently used for the fabrication of β -FeSi₂ thin films. It is a relatively simple and flexible method and meets the requirements of productivity for industrial applications. The main challenge is determined by the proper control of undesired impurities that can be unintentionally incorporated into the film during the process of silicide synthesis. IBS by metal ion implantation, on the other hand, suffers from the implantation damage and defects that require high temperature annealing, which may cause severe inter-diffusion of the Fe and Si atoms or dopant diffusion problems.

The methods based on the atomic and molecular deposition (particularly CVD and MBE) have excellent control of stoichiometry and crystalline structure of silicides. While CVD is commercially viable, it is limited by the choice of the metal-containing gaseous precursors and their purity. MBE is a rather expensive technique, despite the fact that it can produce high quality silicide films.

To fabricate β -FeSi₂ thin films with reasonably good control of its quality and properties, a combination of different approaches is often necessary. This requires an understanding of the materials knowledge and flexible regulations of the experimental conditions in order to produce the optimum results. Combined ion irradiation of Fe/Si bilayers using Fe⁺ ions and subsequent thermal annealing had been used to form high

quality β -FeSi₂ thin films [62]. Laser irradiation of Fe/Si bilayers had also been used to synthesize mixed phases containing FeSi, β -FeSi₂, and metastable γ -FeSi₂ and a complete transformation from mixed phases to pure β -FeSi₂ was obtained after subsequent thermal annealing [63].

Recently, high quality epitaxial β -FeSi₂ thick film has been fabricated by template method [64]. In the work carried out by Kuroda *et al.*, an epitaxial β -FeSi₂ thin layer (<20 nm) was first formed on the Si(111) substrate. This layer serves as the template for the subsequent epitaxial growth of β -FeSi₂ thick films. The epitaxial β -FeSi₂ template layer was prepared by depositing 6 nm Fe at 400 °C and subsequent *in situ* annealing at 600 °C in MBE chamber (i.e., a RDE method), and also by Fe/Si co-deposition method where Fe and Si atoms were deposited simultaneously on Si substrate while keeping the substrate at lower temperature compared with RDE. The template layer formed by co-deposition of Fe and Si was found to exhibit better crystallinity and morphology than that prepared by RDE. The subsequent epitaxial growth of β -FeSi₂ thick film was performed by depositing alternate Fe and Si thin layers, followed by post-deposition annealing of 800 °C for 2 h in Ar ambient.

Direct epitaxial growth of β -FeSi₂ thin films on the Si(111) substrate without annealing was successfully demonstrated by FTS method [65]. In this work by Yoshitake *et al.*, Fe and Si atoms were simultaneously deposited on the Si substrate by FTS using a FeSi₂ alloy target. During the deposition, the substrate was maintained at a temperature of 600 °C. An epitaxial β -FeSi₂ thin film was found to directly form on Si without any post-deposition annealing.

2.3 Solar Cells

2.3.1 Historical development

Historically the PV effect was discovered by A. E. Becquerel in 1839 [66] while experimenting with an electrolytic cell made up of two metal electrodes. Becquerel found that certain materials would produce small amount of electric current when exposed to light. However, progress in solar cells essentially began in 1940 when Russell Ohl discovered that a rod of Si with impurities created a large electrical voltage when it was illuminated with light [67]. In 1941, the Si solar cell was invented by Russell Ohl. In 1953, three American researchers, Pearson, Fuller, and Chapin accidentally observed an electric output almost five times greater than the best selenium cell produced while they were exposing the doped Si to the sunlight. One year later, the first efficient Si solar cell capable of a remarkable 6% conversion efficiency with direct sunlight was made in Bell Labs [68]. This device represented a major development because it was the first PV structure that directly converted light to electricity with reasonable efficiency. From there the simultaneous rise and development of the integrated circuit (IC) industry entrenched the dominance of crystalline Si PV technology.

2.3.2 Photovoltaic effect, solar cells, and sunlight

The *photovoltaic (PV) effect* is a basic physical process through which a solar cell converts sunlight into electricity. This PV energy conversion essentially converts the energy in light into usable electrical energy which may be employed immediately or stored. The basic ingredients for PV energy conversion are shown in Figure 2.6. The process involves light-induced transition of electrons from ground state to excited state

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upon absorbing sufficient energy from incoming photons, thereby creating electron-hole pairs (EHPs) in the materials and a “check valve” action of some sort which prevents photo-generated carriers (electrons and holes) from flowing backwards and recombining [69]. In this general system electrons must go through some external path in order to lose their energy and recombine with holes. This external path may involve an electrical load or some storage mechanisms. This general feature of PV action is similar to the mechanism of natural photosynthesis.

Figure 2.6. Basic features of PV energy conversion. Redrawn from Ref. [69].

Solar cells are man-made PV energy conversion systems of this kind which directly convert light into electricity, and usually use similar physics and technology as that used by the microelectronics industry to make computer chips. The basic energy supply for a solar cell is photons of the solar spectrum and the basic product is usable electrical energy. When sunlight reaches the earth’s surface, the atmosphere attenuates it. The degree to which the atmosphere affects the sunlight received at the earth’s surface is defined by the “*air mass (AM)*”. Formally, air mass x (AM_x) is defined as the secant of the angle between the sun and the zenith, i.e., $x = \sec \theta$. Specifically, the air mass zero

(AM0) condition represents the solar spectrum outside the earth's atmosphere. The radiation intensity corresponding to AM0 condition has an accepted value of 1353 W/m^2 and is known as the *solar constant*. The air mass 1.5 (AM1.5) condition (sun is 48.2° off overhead) represents a satisfactory energy-weighted average for terrestrial applications. The air mass 2 (AM2) condition (sun is 60° off overhead) represents the solar energy distribution available at the earth's surface for average weather conditions. Figure 2.7 shows the solar spectral irradiance for the cases of AM0 and AM1.5 radiation.

Figure 2.7. Solar spectral irradiance for AM0 and AM1.5 radiation [70].

In contrast to the situation outside the earth's atmosphere, terrestrial sunlight is more complex as it varies greatly in both intensity and spectral composition. To allow meaningful comparison between the performances of different solar cells fabricated and tested at different locations, a terrestrial standard has to be defined. The standard testing condition for characterizing the performance of solar cells is AM1.5 at 25°C , with a total

power density content of 1000 W/m^2 (or 100 mW/cm^2). Therefore all measurements are referred to this standard.

The sun constantly emits energy by radiating an essentially continuous spectrum of electromagnetic radiation closely approximating that expected from a black body at a temperature of 6000 K. The radiation spectrum covers a broad wavelength range from deep ultraviolet (DUV) region to long infrared (IR) region. Although sunlight is attenuated by at least 30% during its passage through the earth's atmosphere, the earth receives more energy from the sun in just one hour than the world uses in a whole year [71, 72]. This enormous power that the sun continuously delivers to the earth is estimated to reach $1.2 \times 10^5 \text{ TW}$ ($1 \text{ TW} = 1 \times 10^{12} \text{ W}$), far exceeding the world's energy consumption of 13 TW [72]. Therefore there is definitely enough sunlight to make a contribution to the world's energy needs.

2.3.3 Conventional *pn* junction solar cells

The *pn* junction is one of the primary building blocks of semiconductor devices such as diodes, transistors, solar cells, and ICs. They are active sites where the electronic action of the device takes place and therefore are of fundamental importance to solid state electronics. In this section, we discuss the basic principles and operation of solar cells with the case of conventional *pn* junction.

2.3.3.1 Operating principles

A *pn* junction consists of two different regions of a semiconductor material (usually Si), with one side called the *p*-type region and the other the *n*-type region. A *p*-

type material is a semiconductor doped with acceptor impurities having an increased number of holes in the valence band at normal temperatures. Those doped with donor impurities having an increased number of electrons in the conduction band at normal temperatures are known as *n*-type material. The interface separating the *p*- and *n*-type regions is called the metallurgical junction. The most common solar cells are essentially just large area *pn* junction diodes.

The fundamental device requirement for PV energy conversion is an *electronic asymmetry* in the semiconductor structure. Figure 2.8 shows the space charge region, the build-in electric field, the forces acting on the charged carriers, and the carrier distributions of a *pn* junction at thermal equilibrium. Thermal equilibrium means that there are no external excitations such as voltage, light, and/or temperature gradient applied to the system. When *n*- and *p*-type materials come into contact to form a *pn* junction, as a result of concentration gradient electrons diffuse readily from *n*-type to *p*-type region and vice versa, i.e., majority carriers cross the junction. Once the majority carriers have crossed the junction, they become minority carriers and have a limited lifetime. The ionized dopant atoms left behind are now electrically charged. Consequently, an electric field is set up near the interface between *n*- and *p*-type materials. Under illumination, excess EHPs are generated by light throughout the material. The inherent asymmetry in the carrier transport properties as described promotes a flow of photo-generated electrons from the *p*-type region to the *n*-type, and a flow of holes in the opposite direction. When such illuminated *pn* junction is electrically shorted, a current will flow in the circuit. Therefore a *pn* junction has the required asymmetry for PV energy conversion.

Figure 2.8. The space charge region, the electric field, the forces acting on the charged carriers, and the carrier distributions of a pn junction at thermal equilibrium.

The I - V characteristics of a pn junction can be obtained by solving the basic device equations, which are the Poisson's equation, the current-density equations, and the continuity equations. The solution to the equations is simple only when some further assumptions and approximations are made [73]. Taking into account the effect of recombination in the depletion region, the dark I - V equation of a pn junction can be written as

$$I = I_0 \left[\exp\left(\frac{eV}{kT}\right) - 1 \right] + I_w \left[\exp\left(\frac{eV}{2kT}\right) - 1 \right] \quad (\text{Equation 2.1})$$

where V is the applied bias, e is the elementary electronic charge, k is the Boltzmann's constant, T is the temperature, I_0 and I_w are the dark saturation currents due to recombination in the quasi-neutral regions and depletion region, respectively. More often, it can be expressed in the following form:

$$I = I_s \left[\exp\left(\frac{eV}{nkT}\right) - 1 \right] \quad (\text{Equation 2.2})$$

where I_s is the dark saturation current and n is called the *ideality factor*.

The ideality factor of a pn junction is a measure of how closely the pn junction follows the ideal diode characteristics. It varies with current level as does I_s . At low currents, recombination current in the depletion region dominates and n is close to 2. At higher currents, diffusion current in the quasi-neutral regions dominates and n is close to 1. For diode where recombination in both regions is comparable, n is somewhere between 1 and 2 [73-75]. Figure 2.9 shows the semi-logarithmic plot of the dark I - V characteristics of a pn junction.

Figure 2.9. Semi-logarithmic plot of the dark I - V characteristics of a pn junction.

2.3.3.2 Output characteristics

When light impinges on the pn junction solar cells, a current I_{sc} is developed in short circuit. This current is produced by the sweeping out of photo-generated carriers by

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the depletion region. At open circuit the cells bias themselves to the values of open-circuit voltage V_{oc} necessary to generate a forward current I_F which just cancels out the photo-generated current. At some intermediate voltage $0 \leq V \leq V_{oc}$, the forward current is less than the photo-generated current, producing an electric current in the solar cells. This PV action is responsible for the diode rectifying output characteristics of a PV structure under illumination.

Assume the generation rate of EHPs by the illumination is uniform throughout the device. This would correspond to a situation where the cell was illuminated by long wavelength light consisting of photons of energy close to that of the semiconductor bandgap. Solving the basic device equations for this case of uniform generation rate gives the following results for the illuminated I - V characteristics [74, 76]:

$$I = I_0 \left[\exp\left(\frac{eV}{kT}\right) - 1 \right] - I_L \quad (\text{Equation 2.3})$$

where

$$I_0 = A \left(\frac{eD_n n_i^2}{L_n N_A} + \frac{eD_p n_i^2}{L_p N_D} \right), \quad (\text{Equation 2.4})$$

$$I_L = eAG(L_n + W + L_p). \quad (\text{Equation 2.5})$$

Here I_0 is the ideal saturation current, I_L is the light-generated current, G is the uniform generation rate, and W is the depletion width, whereas other symbols in Equations (2.3)-(2.5) are self-explanatory and have their usual physical meanings. The illuminated characteristics of a solar cell are essentially the dark characteristics displaced downward by a current I_L , as plotted in Figure 2.10. The active region of a solar cell for current

collection is the junction depletion region and the volume of the cell material within a minority carrier diffusion length of either side of this region.

Figure 2.10. I - V characteristics of a pn junction in the dark and when illuminated.

2.3.3.3 Performance parameters

Three parameters are used to characterize the performance of a solar cell. These are the *short-circuit current* I_{sc} , the *open-circuit voltage* V_{oc} , and the *fill factor* FF . Ideally, the short-circuit current is equal to the light-generated current, $I_{sc}=I_L$ and the open-circuit voltage V_{oc} is given by

$$V_{oc} = \frac{kT}{e} \ln \left(\frac{I_L}{I_0} + 1 \right). \quad (\text{Equation 2.6})$$

The power output for any operating point in the fourth quadrant is equal to the area of the rectangle shown in Figure 2.10. This power is maximized when the cell is operating at the *maximum power point* (V_{mp}, I_{mp}). The fill factor FF is defined as

$$FF = \frac{V_{mp} I_{mp}}{V_{oc} I_{sc}}. \quad (\text{Equation 2.7})$$

For cells with reasonable efficiency, it has a typical value in the range from 0.7 to 0.85.

The *conversion efficiency* η is the single most important figure of merit for a solar cell. The conversion efficiency is defined as the ratio of the output electrical power to the incident optical power P_{in} and is given by

$$\eta = \frac{V_{mp} I_{mp}}{P_{in}} = \frac{V_{oc} I_{sc} FF}{P_{in}}. \quad (\text{Equation 2.8})$$

2.3.3.4 Efficiency limits

The ideal limit of conversion efficiency can be estimated by examining the ideal limits of I_{sc} and V_{oc} . Under ideal conditions of unity *quantum efficiency*, each photon incident on the cell of energy greater than the bandgap gives rise to one electron flowing in the external circuit [77]. To calculate the maximum I_{sc} , the photon flux in sunlight must be known. The *photon flux* is defined as the number of photons per second per unit area, given in units of (number of photons)/s/m². It is calculated by dividing the energy content of sunlight (see Figure 2.7) at a given wavelength by the energy of an individual photon of this wavelength. Hence, the maximum I_{sc} can be calculated by integrating these distributions from low wavelengths up to the wavelength corresponding to the bandgap energy E_g . The energy E of a photon is related to its wavelength by the relation

$$E = h\nu = \frac{hc}{\lambda} = \frac{1.24}{\lambda} \text{ eV} \quad (\text{Equation 2.9})$$

where λ is the wavelength in μm and c is the speed of light, 3×10^8 m/s. As E_g decreases, more photons can have sufficient energy to create EHPs and hence I_{sc} increases.

The open-circuit voltage is determined by the properties of the semiconductor through its dependence on I_0 [see Equation (2.6)]. As E_g decreases, the intrinsic carrier concentration (n_i) of the semiconductor increases. This in turn increases the saturation current I_0 [see Equation (2.4)] and therefore reduces the V_{oc} . This trend is opposite from that observed for I_{sc} . It suggests that there will be an optimum bandgap for highest theoretical efficiency [69, 78, 79]. Figure 2.11 shows the ideal conversion efficiency as a function of energy bandgap. The theoretical efficiency limit for single junction cells is 31% [78], which is called the Shockley-Queisser limit. This limiting efficiency is calculated by examining the amount of electrical energy that is extracted per photon of incoming sunlight and assuming that the only recombination mechanism of EHPs is radiative. Note that the efficiency in Figure 2.11 has a broad maximum and does not depend critically on E_g . Therefore, semiconductors with bandgaps in the vicinity of 1 or 2 eV can all be considered as solar cell materials.

Figure 2.11. Ideal conversion efficiency as a function of energy bandgap at 300 K.

The most general efficiency limit for PV is the Carnot thermodynamic limit and is given by [80]

$$\eta = \left(1 - \frac{T_A}{T_S}\right) - \frac{T_A S_G}{E_S} \quad (\text{Equation 2.10})$$

where E_S is the heat energy flux supplied from the sun, S_G is the entropy generation flux associated with the conversion process, and T_A and T_S are the temperatures of the ambient and the sun's photosphere, respectively. This limit has its maximum value of 95% and is known as the Carnot efficiency.

2.3.3.5 Efficiency losses

In practical PV devices, the conversion efficiency is significantly lower than the ideal limits due to the presence of additional loss mechanisms in the system. The loss mechanisms reduce the three performance parameters (I_{sc} , V_{oc} , and FF) and hence the conversion efficiency. The source of I_{sc} loss is mainly due to the optical nature of PV structures. Surface reflection and blockage of the incoming light by the metal grid contact generally reduce the amount of light being coupled into the cell structures and hence I_{sc} . In addition, if the cell is not thick enough, some of the light of appropriate energy will just transmit through the cell. This determines the minimum thickness of cell material needed to avoid significant optical loss. Finally, recombination in the bulk and at surfaces will annihilate some of the photo-generated EHPs that would otherwise contribute to I_{sc} .

The fundamental process determining V_{oc} is the recombination processes in the semiconductor. The lower the recombination rate in the semiconductor, the higher the V_{oc} . Figure 2.12 shows the typical loss mechanisms of a pn junction solar cell under

illumination. The loss mechanisms affect the I_{sc} and establish the V_{oc} and therefore it determines the shape of the I - V characteristics of a cell. The more effective are the processes 1-7 in reducing carrier populations, the more the V_{oc} will be reduced. Hence, it is necessary to minimize the contact losses (processes 2, 3, 6, and 7) and the bulk recombination losses (processes 1, 4, and 5) to improve the cell performance.

The contact losses are mainly due to the ohmic contacts which are sinks for the photo-generated minority carriers. A phenomenological quantity, the minority carrier surface recombination velocity S , is used to characterize the strength of the sink at the ohmic contact. In PV devices, we want $S \rightarrow 0$ for minority carriers and $S \rightarrow \infty$ for majority carriers. This will allow photo-generated minority carriers to be directed to the depletion region which is generally the core of PV response. The bulk recombination losses involve recombination through traps or defects in the forbidden gap, radiative (band-to-band) recombination, and Auger recombination [74]. These recombination processes annihilate the photo-generated EHPs and therefore are important to the operation of solar cells.

Figure 2.12. Typical loss mechanisms of a pn junction solar cell under illumination. Processes 1, 4, and 5 are bulk recombination losses, whereas processes 2, 3, 6, and 7 are contact losses [69].

The parasitic series and shunt resistances present in the solar cells act to reduce the fill factor and hence the conversion efficiency. The major components of series resistance R_s are the bulk resistance of the semiconductor material, the bulk resistance of the metallic contacts and interconnections, and the contact resistance between the metallic contacts and the semiconductor. The shunt resistance R_{sh} is mainly due to the leakage currents in the pn junction. Figure 2.13 shows the equivalent circuit model of a solar cell including both types of parasitic resistances. For the cell design, the two basic goals are (1) maximization of the absorption of photons with energy greater than E_g and (2) minimization of the recombination rates throughout the device.

Figure 2.13. Equivalent circuit model of a solar cell.

2.3.4 Thin film solar cells

2.3.4.1 Advantages and disadvantages

The main advantage of thin film solar cells is their promise of low cost. In thin film solar cells, the active semiconductor layers are polycrystalline or disordered films that have been deposited or formed on various electrically active or passive low-cost substrates such as glass, plastic, ceramic, or metallurgical Si. The formation of active layers is usually performed by low-cost processing methods such as vapor deposition,

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electroplating, evaporation, or sputtering, which is economically viable for large-scale production. In addition, Si is the most weakly absorbing semiconductor of all the viable semiconductors used for thin film PV applications, such as GaAs, CdTe, Cu(In,Ga)Se₂, and even amorphous Si. This is because Si has an indirect bandgap while most of the other semiconductors have a direct bandgap. As a result, more crystalline Si is needed to absorb a given fraction of sunlight compared to other semiconductors. This translates into higher material requirements and hence higher cost, unlike thin film PV devices where much thinner semiconductor materials are used. If the semiconductor thickness is larger than the inverse of the absorption coefficient (also known as the *effective absorption length*, $1/\alpha$), most light will be absorbed. For the β -FeSi₂, an active layer of 200 nm is sufficient to absorb most of the incoming photons of solar spectrum. Table 2.5 shows the comparison of β -FeSi₂ with crystalline Si and GaAs as a PV semiconductor [11]. Another good characteristic of thin film solar cells is the flexibility. Unlike traditional panels, flexible panels can be applied to a wide variety of surfaces.

Table 2.5. Comparison of β -FeSi₂ with crystalline Si and GaAs as a PV semiconductor.

	β -FeSi ₂	Crystalline Si	GaAs
Bandgap (eV)	0.86	1.11	1.43
Optical absorption coefficient (cm ⁻¹)	>10 ⁵	10 ³ -10 ⁴	10 ⁴
Theoretical conversion efficiency (%)	16-23	24	25
Thickness required for solar cell (μm)	1	300	10
Thermal stability (°C)	937	1000	500
Specific gravity (g/cm ³)	4.93	2.33	5.33

The main disadvantages of thin film solar cells are the relatively low efficiency and long-term instability. For the cell efficiencies, the highest laboratory efficiencies of most thin film technologies achieved so far do not exceed that for crystalline Si, despite the fact that they are comparable to each other theoretically. This can be largely attributed to the grain boundary effects and the poor quality of the semiconductor materials formed on foreign substrates, thereby degrading the diffusion length of the photo-generated carriers and hence the conversion efficiency. The stability problems present to most existing thin film PV technologies such as Cu₂S/CdS or amorphous Si is mainly caused by the chemical reaction of the semiconductor with ambient. However, β -FeSi₂ does not pose such concern because it is chemically stable.

2.3.4.2 β -FeSi₂-based solar cells

While β -FeSi₂ is potentially useful in many fields such as optoelectronics and PV, there are only limited β -FeSi₂-based PV devices reported to date. Currently, three major structures based on β -FeSi₂ have been investigated for thin film PV applications. These include (1) β -FeSi₂/Si heterojunction [43, 81-83], (2) β -FeSi₂-based *pn* homojunction [39, 84], and (3) β -FeSi₂-based metal-insulator-semiconductor (MIS) structure [85]. The main problems and challenges concern the control of interface quality and defects, which are the important factors affecting the cell performance.

The reported highest efficiency of β -FeSi₂-based solar cells is only 3.7% [43]. In this work by Liu *et al.*, a high quality thin β -FeSi₂ template buffer layer was first formed on the *p*-Si(111) substrate at low temperature to allow the subsequent epitaxial growth of thick *n*- β -FeSi₂ films. Under the standard AM1.5, 100 mW/cm² illumination, a short-

circuit current density of $J_{sc}=14.84 \text{ mA/cm}^2$, an open-circuit voltage of $V_{oc}=450 \text{ mV}$, and a fill factor of $FF=0.55$ were obtained for a $4 \times 4 \text{ mm}^2$ n - β -FeSi₂/ p -Si heterojunction solar cell without antireflection (AR) coatings. This translates into a promising conversion efficiency of $\eta=3.7\%$. This significant improvement as compared to their previous results was attributed to the usage of the β -FeSi₂ thin template, which significantly improved the crystal quality of the thick β -FeSi₂ film and reduced the diffusion of Fe atoms into the Si at the β -FeSi₂/Si interface [86]. However, such performance is still far from expectation, considering that β -FeSi₂ has high theoretical conversion efficiency of 23% as previously mentioned in Chapter 1.

Figure 2.14. Energy band diagram of n - β -FeSi₂/ p -Si heterojunction [82].

Figure 2.14 shows the energy band diagram of an n -type β -FeSi₂/ p -type Si anisotype heterojunction in thermal equilibrium. The junction build-in potential (qV_{bi}),

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which corresponds to the maximum limit of the open-circuit voltage V_{oc} , was estimated to be about 1.02 eV, which is also higher than that of the crystalline Si homojunction. The obtained V_{oc} is mainly degraded by the recombination processes in the cell structure. This could be attributed to the diffused Fe atoms which form deep level traps in the Si, and the interface states arising from the lattice mismatch between two dissimilar materials.

The β -FeSi₂-based *pn* homojunction was also studied by Liu *et al.* [39], where B and As were used as the *p*-type and *n*-type dopants, respectively. The main problem affecting the homojunction performance was the inter-diffusion of dopants at the junction interface, resulting in poor interface quality and hence non-ideal rectifying characteristics and weak photosensitivity. Nevertheless, clear photoresponse to near-IR light in the range of 1.3-1.6 μm was detected.

The similar problem of Fe diffusion into Si also exists for metal/ β -FeSi₂ Schottky junction. In particular, a thin SiO₂ barrier layer (<10 nm) inserted between the Al and the β -FeSi₂ forming a Al/SiO₂/ β -FeSi₂ MIS structure was found to exhibit good rectifying characteristics depending on the thickness of the SiO₂ layer [85]. Clear photoresponse peaked at a wavelength of around 1.46 μm was obtained for the MIS devices having SiO₂ layer of 5 and 7.5 nm.

The PV properties of β -FeSi₂/Si heterojunctions was found to be enhanced by Al doping [87]. It was suggested that Al doping reduces the density of Si native vacancies or Fe dangling bonds and consequently the recombination centers near the depletion region. Thus, Al doping contributes to the formation of a less defective interface and epitaxial growth of *p*-type β -FeSi₂ on Si(100). This reduces the recombination rate of EHPs near the depletion region and therefore the photoresponse can be enhanced.

Laser annealing has been employed to form device electrodes by converting part of the semiconducting β -FeSi₂ to metallic α -FeSi₂, which serves as the excellent native electrode to β -FeSi₂ [88]. The contact between α -FeSi₂ and β -FeSi₂ was found to possess good ohmic characteristics. The adhesion between the α -FeSi₂ electrode and β -FeSi₂ can be improved because α -FeSi₂ is originally a part of the β -FeSi₂. This greatly simplifies the process of electrode formation, which is usually done by selective sputter deposition of Al on the β -FeSi₂ film.

2.4 First-principles Calculations

First-principles calculations based on the DFT has been the dominant method to simulate and compute the properties of condensed matter. Several calculations have been performed to study the electronic properties of β -FeSi₂ using different methods, including LMTO [22, 23, 89, 90], augmented spherical wave (ASW) [91], full-potential linearized augmented plane wave (FLAPW) [37, 92, 93], and pseudopotential [94, 95]. All of them use either LDA or generalized gradient approximation (GGA) to treat the exchange-correlation functional in the calculations.

The calculations of electronic structure and bandgap properties of β -FeSi₂ have been discussed in Section 2.2.2.2. Some general observations are that the positions of direct and indirect transitions in the BZ were found to vary with calculation method, which could be due to the flat nature of the d -like bands nearby the gap (see Figure 2.2), and the gap estimation ranges from 0.44 eV [89, 91] to 0.825 eV [23]. Furthermore, the nature of the gap was found to be rather structure-sensitive. Nonetheless, most of the calculation results indicated the direct transition to be only a few tens of meV larger than

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the indirect one, so one can speak in terms of a quasi-direct gap. Table 2.6 summarizes the bandgap properties of β -FeSi₂ obtained from the theoretical calculations.

Table 2.6. Bandgap properties of β -FeSi₂ obtained from the theoretical calculations.

Calculation method	Exchange-correlation functional	E_g (eV)	Gap nature	Reference
ASW	LDA	0.44	Indirect	[91]
LMTO	LDA	0.44	Indirect	[89]
FLAPW	GGA	0.68	Indirect	[93]
FLAPW	GGA	0.71	Indirect	[37]
LMTO	LDA	0.74	Indirect	[23]
LMTO	LDA	0.80	Indirect	[22]
ASW	LDA	0.46	Direct	[91]
LMTO	LDA	0.51	Direct	[89]
FLAPW	GGA	0.73	Direct	[93]
FLAPW	GGA	0.74	Direct	[37]
FLAPW	LDA	0.78	Direct	[92]
LMTO	LDA	0.82	Direct	[22]
LMTO	LDA	0.825	Direct	[23]
Pseudopotential	LDA	0.7	...	[95]

The impurity-doped β -FeSi₂ has been studied by first-principles calculations [37, 38]. Most theoretical studies focus mainly on the investigations of TMs as dopants for β -FeSi₂ while only a limited study is devoted to group III and V atoms, which is shown in Table 2.3. Theoretical calculation by Tani and Kido [38] concluded that TMs generally

prefer to substitute Fe atoms in β -FeSi₂. The same conclusion was obtained theoretically for the case of Co by Pan *et al.* [37], where they also found that Al is more energetically favorable to replace Si atoms in β -FeSi₂. The preferential site occupation of the impurity dopants is generally determined from the total energy calculations.

Transport properties such as carrier type, concentration, and mobility of β -FeSi₂ depend strongly on the structural properties such as microstructure and defects as well as the impurity dopants. For the undoped or unintentionally doped β -FeSi₂, native defects are the dominant factor affecting the transport properties. Theoretical calculation by Tani and Kido [96] revealed that Fe vacancies introduce donor-like defect levels below the conduction band, whereas Si vacancies introduce acceptor-like defect levels above the valence band. This suggests that Si-rich (or Fe-deficient) and Fe-rich (or Si-deficient) β -FeSi₂ exhibit *n*-type and *p*-type conductivities, respectively, which has been confirmed experimentally [97-99].

2.5 Summary

The background and related earlier work on β -FeSi₂ have been reviewed. The material properties and formation of β -FeSi₂ as well as its applications to thin film solar cells have been discussed. The fundamental physics and operation of solar cells have been elucidated with the example of conventional *pn* junction. In addition, the theoretical studies on β -FeSi₂ by first-principles calculations were summarized and presented.

CHAPTER 3

EXPERIMENTAL METHODOLOGY

3.1 Introduction

This chapter describes the methods used for the formation of β -FeSi₂ thin films, including silicide film deposition and thermal annealing processes. In addition, the materials and device characterization techniques for the analysis of silicide films and devices will be described in detail.

3.2 Thin Film Silicide Formation

3.2.1 Sputter deposition

Sputter deposition is a physical vapor deposition (PVD) method of depositing thin films by sputtering where no chemical reactions are involved in the growth process. Sputtering is a process whereby atoms are ejected from a solid target material due to bombardment of the target by energetic ions. In sputter deposition, a target containing silicide forming components is bombarded by highly energetic and chemically inert ions (usually argon ions, Ar⁺) which physically sputter atoms off the target. The bombardment causes ejection of the target atoms which are subsequently deposited on the surface of the substrate (usually Si) located below the target [100].

Figure 3.1 shows the schematic of a sputtering system illustrating the sputter deposition process. In a vacuum chamber, the material to be sputtered (sputtering target) is placed at the cathode of negative potential and the substrate at an electrically grounded

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anode. The sputter gas (usually Ar) is then introduced into the chamber. A voltage of several hundred volts is usually applied between these plates, leading to an ignition of a plasma discharge as a result of collisions between the electrons and sputter gas for typical pressure of 10^{-2} - 10^{-4} Torr. The plasma is a fluid of positive ions and electrons in a quasi-neutral electrical state. Under the influence of electric field between these plates (cathode and anode), the positively charged Ar^+ ions are accelerated towards the target at the cathode, which physically sputter some of the target atoms off. The sputtered atoms from the target fly off in random directions, and some of them arrive at the substrate (mostly as neutral atoms) to form a thin film.

Figure 3.1. Schematic of a sputtering system illustrating the sputter deposition process.

In principle, sputtering is driven by momentum exchange between the ions and atoms in the material due to collisions. The incident ions set off collision cascades upon striking the target. This leads to heating of the target and finally also some back-reflected atoms with energy greater than the surface binding energy which can leave the surface of the target. During the sputtering process, the plasma discharge is essentially maintained as the accelerated electrons continuously ionize new ions by collisions with the sputter

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gas. Since the plasma is a good conductor and that the electrons in the plasma are highly mobile, the main voltage drop is observed at the cathode. Such potential distribution is advantageous because the Ar^+ ions are accelerated directly in front of the target which potentially enhances the sputtering yield.

The sputtering yield is the average number of atoms sputtered per incident ion. It depends on the nature and crystallographic orientation of the target material, the mass, energy, and incident angle of the primary ions, and the surface binding energy of atoms in the target. For multi-component or alloy targets, selective sputtering can occur due to the difference in sputtering yields for different components. The component with higher yield becomes depleted after a short initial time while that with lower yield becomes enriched at the surface. However, once equilibrium is reached, the difference in yield is compensated by the enrichment and the sputtered material leaving the surface generally has the same composition as the target material. Due to the self-regulating mechanism, sputtering allows the deposition of films with the same stoichiometry as the target.

The Denton Discovery sputtering system capable of both direct current (DC) and radio frequency (RF) magnetron sputtering was used in this project. DC sputtering was applied for the deposition of FeSi_2 , Ti, Al, and Au films while RF sputtering was used for the deposition of indium tin oxide (ITO) in our experiment. The deposition was carried out at RT using respective targets with an Ar flow rate of 25 sccm.

3.2.2 Ion implantation

Ion implantation is a process where ions of the desired element can be introduced into a material, thereby changing the physical properties of the material. Ion implantation

is an effective method of introducing dopant atoms into the substrate (usually Si) with precise control over the number and position of implanted dopant atoms in the substrate [100-102]. In this method, the desired dopant atoms are vaporized, accelerated, and directed at a Si substrate. They enter the crystal lattice and eventually come to a rest at some depth within the lattice, during which the energetic ions gradually lose their energy through collisions with electrons and nuclei in the substrate.

Figure 3.2 shows the schematic of a typical ion implanter illustrating the ion implantation process. The process begins with the creation of dopant ions in an ionization chamber. The ions are then extracted and subjected to the mass and energy separation through a sector mass analyzer magnet and series of slits followed by ion acceleration, after which the mono-energetic ion beam is directed into the substrate. The energetic ions penetrating into the substrate encounter a series of collisions or stopping mechanisms and finally come to a rest in the lattice. The typical ion energies and doses used are in the range of 10 to 500 keV and 10^{12} to 10^{18} ions/cm², respectively.

Figure 3.2. Schematic of a typical ion implanter illustrating the ion implantation process.

There are two stopping mechanisms by which an ion entering the substrate can be brought to a rest. These are (1) nuclear stopping, $S_n(E)$ and (2) electronic stopping, $S_e(E)$. In nuclear stopping, the energy and momentum of the incident ion are transferred to the target nuclei of the substrate atom after collision. The collision cascades resulted can cause the substrate atoms to displace from the lattice site, leading to the lattice disorder and formation of high concentration of defects. In electronic stopping, the incident ion loses its energy by Coulomb interaction as a result of interaction with the electron cloud of the host atom. The electrons of the substrate atoms may be excited to higher energy levels or even ionized. If E is the energy of an ion at any point x along its path, the total rate of energy loss, dE/dx , due to nuclear and electronic stopping is given by [100]

$$\frac{dE}{dx} = S_n(E) + S_e(E). \quad (\text{Equation 3.1})$$

The stopping mechanisms determine the statistical distribution of the implanted atoms in the material. In amorphous materials, the implanted ion encounters the same number of atoms per unit distance while traveling in the substrate lattice. However, in the case of crystalline materials, there are directions (e.g. Si<110>) in which no nuclei will be encountered and the only stopping mechanism is due to the electrons. Consequently, the incident ions can travel a considerable distance into the substrate with little energy loss. Such channeling effect is more pronounced for light dopant species such as boron and phosphorus. To suppress the ion channeling effect, the substrate is usually tilted by a small angle (typically 7°) during ion implantation so that the ion beam is incident along a random direction. The distribution profile of the implanted ions can be approximately described by a Gaussian distribution function given by [100]

$$n(x) = \frac{\Phi}{\sqrt{2\pi}\Delta R_p} \exp\left[-\frac{(x - R_p)^2}{2\Delta R_p^2}\right] \quad (\text{Equation 3.2})$$

where $n(x)$ is the implanted ion concentration in cm^{-3} as a function of depth x , Φ is the dose in ions/cm^2 , R_p is the projected range, and ΔR_p is the statistical fluctuation in the direction of the projected range.

The Varian D200 ion implanter was used in this project. B^+ , As^+ , and Si^+ ion implantations were performed to introduce B, As, and Si dopants into FeSi_2 films with different doses ranging from 1×10^{13} to 1×10^{15} ions/cm^2 . During the ion implantations, the wafers were positioned at a tilt of 7° and a twist of 22° to suppress the ion channeling effect. The stopping and range of ions in matter (SRIM) code [103] was used to simulate the stopping powers, projected range and straggling distributions for B, As, and Si ions at different energies in FeSi_2 target.

3.2.3 Annealing processes

3.2.3.1 Rapid thermal annealing

Rapid thermal annealing (RTA) is an important thermal processing technique for a number of steps such as silicide formation, activation of implanted dopants, removal of implantation damage, formation of gate dielectrics, etc. The main feature of RTA is the short duration of anneals in seconds which reduces the overall thermal budget such that desired physical and chemical processes are completed while unwanted reactions are suppressed. In RTA, the sample is typically annealed in seconds using incoherent light sources such as tungsten halogen lamps, arc lamps, or graphite heaters. Since the light beam is defocused, the entire wafer can be uniformly exposed and annealed isothermally.

Figure 3.3 shows the typical RTA processing cycle. The RTA processing cycle generally consists of three phases: heating, annealing, and cooling. During heating, the temperature is ramped up at a rate of 30-60 °C/s to the desired temperature at which the sample is annealed for a certain period of time. After annealing, the energy sources for achieving high temperature and short time annealing are removed and the sample is subjected to cooling. The heating and cooling processes are dominated by radiation. Assuming the sample is uniformly exposed, the heat flow produced by the incoherent light source for the case of one-dimensional treatment is given by [104]

$$\rho C_p (T) \frac{\partial T(x,t)}{\partial t} = \frac{\partial}{\partial x} \left[\kappa(T) \frac{\partial T(x,t)}{\partial x} \right] + P(x,T,t) \quad (\text{Equation 3.3})$$

where T is the temperature, t is the time, ρ is the density, C_p is the specific heat capacity, κ is the thermal conductivity of the sample, and P is the absorbed power distribution for the radiation source.

Figure 3.3. Typical RTA processing cycle showing three different phases of processes: heating, annealing, and cooling.

In our experiment, the RTA processes were performed under a flowing purified N₂ ambient at various temperatures ranging from 300 to 850 °C for 60 s using Uniaxis Addax XM80 rapid thermal processing (RTP) system. A chromel-alumel thermocouple coupled with a well-calibrated high temperature optical pyrometer was used to measure the temperature of the sample at the bottom during annealing processes.

3.2.3.2 Furnace annealing

Furnace annealing (FA) exhibits relatively high thermal budget and long thermal cycle due to its long duration of anneals in hours or more. In FA, the sample is usually placed in a cylindrical tube (tube furnaces) or closed box (box furnaces) surrounded by heating elements, which are embedded in a thermally insulating matrix. Electric current passing through the heating element results in heating of the element via Joule heating, which produces the desired temperature for annealing. Typically, the heating and cooling rates in FA are significantly lower as compared to RTA and the duration of anneals can be up to a few hours. In our experiment, the FA processes were done in a forming gas (N₂/H₂, with 5% H₂) ambient using Thermcraft tube furnace. A thermocouple was used for the temperature measurement during annealing processes.

3.3 Physical and Chemical Characterization

3.3.1 X-ray diffraction

X-ray diffraction (XRD) is a versatile and non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of materials. Figure 3.4 shows a series of parallel planes of atoms in a periodic lattice

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separated from one another by a distance d , which varies according to the nature of the material. For any crystal, such parallel planes exist in a number of different orientations, each having its own specific d -spacing. When a monochromatic X-ray beam with wavelength λ is incident on the parallel lattice planes at an angle θ , constructive interference of the reflected rays from successive planes occurs when the path difference is an integral number n of wavelengths. This gives the Bragg's law for diffraction [105]:

$$2d \sin \theta = n\lambda . \quad (\text{Equation 3.4})$$

Figure 3.4. Bragg's law for diffraction: $2d \sin \theta = n\lambda$. Constructive interference of the reflected rays occurs when the path difference is an integral number of wavelengths.

The Bragg's law is a consequence of the periodicity of the lattice. Reflection can occur only for wavelength $\lambda \leq 2d$, as suggested by Equation (3.4). This explains why visible light, which produces only ordinary optical refraction, cannot be used. X-ray wavelength (1.54 Å for Cu $K\alpha$ radiation) is comparable with the inter-atomic distances and hence is excellent candidate for probing crystals. When the Bragg's condition is satisfied, the reflected rays interfere constructively to produce a diffraction pattern which can be detected. The relative intensity of the various orders of diffraction (denoted by n)

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is determined by the composition of the basis of atoms associated with each lattice point of the crystal.

In XRD experiment, the incident angle θ is continuously varied over a range of values such that the Bragg's condition is satisfied by different d -spacings in a material. Plotting the diffraction intensity as a function of diffraction angle (2θ) produces the diffraction pattern or the XRD spectrum, which is the characteristic of the sample. By comparison with the standard diffraction pattern from the joint committee on powder diffraction standards (JCPDS) library [106], detailed information about phase and crystal structure can be extracted.

The Siemens D5005 XRD and Bruker AXS general area detector diffraction systems (GADDS) were used in this project. The Siemens D5005 XRD is a conventional diffractometer equipped with a point detector whose diffraction measurement is confined within a plane, during which the point detector makes a 2θ scan along a detection circle. The Bruker AXS GADDS utilizes a two-dimensional (2D) area detector and high speed electronics for rapid scan and processing of XRD patterns. Each 2D pattern, i.e., the Debye ring, is a plot of diffraction intensity for a particular diffraction angle 2θ (x -axis) with χ (y -axis). The main advantages are the improved speed of data collection and 2D detection of diffracted X-ray beams with greater sensitivity.

Figure 3.5 illustrates the principle of 2D detection for XRD. When an incident X-ray beam interacts with a sample, a diffraction cone with its rotation axis lying along the incident beam is produced. Here, D is the distance between the sample and the detector and α is the detector swing angle, also referred to as detector 2θ angle. The surface of the 2D detector can be considered as a plane, which intersects the diffraction cone to form a

conic section. This conic section is known as the diffraction ring or Debye ring, which takes different shapes for different α angles. In particular, when imaged on-axis ($\alpha=0^\circ$), the conic section appears as circle, producing a circular diffraction pattern or Debye ring.

Figure 3.5. A diffraction cone and the Debye ring with a 2D detector plane.

In our experiment, the Seeman-Bohlin scan was performed for thin film analysis with a glancing angle of incidence of 2° using Siemens D5005 XRD. The Seeman-Bohlin scan is important for lateral resolution because a large area of the thin film sample can be analyzed by using a small glancing angle of incidence. The Bragg-Brentano scan (i.e., the θ - 2θ scan) was performed for depth resolution analysis using Bruker AXS GADDS. The diffraction angle 2θ used ranges from 25° to 55° .

3.3.2 Scanning electron microscopy

Scanning electron microscopy (SEM) is a type of electron microscopy capable of high resolution imaging of a sample surface. SEM uses an electron beam to produce a

magnified image of the sample. The image is produced by scanning the sample with a focused electron beam with typical energy of 10-30 keV and detecting the secondary and backscattered electrons [107]. The use of electrons enables much larger magnifications and better depth of field as compared to optical microscopes since electron wavelengths are much smaller than photon wavelengths. The electron wavelength λ_e depends on the electron velocity v_e or the accelerating voltage V and is given by de Broglie equation:

$$\lambda_e = \frac{h}{p} = \frac{h}{m_0 v_e} = \frac{h}{\sqrt{2m_0 e V}} \quad (\text{Equation 3.5})$$

where h is the Planck's constant, p is the momentum of the electron, and m_0 is the mass of the electron. For an accelerating voltage of 10 kV, the electron wavelength is about 0.012 nm, which is significantly below the wavelength of visible light (~400-700 nm).

In a typical SEM, the electron beam is thermionically emitted from an electron emitter of tungsten or lanthanum hexaboride. The interaction between incident electrons and surface atoms produces signals (mainly secondary electrons) that contain information about sample topography and composition which can be detected to form SEM image. In field-emission SEM (FESEM), due to the highly intense and more coherent electron beam, the system is capable of both high resolution imaging and high quality real time image displays at all scan speeds. The detection of the emitted characteristic X-rays from the specimen caused by the shell transitions as a result of electron-atom interaction can be used for elemental analysis and is known as energy dispersive X-ray spectroscopy (EDS). In our experiment, a JEOL FESEM JSM 6700 was used.

3.3.3 Transmission electron microscopy

Transmission electron microscopy (TEM) is an electron microscopy technique capable of extremely high resolution imaging in the limit of sub-atomic regime [108]. In TEM, a beam of electrons is transmitted through an ultrathin specimen. The transmitted and forward scattered electrons form a diffraction pattern and produce an image which is magnified and focused onto a fluorescent screen. The three primary imaging modes are bright field, dark field, and high resolution TEM (HRTEM). Images formed with only the transmitted electrons are bright field images and images formed with a specific diffracted beam are dark field images. HRTEM gives structural information on the atomic size level and is very important for interface analysis.

In principle, TEM operates similar to an optical microscope, except that it utilizes high energy electron beam (typically in the range from 100 to 400 keV) instead of visible light. The extremely high resolution imaging capability in the nanometer scale of TEM can be understood from the electron wavelength being used. For an accelerating voltage of 100 kV, the electron wavelength is about 0.004 nm by Equation (3.5), which enables magnifications of several hundred thousand. In our experiment, a FEI FETEM CM200 with an accelerating voltage of 200 keV was used.

3.3.4 Secondary ion mass spectroscopy

Secondary ion mass spectroscopy (SIMS) is one of the most powerful surface analytical techniques for studying the composition of solid surfaces and thin films with excellent sensitivity. The technique is element specific and is capable of detecting most elements as well as isotopes and molecular species present in the parts per billion range.

The basis of SIMS is a destructive removal of material from the sample by sputtering and an analysis of the ejected material by a mass spectrometer [107].

In a typical SIMS, the primary ions (mostly Cs^+ , O_2^+ , O^- , Ar^+ , or Ga^+ ions) of energies between 1 and 30 keV are incident on the sample. In this energy range, the penetration depth of primary ions into the sample essentially remains below 10 nm which is the surface layer of the sample. The primary ions set off collision cascades and eject some of the surface atoms from the sample (sputtering). The ejected atoms are mostly neutral, but some can be ionized to become positively or negatively charged, which are referred to as secondary ions. The mass/charge ratio of the secondary ions is then analyzed and detected as a mass spectrum or a count by mass spectrometer and displayed on a fluorescent screen.

Quantitative depth profiling is undoubtedly the major strength of SIMS. In depth profiling, the secondary ion yield for one particular mass is recorded as a function of sputtering time. In practice, such plots must be converted to density versus depth. The conversion of signal intensity or ion yield to density is routinely performed with the use of calibrated standards. The time-to-depth conversion is usually made by measuring the sputter crater depth.

In our experiment, an ION-TOF GmbH time-of-flight SIMS (TOF-SIMS) IV was used. In TOF-SIMS, the incident beam consists of pulsed ions from a liquid Ga^+ gun with pulse width on the order of nanoseconds which generates pulsed secondary ions. These ions are separated in a field-free drift path according to their kinetic energy and the time taken for them to travel to the detector (i.e., the transit time) is measured. The

mass/charge ratio m/q of the ions can be obtained by equating their kinetic and potential energies and is given by

$$\frac{m}{q} = \frac{2Vt_i^2}{L^2} \quad (\text{Equation 3.6})$$

where V is the accelerating voltage, t_i is the transit time, and L is the path length from the sample to the detector. A major advantage of TOF-SIMS is the absence of narrow slits in the spectrometer which increases the ion collection by 10-50%. The sputtering rate can be reduced which allows for more accurate depth profiling. Since m/q is determined by time of flight, all generated secondary ions can be detected simultaneously.

3.4 Optical Characterization

3.4.1 Absorption, transmission, and reflection

Optical characterization techniques are attractive because they are mostly non-contacting with minimal sample preparation, which is a major advantage when contacts are detrimental [107]. Optical measurements can have very high sensitivity. In practice, the measurements utilize essentially the entire electromagnetic spectrum from the DUV to the far IR region. The relationship between light energy and wavelength has already been given by Equation (2.9) in Chapter 2.

When light impinges on a semiconductor, there are three fundamental photon-semiconductor interaction mechanisms: absorption, transmission, and reflection. Figure 3.6 shows the interaction mechanisms between light and semiconductor. The process mainly depends on the photon energy $E=h\nu$ (h is the Planck's constant and ν is the frequency) and the bandgap energy E_g . If the photon energy is less than E_g , the photons

are not readily absorbed. In this case, the light is transmitted through the material and the semiconductor appears to be transparent. If $E > E_g$, the photon can interact with the valence electrons and elevate the electrons into the conduction band creating EHPs, giving rise to the absorption process. Reflection occurs for almost all materials. It is characterized by the refractive index of the material.

Figure 3.6. Interaction mechanisms between light and semiconductor.

3.4.2 Photo-absorption measurements

The optical properties of semiconductors are most commonly measured by a spectrophotometer, which is the instrument to measure the interaction between light energy and matter to obtain qualitative and quantitative information about samples. There are three different modes of measurement, namely the absorbance, transmittance, and reflectance. During measurement, the instrument measures the ratio of the incident light to the transmitted light. The logarithm of this ratio is defined as the absorbance A of the sample given by

$$A = \log_{10} \frac{I_i}{I_t} \quad (\text{Equation 3.7})$$

where I_i and I_t are the incident and transmitted light, respectively (see Figure 3.6).

A Shimadzu UV3101 UV-VIS-NIR spectrophotometer was used in this project. The system is a double beam instrument capable of all different modes of measurement. Figure 3.7 shows the schematic of a double monochromator spectrophotometer. In this double beam instrument, a beam splitter is used to obtain two light beams I_i of equal energy with equivalent optical paths from the incident light. One of these beams passes through the sample (I) while the other passes through a reference sample (I_0). These beams are then detected and measured by a sample and reference detector, respectively.

Figure 3.7. Schematic of a double monochromator spectrophotometer.

In our experiment, the photo-absorption measurements were performed in an absorbance mode to determine the absorption spectra of β -FeSi₂ based on the proposed optical absorption model. In absorbance mode, the ratio I_0/I was measured to give the absorbance of the sample according to Equation (3.7). In general, the optical properties of

interest such as optical absorption coefficient and index of refraction are not directly measurable quantities. However, based on the physical structure of the sample, a model relating optical constants to the experimentally measured absorbance was developed. The model was then applied to calculate the optical constants of the sample.

3.5 Electrical Characterization

3.5.1 Four-point probe measurement

Four-point probe measurement is an electrical impedance measuring technique that uses separate pairs of current-carrying and voltage-sensing electrodes for accurate measurements [107]. Figure 3.8 shows a four-point probe measurement configuration. In this configuration, the current I is typically carried through the outer two probes into the sample while the voltage V is measured across the inner two probes. Although the voltage path contains the probe and contact resistances, the measured voltage is essentially the voltage drop across the sample because the current flowing through the voltage path is very low due to the high input impedance of the voltmeter (around $10^{12} \Omega$ or higher). Hence, the influence of the parasitic voltage drops can be eliminated and the resistance of the sample can be accurately determined.

The four-point probe is commonly used to measure the sheet resistance of thin films. For an arbitrarily shaped thin sample, the measured sheet resistance R_s is given by

$$R_s = F \times \frac{V}{I} \quad (\text{Equation 3.8})$$

where F is a correction factor depending on the sample geometry, probe spacing, and probe placement relative to the sample edges. The sheet resistance is a measure of the

resistivity averaged over the sample thickness, given in units of Ω/square . It is related to the resistivity ρ and thickness t of the film by the relation

$$R_s = \frac{\rho}{t}. \quad (\text{Equation 3.9})$$

Figure 3.8. Four-point probe measurement configuration.

3.5.2 Hall effect measurements

Hall effect measurements have found wide application in the characterization of semiconductor materials because it has the ability to determine the resistivity, the carrier type and density, and the mobility. The Hall effect was discovered by Hall in 1879 while investigating the nature of the force acting on a current-carrying conductor in a magnetic field [109]. Hall found that a magnetic field applied to a conductor perpendicular to the current flow direction produces an electric field perpendicular to the magnetic field and the current.

Figure 3.9 shows the schematic illustrating the Hall effect in a semiconductor, in which a current I flows in the x -direction and a uniform magnetic field B is applied in the

z -direction. In the presence of the uniform magnetic field, free carriers (electrons in the n -type samples and holes in the p -type samples) experiencing the Lorentz force initially drift away from the current path towards the negative y -axis, leading to an excess surface electrical charges on this side of the sample. This produces a Hall voltage and induces an electric field in the y -direction opposing the Lorentz force. In steady state, the Lorentz force is exactly balanced by the force acting on the free carriers due to the electric field.

Figure 3.9. Schematic illustrating the Hall effect in a semiconductor.

The Hall voltage V_H is given by [107]

$$V_H = \frac{IB}{eNt} \quad (\text{Equation 3.10})$$

where N is the carrier concentration. Therefore, by measuring the current I , the magnetic field B , and the Hall voltage V_H , the carrier concentration can be determined from

$$N = \frac{1}{e|R_H|} \quad (\text{Equation 3.11})$$

where R_H is the Hall coefficient defined as

$$R_H = \frac{tV_H}{IB}. \quad (\text{Equation 3.12})$$

Note that the carrier type can be deduced from the sign of the Hall coefficient R_H ; it is positive for p -type semiconductor and negative for n -type semiconductor. The Hall mobility μ_H can be calculated by

$$\mu_H = \frac{|R_H|}{\rho}. \quad (\text{Equation 3.13})$$

An Accent HL 5500 system was used for the Hall effect measurements in this project. The Hall effect measurements were conducted at RT under an applied constant magnetic field of 0.32 T with the van der Pauw technique to determine the carrier conductivity type, concentration, and mobility in the β -FeSi₂ thin films. In the van der Pauw technique, a resistivity measurement was first carried out to measure the resistivity of the sample, and a Hall measurement was then performed to determine the Hall coefficient. Carrier density and mobility are then calculated from these quantities by Equations (3.11) and (3.13). This technique requires four contacts to the sample and is applicable to sample of arbitrary shape. In our experiment, all samples have a square geometry of area $1 \times 1 \text{ cm}^2$. Ohmic contacts were fabricated by soldering of In metal at the corners of the sample.

3.5.3 Current-voltage measurements

The current-voltage (I - V) characteristics of the β -FeSi₂/Si heterojunction diodes were extracted using MDC CSM/Win semiconductor measurement system equipped with a QuietCHUCK DC 490 system capable of temperature dependent I - V measurements. In

theory, the current of a pn junction is often written as a function of the diode voltage V_d similar to Equation (2.2) as [107]

$$I = I_s \left[\exp\left(\frac{eV_d}{nkT}\right) - 1 \right] \quad (\text{Equation 3.14})$$

where $V_d = V - IR_s$, V is the applied terminal voltage and the term IR_s represents the voltage drop due to the series resistance R_s . The diode voltage is the voltage across the depletion region and excludes any voltage drops across the quasi-neutral regions. For $V_d \gg nkT/e$, a plot of $\log(I)$ versus V_d generally yields a straight line whose slope and $V_d = 0$ intercept give the ideality factor n and saturation current I_s , respectively. The R_s can be determined from the deviation of the $\log(I)$ - V curve from linearity at high currents as $R_s = \Delta V/I$.

The output characteristics of the β -FeSi₂/Si heterojunction solar cells were measured using a SAN-EI Electric XES-301S solar simulator. The solar simulator utilizes a 300 W Xe short arc lamp exposure unit to produce a continuous light spectrum with an energy distribution close to that of sunlight, which provides uniform illumination over an effective irradiated area of 100 mm in diameter. In our experiment, the solar cells were characterized under the AM1.5 illumination with a total power density of 100 mW/cm². The performance parameters I_{sc} , V_{oc} , and FF and conversion efficiency η of the solar cells were extracted from the illuminated I - V characteristics.

3.6 Summary

The experimental approaches used for the formation of β -FeSi₂ thin films have been discussed. Different annealing processes, including RTA and FA, were covered. The materials and optical as well as electrical characterization techniques used for the

analysis of silicide films and devices were also described. Unless otherwise stated, the subsequent chapters follow the experimental procedures described in this chapter.

CHAPTER 4

FIRST-PRINCIPLES STUDY OF BETA-PHASE IRON DISILICIDE

4.1 Introduction

In this chapter, we present the theoretical study of β -FeSi₂ by first-principles calculations based on the DFT. The basic principles and simulation approaches of first-principles calculations are described. The equilibrium crystal structure and properties of β -FeSi₂ are studied and analyzed in terms of the band structure, density of states (DOS), and structural parameters. The effects of Fe and Si vacancies on the electrical properties of β -FeSi₂ are also investigated. In addition, the effects of impurity doping in β -FeSi₂ by B and As dopants are discussed.

4.2 Atomistic Simulation and Approaches

4.2.1 Basic principles

First-principles (also known as the *ab initio*) calculations based on the density-functional theory (DFT) is a powerful and reliable means to simulate and compute the properties of condensed matter. Since the behavior of electrons governs most of the properties of materials, such as that of a single atom or an assembly of atoms in solids, one can understand the physical properties of any material from first-principles, i.e., by solving the Schrödinger equation for the electrons in that material based on the

fundamental physical laws and without using any free parameters. However, such many-body problem is unquestionably formidable and often requires a computational approach because electrons interact strongly with each other.

In practice, most first-principles approaches recast the problem to one where electron interactions are represented by an effective potential acting on the apparently independent and non-interacting electrons. The effective potential takes into account the electron interactions and allows one to deal with one electron at a time. This reduces the many-body problem to the solution of the dynamics of non-interacting electrons in some specific configuration of the nuclei (effective potential field). The result is a set of one-electron Schrödinger-like equations given by

$$H\psi_n = \left(-\frac{\hbar^2}{2m} \nabla^2 + V_{ext} + V_{eff} \right) \psi_n = \varepsilon_i \psi_n \quad (\text{Equation 4.1})$$

where ψ_n are the n one-electron wavefunctions, V_{ext} is the external potential of the nuclei, and V_{eff} is the effective potential including Hartree and exchange-correlation potentials.

For practical implementation of the calculations, further simplifications must be introduced to allow calculations to be performed more accurately and efficiently. These include DFT to model the electron-electron interactions, pseudopotential theory to model the electron-core interactions, supercells to model the systems with aperiodic geometries, and iterative minimization techniques to relax the electronic coordinates for total energy minimization [110]. DFT is an exact theory for describing interacting electrons. It states that the total energy of a system of electrons and nuclei is a unique functional of the electron density [111]. Therefore, by applying DFT, one makes no attempt to compute the many-body electron wavefunctions and instead working with a simple scalar field of

density functional of the energy. The energy E of a system of electrons and nuclei is written in terms of the electron density $\rho(\vec{r})$ as

$$E = E[\rho(\vec{r})] = \int V_{ext}(\vec{r})\rho(\vec{r})d\vec{r} + F[\rho(\vec{r})] \quad (\text{Equation 4.2})$$

where F is an effective functional taking into account the electron kinetic energy and exchange-correlation effects, and the electron density is given by [112]

$$\rho(\vec{r}) = \sum_{n=1}^N |\psi_n(\vec{r})|^2. \quad (\text{Equation 4.3})$$

The degree of simplification is immense, and yet the theory remains completely general. The true ground state energy of a system for a given external potential can be determined via the variational principle of DFT.

4.2.2 Simulation methods

Figure 4.1 shows the flowchart describing the simulation process flow. Atomistic simulation generally requires first the construction of the material structures of interest. After the crystal structure is created, the basis set parameters and convergence tolerances used in the calculation are specified. The basis set parameters are the cutoff energy and the Monkhorst-Pack (MP) grid density which determine the finite plane wave basis set and the number of k -point sampling in the reciprocal space, respectively. The crystal structure is then subjected to geometry optimization process until it is fully relaxed and stable by total energy minimization. At the optimized structure, static calculation is finally performed to compute the physical properties of interest, such as total energy, band structure and DOS, etc.

Figure 4.1. Flowchart describing the atomistic simulation process flow.

In essence, geometry optimization ensures the ions and electrons in the supercell are moved around stepwise until the forces and stresses acting on the atoms and the change in total energy between steps fall below some predefined convergence tolerances. Figure 4.2 shows the flowchart describing the geometry optimization process. During optimization process, the ionic positions are adjusted using quasi-Newton methods. For each configuration of the ionic positions, the electronic configuration is then optimized via conjugated gradient technique. The system now compares the total energy with the previous configuration and checks if the forces and stresses are within the tolerance limits. If the structure is not optimized, a new set of ionic positions will be generated. This cycle is performed until the tolerance limits are satisfied and the energy should then be a local minimum.

Figure 4.2. Flowchart describing the geometry optimization process.

In our simulation, the Materials Studio 4.0 was used to construct, visualize, and manipulate the crystal structures under study. First-principles calculations based on the DFT were performed using the Cambridge serial total energy package (CASTEP) developed by Payne *et al.* [110]. The Perdew-Burke-Ernzerhof (PBE) form of generalized gradient approximation (GGA) [113] was used to treat the exchange-correlation functional. The Vanderbilt ultrasoft pseudopotentials (USP) [114] were employed for the $3d^6 4s^2$, $3s^2 3p^2$, $2s^2 2p^1$, and $4s^2 4p^3$ atomic configurations of Fe, Si, B, and As, respectively, to describe the electron-ion interaction. The geometry optimization was performed using Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [115].

4.3 Crystal Structures

4.3.1 Structural model of β -FeSi₂

We start our theoretical study on the equilibrium crystal structure and properties of β -FeSi₂. We constructed a conventional 48-atom simple orthorhombic unit cell to model β -FeSi₂ using the accepted experimental lattice constants $a=9.863$ Å, $b=7.791$ Å, and $c=7.833$ Å and atomic coordinates shown in Table 4.1 given by Dusausoy *et al.* [16]. Figure 4.3 shows the orthorhombic unit cell of β -FeSi₂ and its projection onto the x - y and y - z plane, i.e., (001) and (100) direction, respectively. There are two crystallographically non-equivalent sites for Fe (8 Fe_I and 8 Fe_{II}) and Si (16 Si_I and 16 Si_{II}) and 16 formula units distributed over these atoms per unit cell. In the lattice, each Fe has 8 Si neighbors and each Si has 4 Fe neighbors.

Table 4.1. Atomic coordinates of β -FeSi₂.

Non-equivalent site	Wyckoff position	Fractional coordinate
Fe _I	8d	(0.21465, 0.00000, 0.00000)
Fe _{II}	8f	(0.00000, 0.30861, 0.31504)
Si _I	16g	(0.12823, 0.27465, 0.05120)
Si _{II}	16g	(0.37271, 0.04499, 0.22608)

Figure 4.3. A conventional 48-atom simple orthorhombic unit cell of β -FeSi₂ and its projection onto the x - y and y - z plane, i.e., (001) and (100) direction, respectively.

In the calculations, we expanded the electron wavefunction using plane waves with a cutoff energy of 300 eV. The BZ in the reciprocal space was sampled using a $6 \times 6 \times 6$ k -point mesh based on the Monkhorst-Pack (MP) scheme [116]. The cell structure was allowed to fully relax by total energy minimization until the Hellmann-Feynman forces and stresses acting on the atoms were smaller than 0.03 eV/Å and 0.05 GPa,

respectively, and the convergence in the total energy was better than 0.01 meV/atom. In the relaxation process, both atomic coordinates and lattice parameters of β -FeSi₂ were optimized. The static calculation was performed at the relaxed β -FeSi₂ crystal structure.

4.3.2 Band structure and density of states

Figure 4.4 shows the electronic band structure of relaxed β -FeSi₂ obtained by the pseudopotential calculations within the GGA scheme. The labels along the x -axis of the band structure correspond to the standard definitions of high symmetry points for the given lattice type [117]. In particular, the Γ point is denoted by a G , which is the center of the BZ. It can be seen that an energy gap clearly exists in the band structure, suggesting a semiconducting behavior for β -FeSi₂. In order to investigate the gap nature and value, it is necessary to resolve the region of band structure near the band edges.

Figure 4.5 shows the band structure and the corresponding DOS of relaxed β -FeSi₂ in the vicinity of the Fermi level E_F . The total number of valence electrons in the unit cell is 256 and the gap is formed between the 128th and 129th bands. The origin of the gap formation was related to a Jahn-Teller-like effect [118] of crystal distortion from the metastable fluorite form of FeSi₂ as pointed out in Ref. [22]. The band structure is characterized by an indirect transition of 0.787 eV between the valence band maximum (VBM) at the G point and a point located at approximately $0.6 \times (G-Z)$ (conventionally denoted as Λ^*) which is the CBM, and a direct transition of 0.836 eV at the Λ^* point.

This result correlates well with the calculations in Refs. [23, 93], considering that the Y point in the base-centered orthorhombic BZ is folded into the G point in the simple orthorhombic BZ. The gap values obtained are slightly larger; however, the energy

difference between the direct and indirect transitions is quantitatively meaningful. This energy difference was found to be 49 meV, which is consistent with the observations in other calculations (see Table 2.6). The direct gap of 0.836 eV for β -FeSi₂ agrees well with our optical results of ~ 0.86 eV shown in Chapter 5 (Section 5.4.3) [7] and that reported in the literatures (see Table 2.2). It is well known that the electronic structure calculations within the GGA generally underestimate the bandgap energies [119, 120]. Therefore, the observed underestimation of $\sim 3\%$ in the gap size is expected.

It is clear from Figure 4.5 that the band structure of β -FeSi₂ is rather complicated. However, it can be understood from the energy dependence of the total and partial DOS (PDOS) as presented in Figure 4.6. The valence band extends down to about -13.5 eV below the Fermi energy. The bands in the region from the bottom up to about -7.0 eV correspond mainly to the Si-*s* states. The contribution of the Fe-*d* states in this region is relatively insignificant. In the region from -7.0 to about -3.0 eV, the Si-*p* states hybridize with the Fe-*d* states with t_{2g} character, thereby forming strong bonding orbitals in the Fe-Si directions. The remaining non-bonding Fe-*d* states with e_g character (i.e., the lowest unoccupied states) are located above -3.0 eV up to the Fermi level E_F . These results are in good agreement with the theoretical results reported in Refs. [23, 92].

Figure 4.4. Electronic band structure of relaxed β -FeSi₂ obtained by the pseudopotential calculations within the GGA scheme.

Figure 4.5. Band structure and the corresponding DOS of relaxed β -FeSi₂ in the vicinity of the Fermi level E_F .

Figure 4.6. Total and partial DOS of (a) β -FeSi₂ and the subshells of (b) Fe and (c) Si.

4.3.3 Equilibrium lattice parameters

Table 4.2 shows the comparison between the calculated and experimental values for the lattice parameters of β -FeSi₂. Our theoretical calculations predict an orthorhombic lattice (a , b , and c are distinct while α , β , and γ are mutually orthogonal) for β -FeSi₂ with the equilibrium lattice constants $a=9.8442478$ Å, $b=7.7291945$ Å, and $c=7.7759268$ Å of less than 0.8% from the experimental values. Therefore they are in excellent agreement with the experimental results. The calculated lattice constants were found to be smaller than its experimental values. This translates into 1.7% shrinkage in the unit cell volume from 601.908344 to 591.655541 Å³.

Table 4.2. Comparison between the calculated and experimental values for the lattice parameters of β -FeSi₂.

Lattice parameter	Calculated (Å)	Experimental (Å)	Error (%)
a	9.8442478	9.863	-0.190
b	7.7291945	7.791	-0.793
c	7.7759268	7.833	-0.729
α	90°	90°	0
β	90°	90°	0
γ	90°	90°	0

Since the simulation was done at absolute zero (0 K), the actual lattice constants are expected to be closer to the experimental values after taking into account the effect of thermal expansion at RT (300 K). Consequently, the actual error is also expected to be

smaller. A simple estimation can be performed as follows to quantify the actual error.

When the temperature changes, the final length L' after expansion is given by

$$L' = (1 + \alpha_i \Delta T) L_0 \quad (\text{Equation 4.4})$$

where L_0 is the original length, ΔT is the temperature difference in K, and α_i is the thermal expansion coefficient in K^{-1} along the i direction. Using the anisotropic and linear thermal expansion coefficient of β -FeSi₂ for different crystal orientations given in Ref. [33], the lattice constants of β -FeSi₂ at 300 K can readily be calculated.

Table 4.3 shows the result of the calculation. The calculated lattice constants now become $a=9.8948362 \text{ \AA}$, $b=7.7304186 \text{ \AA}$, and $c=7.7782050 \text{ \AA}$ after expansion at 300 K. This gives an error of +0.323%, -0.778%, and -0.7%, respectively. The unit cell volume was found to decrease from 601.908344 to 594.964435 $\text{\AA}^3$, corresponding to 1.15% reduction. Therefore our first-principles study predicts an orthorhombic crystal structure for β -FeSi₂ that closely matches with the experimental findings, which also justifies the correctness of our theoretical results.

Table 4.3. Calculated lattice constants of β -FeSi₂ taking into account the thermal expansion at 300 K and its comparison with the experimental values.

Lattice constant	$\alpha (10^{-6} \text{ K}^{-1})$	Calculated ($\text{\AA}$) (at 300 K)	Experimental ($\text{\AA}$)	Error (%)
a	$16.697+0.001442 \times T$	9.8948362	9.863	+0.323
b	$0.026+0.001673 \times T$	7.7304186	7.791	-0.778
c	$0.415+0.001872 \times T$	7.7782050	7.833	-0.7

While the present study generally produces accurate results, it is important to recognize the two main sources of errors in the calculation: (1) fundamental error associated with the use of GGA to treat the exchange-correlation functional and (2) systematic error associated with inaccuracy in the wavefunctions introduced by using a finite basis set and k -point sampling in the reciprocal space. The former is essentially unavoidable, but the latter can be minimized by using optimal basis set parameters, i.e., cutoff energy and MP grid density. Increasing the precision of cutoff energy and MP grid density should decrease the systematic error and hence improve the accuracy in the calculation. However, this will be achieved at a trade-off of increased computational cost.

4.4 Effects of Fe and Si Vacancy Defects

Structural imperfections such as chemical impurities or point defects (interstitials or vacancies) are commonly found in the real crystals. Some important properties of crystals can be controlled or influenced as significantly by imperfections as by the host crystal. In the case of β -FeSi₂, native point defects (mainly Fe and Si vacancies) are known to be closely related to the transport properties of carriers in the undoped or unintentionally doped silicide film, and even in the impurity-doped β -FeSi₂ where both electrical and optical properties can be greatly affected, particularly when defects are present at high concentrations. It is therefore important to study the effects of these vacancy defects.

We focus our investigation on the Fe and Si vacancies and exclude other possible point defects such as interstitials or antisites. To model β -FeSi₂ crystal containing a vacancy (Fe or Si), we used the conventional 48-atom simple orthorhombic unit cell of β -

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FeSi₂ as depicted in Figure 4.3 and replaced one of each type of the Fe or Si site by a vacancy ($V[\text{Fe}_\text{I}]$, $V[\text{Fe}_\text{II}]$, $V[\text{Si}_\text{I}]$, and $V[\text{Si}_\text{II}]$) to form the defect structures for calculations. Figure 4.7 shows the defective β -FeSi₂ crystals containing each Fe and Si vacancy. These supercells are two times larger than the primitive cell of β -FeSi₂ and thus are effective in reducing the inter-vacancy interactions.

Figure 4.7. Defective crystal models of β -FeSi₂ containing a vacancy of (a) Fe_I, (b) Fe_{II}, (c) Si_I, and (d) Si_{II} in the (001) projection.

In the calculation of the defective crystals, the electron wavefunction was expanded using plane waves with a cutoff energy of 280 eV. A $2 \times 3 \times 3$ k -point mesh

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generated by the MP scheme was employed for numerical integrations over the BZ. Structural relaxation was performed by total energy minimization such that the atomic arrangements around a vacancy were optimized, allowing relaxation of the first and second nearest neighboring atoms. The relaxation procedures were truncated when the Hellmann-Feynman forces acting on the atoms were smaller than 0.05 eV/Å. In order to calculate the atomic chemical potentials of the constituent elements, we also carried out calculations for the reference materials, i.e., bulk Fe ($Im\bar{3}m$) and Si ($Fd\bar{3}m$) as well as Fe₁₆Si₃₂ ($Cmca$) crystals using the same convergence tolerances for consistency.

4.4.1 Defect formation energy

In a perfect crystal, we create a vacancy by transferring an atom from a lattice site in the interior to the surface of the crystal. In thermal equilibrium, a certain number of these lattice vacancies are always present in an otherwise perfect crystal because the entropy is increased by the presence of disorder in the structure. The formation energy of defects in general depends strongly on the atomic chemical potentials of the constituent elements and the electron chemical potential. For an elemental system where the total energy of a single bulk atom is well defined, the defect formation energy can be unambiguously obtained as the difference between the calculated energy of an N -atom defect-containing supercell and N times the energy of a single bulk atom. However, this analysis cannot be applied to compound semiconductors such as FeSi₂ where the energy of a pair of Fe and 2 Si atoms is well defined, but the energy of a single Fe or Si atom depends on the interactions between the crystal and its external environment.

By introducing an external reservoir of Fe (or Si) atoms, Fe (or Si) atoms can be added to the crystal from the reservoir (forming interstitials), or removed from the crystal and transferred to the reservoir (forming vacancies). This allows us to assign any constant energy (a reference state) to the Fe (or Si) atom, whose energy at $T=0$ K is defined as the chemical potential. Since the sum of the Fe and Si energies is determined by the total energy of the perfect FeSi₂ cell, the Fe energy determines the Si energy, and vice versa. Therefore the formation energy of any defect can be clearly defined and determined from the total energies of the relevant crystals.

For a neutral vacancy defect X , the formation energy $E_f[X]$ of the defect in a compound is given by [121, 122]

$$E_f[X] = E_T[X] - E_T + \mu_X \quad (\text{Equation 4.5})$$

where $E_T[X]$ is the total energy of the supercell with a vacancy X ($X=\text{Fe}_\text{I}$, Fe_II , Si_I , and Si_II in $\beta\text{-FeSi}_2$), E_T is the total energy of the perfect crystal ($\text{Fe}_{16}\text{Si}_{32}$), and μ_X is the chemical potential of the corresponding constituent element (Fe or Si). The chemical potential depends on the environmental constraints of the system. In particular, the chemical potential of a given atomic species cannot exceed that of a corresponding bulk atom. This leads to the following constraints on the chemical potentials of Fe and Si:

$$\mu_{\text{Fe}} \leq \mu_{\text{Fe}(\text{bulk})}, \quad (\text{Equation 4.6})$$

$$\mu_{\text{Si}} \leq \mu_{\text{Si}(\text{bulk})}. \quad (\text{Equation 4.7})$$

Furthermore, the chemical potentials of Fe and Si should be correlated to each other to satisfy the following equation:

$$\mu_{\text{Fe}} + 2\mu_{\text{Si}} = \mu_{\text{FeSi}_2(\text{bulk})}. \quad (\text{Equation 4.8})$$

It should be noted that for the elemental system, the chemical potentials $\mu_{\text{Fe(bulk)}}$ and $\mu_{\text{Si(bulk)}}$ are the energies of a single bulk Fe and Si atom, respectively, which can be determined from the bulk calculations as the energy per atom in the unit cell, whereas the chemical potential of the bulk $\beta\text{-FeSi}_2$, $\mu_{\text{FeSi}_2(\text{bulk})}$, is calculated as the total energy of the crystal per unit formula. Table 4.4 shows the calculated total energies of the perfect and defective $\beta\text{-FeSi}_2$ crystals as well as the Fe and Si atoms. Using the relevant total energy values, the defect formation energy can be calculated by Equation (4.5) subjected to the constraints in Equations (4.6)-(4.8). Here, we examine two limiting cases:

- (1) Fe-rich limit where $\mu_{\text{Fe}} = \mu_{\text{Fe(bulk)}}$ and $\mu_{\text{Si}} = 0.5(\mu_{\text{FeSi}_2(\text{bulk})} - \mu_{\text{Fe(bulk)}})$, and
- (2) Si-rich limit where $\mu_{\text{Si}} = \mu_{\text{Si(bulk)}}$ and $\mu_{\text{Fe}} = \mu_{\text{FeSi}_2(\text{bulk})} - 2\mu_{\text{Si(bulk)}}$.

Table 4.4. Total energies of the perfect and defective $\beta\text{-FeSi}_2$ crystals as well as the Fe and Si atoms.

Crystal structure	Total energy (eV)
$\text{Fe}_{16}\text{Si}_{32}$ (perfect)	-17355.1217
$\text{Fe}_{15}\text{Si}_{32}$ with $V[\text{Fe}_I]$	-16485.0623
$\text{Fe}_{15}\text{Si}_{32}$ with $V[\text{Fe}_{II}]$	-16485.1841
$\text{Fe}_{16}\text{Si}_{31}$ with $V[\text{Si}_I]$	-17243.3254
$\text{Fe}_{16}\text{Si}_{31}$ with $V[\text{Si}_{II}]$	-17243.2766
Fe atom	-864.678
Si atom	-107.232

Table 4.5 shows the results of the calculation for Fe and Si vacancies at these conditions. At the Fe-rich limit, the energy required to remove a Fe_I , Fe_{II} , Si_I , and Si_{II}

atom from the perfect β -FeSi₂ lattice was 5.381, 5.260, 1.788, and 1.837 eV, respectively, which is in good agreement with that reported by Tani and Kido [96]. On the other hand, the formation energies for Fe_I, Fe_{II}, Si_I, and Si_{II} vacancies at the Si-rich limit were found to be -0.172, -0.293, 4.564, and 4.613 eV, respectively. This is in contrast to the results of Tani and Kido, where they observed lower E_f values for Si vacancy than Fe vacancy at this condition.

Table 4.5. Formation energies of the neutral Fe_I, Fe_{II}, Si_I, and Si_{II} vacancies in β -FeSi₂ at the Fe- and Si-rich limits.

Vacancy defect	Fe-rich limit	Si-rich limit
X	$E_f[X]$ (eV)	$E_f[X]$ (eV)
Fe _I	5.381	-0.172
Fe _{II}	5.260	-0.293
Si _I	1.788	4.564
Si _{II}	1.837	4.613

Figure 4.8 shows the formation energies of the Fe and Si vacancies as a function of the atomic chemical potential. It was observed that Fe and Si vacancies exhibit lower formation energies under Si- and Fe-rich conditions, respectively. The formation of Fe vacancy is energetically more favorable under Si-rich conditions. In particular, at the Si-rich limit it shows a small negative value, indicating an abundance of Fe vacancies in β -FeSi₂ at this point where the contribution of Si vacancies is relatively insignificant. The formation of Si vacancy is preferable under Fe-rich conditions, suggesting that Si vacancies could dominate in β -FeSi₂ at this condition. A comparison of the E_f values over

the entire range revealed that vacancy formation at the site II and site I are more likely for Fe and Si, respectively.

Figure 4.8. Formation energies of the neutral Fe and Si vacancies as a function of the atomic chemical potential of Fe or Si. The left- and right-hand limits correspond to the Fe- and Si-rich limits considered, respectively.

4.4.2 Effects of Fe vacancies

Figure 4.9 shows the band structures of the defective β -FeSi₂ crystals with Fe vacancy at the site I and site II. It is evident that certain energy bands were formed below the conduction band in the forbidden gap of the defective crystals. These energy bands correspond to the defect bands caused by the defect states associated with Fe vacancies in the β -FeSi₂. The Fermi level was found to shift towards the conduction band, implying that Fe vacancies could produce donor-like defect states in β -FeSi₂.

The calculated total DOS for the defective crystals are shown in Figure 4.10. It can be seen that distinct defect levels were produced between the valence band and the

conduction band as a result of the presence of Fe vacancies. The Fermi level was found to exist at these levels, which were located below the conduction band. If the electrons in the defect levels can be elevated into the conduction band by thermal energy, additional electrons would be produced in the conduction band. This confirmed that Fe vacancies introduce donor states in β -FeSi₂. It can therefore be concluded that Fe-deficient (or Si-rich, $x > 2$) β -FeSi_x crystals exhibit *n*-type electrical conductivity. By comparing the DOS spectra of the defective crystals with that of the perfect crystal as shown in Figure 4.6(a), it was found that their band shapes were generally very similar, except in the region near or between the band edges. This suggests that the presence of Fe vacancies would not induce drastic change in the electronic structure of β -FeSi₂ even at high concentrations.

Figure 4.9. Band structures of the defective β -FeSi₂ crystals with Fe vacancy at the (a) site I and (b) site II. Zero of the energy scale corresponds to the top of the 128th band. The dashed line and circle indicate the position of the Fermi level E_F and the defect bands, respectively.

Figure 4.10. Total DOS of the defective β -FeSi₂ crystals with Fe vacancy at the (a) site I and (b) site II. E_F exists at the defect levels below the conduction band, indicating n -type conductivity for Fe-deficient (or Si-rich) crystals.

4.4.3 Effects of Si vacancies

Figure 4.11 shows the band structures of the defective β -FeSi₂ crystals with Si vacancy at the site I and site II. It can be clearly seen that defect bands corresponding to the defect states associated with Si vacancies were formed in the forbidden gap of the defective crystals. The Fermi level was found to exist at the top of the valence band,

indicating *p*-type conductivity for Si-deficient (or Fe-rich, $x < 2$) β -FeSi_x crystals. This can be confirmed from the analysis of the total DOS spectra as shown in Figure 4.12, where we observed sharp defect levels appeared in the gap near the valence band edge. These defect levels can capture electrons with sufficient thermal energy from the valence band, thereby leaving behind excess holes in the valence band. This proves that Si vacancies produce acceptor-like defect states in β -FeSi₂. Moreover, by comparing Figures 4.12 and 4.10, we found that the band shapes of the defective crystals with Si or Fe vacancies were highly similar, except in the vicinity of the band edges. This leads to the same conclusion that the presence of Si vacancies even at high densities would not noticeably affect the electronic structure of β -FeSi₂.

Figure 4.11. Band structures of the defective β -FeSi₂ crystals with Si vacancy at the (a) site I and (b) site II. Zero of the energy scale corresponds to the top of the 128th band. The dashed line and circle indicate the position of the Fermi level E_F and the defect bands, respectively.

Figure 4.12. Total DOS of the defective β -FeSi₂ crystals with Si vacancy at the (a) site I and (b) site II. E_F exists at the top of the valence band, indicating p -type conductivity for Si-deficient (or Fe-rich) crystals.

4.5 Effects of B and As Doping

Impurity doping by adding small and controlled amount of specific dopant is of fundamental importance for conductivity modulation in any semiconductors. This doping process can greatly alter the electrical characteristics of the semiconductor by changing the active carrier concentrations. For β -FeSi₂, despite the fact that most studies focus

mainly on the investigations of TMs as suitable dopants, one could consider group III and V atoms as alternative elements for doping, in particular, boron (B) and arsenic (As), which are the most common dopants used in Si-based microelectronics. It is therefore important to study the effects of B and As doping in β -FeSi₂ and to investigate whether B and As could be effective dopants for β -FeSi₂.

An impurity atom in a semiconductor can be located at a lattice site where it replaces a host atom as a substitutional impurity or it can exist in the space between the host atoms as an interstitial impurity. In our calculations, we focused on the substitutional impurities (B and As) since they have a very profound effect on controlling the conductivity type and magnitude of a semiconductor. In contrast, the interstitial impurities are often electrically inactive and hence they do not have a significant effect on the electrical properties of a semiconductor as the substitutional impurities.

We used the orthorhombic unit cell of β -FeSi₂ (see Figure 4.3) and substituted one of each type of the Fe or Si site by an impurity (B or As) atom to form the impurity-doped structures (similar to Figure 4.7) for calculations. The electron wavefunction was expanded using plane waves with a cutoff energy of 280 eV. A $2 \times 3 \times 3$ k -point mesh based on the Monkhorst-Pack (MP) scheme was employed for the BZ integrations. All structures were allowed to fully relax by total energy minimization until the Hellmann-Feynman forces acting on the atoms were smaller than 0.05 eV/Å. In the relaxation process, only the atomic coordinates were optimized while the lattice parameters were fixed at the accepted experimental values [16]. The static calculation was performed at the relaxed B- and As-doped β -FeSi₂ crystal structures.

4.5.1 Preferential site substitution

Figure 4.13 shows the calculated total energies of relaxed B- and As-doped β -FeSi₂ crystals with the B and As atoms situating at different substitutional sites. The preferential site occupation of B and As in β -FeSi₂ can be determined by comparing the total energy of various doped crystals. It was found that the replacement of Fe in β -FeSi₂ by the B and As atoms produced crystals with higher total energies that were relatively unstable. On the other hand, the impurity-doped β -FeSi₂ crystals with the B and As atoms substituting for the Si sites possessed lower total energies that were energetically more favorable. This shows that the B and As atoms prefer to occupy the Si site in the β -FeSi₂.

Figure 4.13. Total energies of relaxed B- and As-doped β -FeSi₂ crystals with B and As atoms situated at different substitutional sites.

As mentioned previously, there are two crystallographically non-equivalent sites for Si (Si_I and Si_{II}) in β -FeSi₂. While the replacement of both sites generally yields a stable structure, there is an energy difference ΔE associated with both substitutional sites as shown in Table 4.6. By comparison, it can therefore be concluded that the preferential

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substitutional site of B and As atoms in β -FeSi₂ are Si_{II} and Si_I, respectively. It now becomes straightforward that *p*-type conduction is expected for B-doped β -FeSi₂ whereas *n*-type conduction is expected for As-doped β -FeSi₂. When B substitutes for a Si host atom, they are deficient of one electron per atom to complete the bonding with the adjacent Si and Fe host atoms. Such deficiency can be overcome by accepting a valence electron, thereby leaving behind a hole in the valence band. When As substitutes for a Si host atom, there is one excess electron from each atom that can contribute to the conduction band.

Table 4.6. The energy difference (ΔE) between both substitutional Si sites and the preferential substitutional site of B and As in steady state.

Impurity element	Substitutional site	Total energy (eV)	ΔE (meV)	Preferential substitutional site
B	Si _I	-17322.0658	104.20	Si _{II}
	Si _{II}	-17322.1700		
As	Si _I	-17420.3770	75.90	Si _I
	Si _{II}	-17420.3011		

Table 4.7 shows the atomic charges in the perfect and B- and As-doped β -FeSi₂ crystals obtained by Mulliken population analysis [123, 124], which provides a means of estimating partial atomic charges or electrons associated with an atom, given in units of elementary charge e (1.602×10^{-19} C). In the perfect β -FeSi₂, the Fe_I and Fe_{II} atoms indicate a negative value of -0.35 and -0.34, respectively, whereas the Si_I and Si_{II} atoms show a positive value of +0.18 and +0.16, respectively. However, in the impurity-doped

β -FeSi₂, B was observed to be negatively charged in the range of -0.43 to -0.45, whereas As was found to be positively charged in the range of +1.51 to +1.53. The charges of Si atoms remained essentially unaffected and insensitive to the types of dopants, while that of Fe atoms were decreased and increased (in magnitude) by B and As doping, respectively. This result clearly suggests that electron transfer from Fe to B and from As to Fe occurred by impurity doping. This is fully consistent with our physical expectation and correlates well with our DOS results in Figure 4.6 indicating that the behavior of β -FeSi₂ is mainly dominated by the Fe atoms having *d*-electrons. It should be noted that the absolute magnitude of the atomic charges given by population analysis have little physical meanings since they vary with the atomic basis set with which they were calculated and instead, their relative values are qualitatively meaningful [125].

Table 4.7. Electronic charges (in *e*) of the atoms in perfect and B- and As-doped β -FeSi₂ crystals obtained by Mulliken population analysis. The atomic charge of a given atom is the average of the charges of atoms at the same site in the unit cell. *M* represents B or As.

Crystal structure	Fe _I	Fe _{II}	Si _I	Si _{II}	<i>M</i>
Fe ₁₆ Si ₃₂ (perfect)	-0.35	-0.34	+0.18	+0.16	...
Fe(Si _{0.96875} B _{0.03125}) ₂ with B at Si _I site	-0.313	-0.306	+0.185	+0.164	-0.43
Fe(Si _{0.96875} B _{0.03125}) ₂ with B at Si _{II} site	-0.318	-0.309	+0.183	+0.168	-0.45
Fe(Si _{0.96875} As _{0.03125}) ₂ with As at Si _I site	-0.416	-0.406	+0.172	+0.154	+1.53
Fe(Si _{0.96875} As _{0.03125}) ₂ with As at Si _{II} site	-0.416	-0.405	+0.172	+0.154	+1.51

4.5.2 Effects on conductivity modulation

Figures 4.14 and 4.15 show the band structures and the corresponding DOS of the relaxed $\text{Fe}(\text{Si}_{0.96875}\text{B}_{0.03125})_2$ and $\text{Fe}(\text{Si}_{0.96875}\text{As}_{0.03125})_2$ in the vicinity of the Fermi level E_F , respectively. As shown clearly, the Fermi level shifts into the valence band after B doping, indicating p -type conductivity for the B-doped β - FeSi_2 (see Figure 4.14), whereas it shifts into the conduction band after As doping, suggesting n -type conductivity for the As-doped β - FeSi_2 (see Figure 4.15). This result is consistent with the conclusion of the total energy calculations and population analysis. Furthermore, it can be concluded from the position of Fermi level in the respective band structure that both $\text{Fe}(\text{Si}_{0.96875}\text{B}_{0.03125})_2$ and $\text{Fe}(\text{Si}_{0.96875}\text{As}_{0.03125})_2$ were highly degenerated as expected due to the extremely high impurity concentration ($\sim 1.7 \times 10^{21} \text{ cm}^{-3}$) in the structure, which also causes the observed gap reduction as compared to Figure 4.5.

While it is hopeful that one could perform calculations on the structures with impurity concentration matching with the typical experimental values, this can be hardly achieved and is certainly impractical due to the constraint in the computational resources. In fact, calculations generally scale with the cube of the number of atoms involved. This implies that one would require tremendous amount of computational cost to simulate such structures with a large number of atoms which is physically impossible. However, this limitation should not inflict our predictions of the electronic properties such as conductivity modulation and site occupation of dopants.

A significant tailing of the conduction band and valence band states was observed in the DOS curves as shown in Figures 4.14 and 4.15. Such band tailing was partially due to the Gaussian smearing in the DOS calculations but it was largely a consequence of the

impurity band formation and could be closely correlated with the impurity concentration in β -FeSi₂. In theory, impurities can perturb the band edges by forming a band of impurity states, thereby inducing tails in the conduction band and valence band states. Such impurities may involve substitutional atoms or point defects such as interstitials and vacancies. As the impurity concentration increases, the electron wavefunctions at the impurity level begin to overlap, resulting in the formation of a band of states (formally known as the impurity band) whose distribution tails into the forbidden bandgap [126]. The extent of the band tailing generally varies in accordance with the impurity concentration. Consequently, a significant band tailing appeared in the DOS spectra of the degenerate B- and As-doped β -FeSi₂.

Figure 4.14. Band structure and the corresponding DOS of relaxed Fe(Si_{0.96875}B_{0.03125})₂ with B substituting one Si atom at the Si_{II} site in the vicinity of the Fermi level E_F . Zero of the energy scale corresponds to the top of the 128th band.

Figure 4.15. Band structure and the corresponding DOS of relaxed $\text{Fe}(\text{Si}_{0.96875}\text{As}_{0.03125})_2$ with As substituting one Si atom at the Si_{I} site in the vicinity of the Fermi level E_F . Zero of the energy scale corresponds to the top of the 128th band.

4.5.3 Effects on lattice distortion

It is well known that impurities induce structural relaxation in the host lattice and modify the electronic structure of the system. Tables 4.8 and 4.9 show the change in the atomic bond lengths of B and As with its neighboring Si and Fe host atoms in the B-doped $\beta\text{-FeSi}_2$ with B substituting one Si atom at the Si_{II} site and As-doped $\beta\text{-FeSi}_2$ with As substituting one Si atom at the Si_{I} site, respectively. From the relaxation results, it can be seen that As doping caused elongation of the As-Si bonds and contraction of the As-Fe bonds with an absolute bond length change of less than 4.8% (see Table 4.9), whereas it is not so conclusive for the B doping since both inward and outward relaxations of the Si and Fe host atoms relative to the B impurity occurred and the bond length change was relatively larger (see Table 4.8).

Table 4.8. Change in atomic bond length of B with its surrounding Si and Fe host atoms in B-doped β -FeSi₂ with B substituting one Si atom at the Si_{II} site. The superscript indicates the number of the same bond name with different bond lengths.

Atomic bond	Bond length before relaxation (Å)	Bond length after relaxation (Å)	Change (%)
¹ B-Si _I	2.54540	2.56695	0.847
² B-Si _I	2.57817	2.45328	-4.844
³ B-Si _I	2.44385	2.36397	-3.268
¹ B-Si _{II}	2.51213	2.40552	-4.244
² B-Si _{II}	2.45065	2.31614	-5.489
¹ B-Fe _I	2.39789	2.40347	0.233
² B-Fe _I	2.35152	2.23757	-4.846
¹ B-Fe _{II}	2.36312	2.43770	3.156
² B-Fe _{II}	2.39717	2.23558	-6.741

Table 4.9. Change in atomic bond length of As with its surrounding Si and Fe host atoms in As-doped β -FeSi₂ with As substituting one Si atom at the Si_I site. The superscript indicates the number of the same bond name with different bond lengths.

Atomic bond	Bond length before relaxation (Å)	Bond length after relaxation (Å)	Change (%)
¹ As-Si _I	2.56138	2.59660	1.375
² As-Si _I	2.52946	2.57241	1.698
¹ As-Si _{II}	2.58688	2.68435	3.768
² As-Si _{II}	2.51251	2.63073	4.705
³ As-Si _{II}	2.49902	2.54296	1.758
¹ As-Fe _I	2.37588	2.36592	-0.419
² As-Fe _I	2.33797	2.32013	-0.763
¹ As-Fe _{II}	2.43734	2.40458	-1.344
² As-Fe _{II}	2.33286	2.33155	-0.056

The geometrical distortion associated with the β -FeSi₂ lattice upon impurity doping manifests itself by a spontaneous displacement of the atoms with respect to the surroundings, thereby elongating or shortening the atomic bonds, and the overall effect of such distortion is to lower the system total energy resulting in a stable crystal structure (i.e., a Jahn-Teller type effect) [118]. This effect is most pronounced when the impurity concentration becomes very high, in which case the lattice will undergo distortion to modulate the Coulomb force acting on the atoms and to remove the ground state degeneracy of the impurity states so as to minimize the overall energy. In our calculations, the impurity concentration in the proportion of 1 impurity atom to 31 silicon atoms is extremely high, making Fe(Si_{0.96875}M_{0.03125})₂ ($M=B$ and As) a degenerate semiconductor. Nonetheless, in most cases with low or moderate impurity doping levels, the interaction between impurities and the surrounding host atoms should mainly exist in the form of local deformation potential [127].

4.5.4 Positions of impurity levels

The present calculations performed on the degenerately doped β -FeSi₂ crystals do not permit the direct determination of the actual impurity energy levels in the bandgap of β -FeSi₂ since the Fermi level E_F essentially pins at the conduction band and valence band as a consequence of heavy doping. The knowledge of the impurity level in the bandgap is important because it determines whether a substitutional impurity is an effective dopant in β -FeSi₂. However, it is possible to estimate the binding or ionization energy of an electron trapped to a As donor and a hole to a B acceptor based on the Bohr theory of the hydrogen atom. This simple hydrogen atom model must be modified to take into account

the dielectric constant ε of the medium for screening of the Coulomb force which the impurity ion exerts on the bound electron or hole and the effective masses m^* of the electron and the hole in the periodic potential of the crystal. The modified Bohr formulas are therefore given by [128]

$$E_n = -\frac{m^* e^4}{2\hbar^2 (4\pi\varepsilon)^2 n^2} = -\left(\frac{13.6}{\varepsilon^2}\right)\left(\frac{m^*}{m}\right)\left(\frac{1}{n^2}\right) \quad (\text{Equation 4.9})$$

and

$$a_n = \frac{(4\pi\varepsilon)\hbar^2 n^2}{m^* e^2} = \left(\frac{0.53\varepsilon}{m^*/m}\right)n^2, \quad (\text{Equation 4.10})$$

where E_n is the ionization energy in eV, a_n is the Bohr radius in Å, e is the elementary electronic charge, $\hbar$ is the reduced Planck's constant, m is the mass of the electron in vacuum, and n is a quantum number ≥ 1 . Equation (4.9) suggests that the ionization from the successively higher quantum states requires rapidly decreasing increment in the energy. When the electron of the donor is in the conduction band, it is essentially free; therefore, its ground state, the donor level, is one ionization energy below the conduction band. Similarly, the acceptor level is one binding or ionization energy above the valence band. Noting that the effective mass ratio m^*/m is less than 1, by making $n=1$ in Equations (4.9) and (4.10) and using the relation $\varepsilon = n_0^2$ with the value of the refractive index $n_0=5.6$ for β -FeSi₂ [28], the ground state ionization energy and Bohr radius of the bound electron and hole were calculated to be at least smaller than about 13.8 meV and greater than about 16.6 Å, respectively. It should be pointed out that this estimation based on the simple hydrogen atom model is accurate only to the first approximation because the effective mass generally varies considerably around the impurity atom. In addition,

we have neglected the anisotropy of the effective mass and assumed identical effective masses for both bound electron and hole. Nonetheless, the ionization energy is smaller than the thermal energy at RT (~ 25.9 meV) and much smaller than the energy bandgap of β -FeSi₂ (~ 0.86 eV). Consequently, we would expect that most of the trapped electrons are freed from the As donors and similarly, holes from the B acceptors at RT. It can therefore be concluded that most of the As donor and B acceptor impurity atoms are ionized at RT, and they are shallow impurities in β -FeSi₂ since their bound state energy levels are located very near to the respective band edges. Furthermore, the orbit radius is large compared with the inter-atomic spacing in β -FeSi₂ (typically less than 3 Å), indicating that the bound electron and hole can travel through many lattice sites in the neighborhood of the impurity and hence they are delocalized. These results suggest that boron and arsenic are effective dopants for β -FeSi₂ and therefore should be of technological importance for the doping control in β -FeSi₂.

4.6 Summary

The first-principles study of β -FeSi₂ has been performed based on the DFT. First-principles calculations revealed the existence of both direct and indirect transitions in β -FeSi₂ and confirmed its semiconducting property. A direct and an indirect bandgap of 0.836 and 0.787 eV were obtained for β -FeSi₂, respectively. The presence of Fe or Si vacancies was found to introduce energy levels in the forbidden gap and affect the electrical conductivity of β -FeSi₂ depending on the types of vacancy defects, with Fe vacancies produce donor-like defect states below the conduction band while Si vacancies produce acceptor-like defect states above the valence band. The B and As were shown to

be shallow impurities in β -FeSi₂ and therefore could be effective dopants for β -FeSi₂. In particular, p -type and n -type conductivities were suggested for the B- and As-doped β -FeSi₂, respectively. The impurity doping was found to induce structural relaxation via lattice distortion, with As doping causing elongation of the As-Si bonds and contraction of the As-Fe bonds while B doping resulting in both inward and outward relaxations of the neighboring Si and Fe host atoms.

CHAPTER 5

STRUCTURAL, OPTICAL, AND ELECTRICAL PROPERTIES OF BETA-PHASE IRON DISILICIDE

5.1 Introduction

This chapter presents the structural, optical, and electrical study on the FeSi₂ thin films formed by direct sputter deposition from a stoichiometric iron disilicide target via RTA. The phase evolution and microstructures of silicide thin films are investigated. The optical absorption and bandgap properties are studied based on the proposed optical absorption model. The carrier type, concentration, and mobility in FeSi₂ as well as diode characteristics are also discussed.

5.2 Experiment

Bare *p*-type Si(100) substrates with resistivity of $\rho=6\text{-}10\ \Omega\text{-cm}$ were used in this study. Prior to the silicide film deposition, the *p*-Si(100) substrates were cleaned using standard Radio Corporation of America (RCA) wet cleaning process to remove the organic and metal contaminants, followed by chemical cleaning in hydrofluoric acid (HF) solution (4% by volume) for 10 s to remove the native oxide on the Si surface. After cleaning, the Si substrates were immediately loaded into a DC magnetron sputtering chamber with a base pressure of 3×10^{-7} Torr. A layer of 55 nm FeSi₂ was sputter-deposited at RT from a stoichiometric iron disilicide target (purity=4N, 99.99%). The

samples were then subjected to RTA in an N₂ ambient at temperatures of 300-800 °C for 60 s for structural, optical, and electrical characterization.

5.3 Structural Properties

5.3.1 Phase analysis

We start our experimental study on the structural properties of β -FeSi₂ thin films. Figure 5.1 shows the XRD spectra of both as-deposited and RTA-annealed samples obtained under glancing angle incidence configuration ($\Omega=2^\circ$). As illustrated clearly, no diffraction peaks were observed for the as-deposited films and the samples annealed at temperatures ≤ 400 °C. The absence of the XRD peaks suggests an amorphous nature of the FeSi₂ films in these samples. The XRD peaks corresponding to the semiconducting β -FeSi₂ phase start to appear after RTA at 500 °C and above. The intensity of the β -FeSi₂ peaks was found to increase with annealing temperature, indicating an enhancement in the film crystallinity with annealing temperature. This could have resulted from the growth of β -FeSi₂ grains with preferential orientation relationship with the underlying substrates. However, no obvious texturing of the β -FeSi₂ films was observed and instead, the grains were seen to grow in all those orientations as identified with the ratios of the peak intensities being independent of the annealing temperatures and underlying substrates. This observation is not surprising since typically in a post-deposition annealing the random crystallization process is mainly controlled by bulk diffusion and therefore the substrate has minimal influence on the resulting structure. Our observation on the transition from amorphous to polycrystalline β -phase FeSi₂ agrees with that reported in the literature for the case of cosputtered FeSi₂ films [129].

Figure 5.1. XRD spectra of as-deposited and RTA-annealed samples under glancing angle incidence configuration ($\Omega=2^\circ$) for FeSi₂ on *p*-Si(100).

Figure 5.2 shows the GADDS patterns of the as-deposited FeSi₂ on *p*-Si(100) and the samples RTA-annealed at selected temperatures. The GADDS scans can provide a quick overview of the crystallinity, composition, and orientation of the sample. If the observed Debye rings are smooth and continuous, the sample is polycrystalline and fine-grained. If the rings are continuous but spotty, the material is polycrystalline and large-grained. Incomplete Debye rings indicate orientation or texturing of the sample. If only individual spots are observed, the material is single crystal, which can be considered as the extreme case of crystallographic texture.

Figure 5.2. GADDS θ - 2θ XRD scans of (a) as-deposited FeSi₂ on *p*-Si(100) and the samples RTA-annealed at (b) 400, (c) 500, and (d) 800 °C.

As shown clearly, the absence of the Debye rings in the as-deposited film and the sample annealed at 400 °C confirmed that the silicide films remained fully amorphous up to 400 °C. At 500 °C and above, the Debye rings corresponding to the semiconducting β -FeSi₂ appeared, indicating the formation of β -FeSi₂ at these temperatures. These results are fully consistent with the conclusion of the thin film analysis as previously discussed. Furthermore, it can be seen that the Debye rings are relatively smooth and continuous,

implying that the silicide films are polycrystalline and fine-grained. Since there is no evidence of incomplete rings or single crystal spots, the samples did not exhibit textures.

5.3.2 Microstructure and morphology

Figure 5.3(a) shows the SEM micrograph of the as-deposited FeSi₂ on *p*-Si(100). The as-deposited film is amorphous as expected because it is simply a mixture of Fe and Si atoms at the atomic scale and therefore a post-deposition annealing is generally required for the β -FeSi₂ formation. Figures 5.3(b) and (c) show the SEM micrographs of the samples annealed at 800 °C at different magnifications. As shown clearly, the surface of the silicide film consists of uniformly distributed grains which indicate polycrystalline in nature. These grains correspond to the β -FeSi₂ grains since at 800 °C only a single phase β -FeSi₂ was formed as confirmed by the XRD analysis. It is apparent from the cross-sectional TEM micrograph shown in Figure 5.3(d) that the grains exhibit columnar structure. The size of the β -FeSi₂ grains should be of nanoscale (~20 nm) which can be inferred from the higher magnification SEM micrograph shown in Figure 5.3(c) and the TEM micrograph depicted in the inset in Figure 5.3(d), which also shows that some complexes between Fe and Si and possibly O are formed at the interface.

To further study the surface morphology of the samples, atomic force microscopy (AFM) was performed in a tapping mode on the samples annealed at different RTA temperatures. Figure 5.4 shows the AFM images of the as-deposited FeSi₂ on *p*-Si(100) and the samples annealed at selected temperatures. Quantitative analysis from the AFM revealed that the surface roughness of the silicide films measured in root mean square (RMS) value is 0.974 nm for the sample annealed at 800 °C and less than 1 nm for other

samples. This suggests that the surface of the silicide films is generally flat and smooth. The average grain size was estimated to be about 691 nm² for the sample annealed at 800 °C, indicating that the samples contain uniformly distributed nanosize β -FeSi₂ grains.

Figure 5.3. (a) SEM micrograph of as-deposited FeSi₂ on *p*-Si(100). (b) SEM micrograph of the sample RTA-annealed at 800 °C. (c) SEM micrograph of the sample RTA-annealed at 800 °C at higher magnification. (d) Cross-sectional TEM micrograph of β -FeSi₂ on *p*-Si(100) and the interface (inset).

Figure 5.4. AFM images of as-deposited FeSi₂ on *p*-Si(100) and the samples RTA-annealed at (b) 400, (c) 500, and (d) 800 °C.

5.4 Optical Properties

Optical properties of semiconductors are of fundamental importance to the operation and design of solar cells. In particular, the optical absorption coefficient is a critical parameter since it determines the effective absorption length of a semiconductor, which in turn determines the required or optimum thickness of the absorber layer in the PV devices. Moreover, the optical generation rate of carriers is also strongly dependent on the absorption coefficient of the material. It is therefore important to study the optical absorption coefficient of β -FeSi₂ and to deduce the bandgap from the absorption spectra.

5.4.1 Optical absorption model

In principle, the optical properties such as optical absorption coefficient or index of refraction cannot be directly obtained by optical measurements. Based on the physical structure of the sample, we develop an optical absorption model that allows a direct determination of the absorption spectrum of silicide in double-layer structure from absorbance measurements. The physical model relates the optical absorption coefficient α_f of silicide to the experimentally measured absorbance A , reflection coefficients at various interfaces R , and silicide film thickness d_f . The theoretical formulation of the optical absorption model is presented in Appendix A.

The optical absorption coefficient α_f of FeSi_2 as derived for the double-layer model [see Appendix A for Equations (A.6)-(A.8)] can be summarized in a functional form $\alpha_f \equiv f(d_f, R, A)$ and given by

$$\alpha_f = \frac{1}{d_f} \ln \left(\frac{2bR' \times 10^{-A}}{\sqrt{a^2 + 4b^2 R' \times 10^{-2A}} - a} \right), \quad (\text{Equation 5.1})$$

where R' represents the product $R_f R_{int}$ for the double-layer system, and a and b are the parameters defined in the model. The reflection coefficient R between any two media of refractive indices n_1 and n_2 can be determined according to this equation:

$$R = \left(\frac{n_2 - n_1}{n_2 + n_1} \right)^2. \quad (\text{Equation 5.2})$$

Equation (5.2) suggests that the reflection coefficient R depends strongly on the refractive index n which is a strong function of photon wavelength λ or energy E . In order to determine the absorption spectrum, the values of n of various layers over the measured energy range of 0.7-1.0 eV need to be known. This energy range was deliberately chosen

to cover the energy bandgap of β -FeSi₂. In the calculation, we assumed constant values for the refractive indices of $n_{Si}=3.5$ and $n_{air}=1.0$ but retained the energy dependence of n_f for FeSi₂ for improved accuracy. The values of n_f as a function of energy were obtained from the published data (see Figure 2.4 in Chapter 2). However, these accepted values of the refractive index for FeSi₂ are present only at certain energy values, whereas a continuous value of n_f in the energy range of 0.7-1.0 eV is required. It is instructive to perform curve fitting to the data over the energy range from 0.2 to 1.5 eV.

Figure 5.5. Refractive index of FeSi₂ as a function of photon energy over the energy range from 0.2 to 1.5 eV. Curve fitting to the discrete data points was performed using the polynomial function in Equation (5.3) (solid line).

Figure 5.5 shows the result of the polynomial fitting for the refractive index n_f . The polynomial function used in this fitting is given by

$$n(E) = \begin{cases} A_0 + A_1E + A_2E^2, & 0.2 \leq E \leq 0.9 \text{ eV} \\ B_0 + B_1E + B_2E^2, & 0.9 < E \leq 1.5 \text{ eV} \end{cases} \quad (\text{Equation 5.3})$$

where the fitting parameters $A_0=5.93602$, $A_1=-1.59911$, $A_2=2.79821$, $B_0=12.47267$, $B_1=-8.72821$, and $B_2=2.60833$. The fitted polynomial function in Equation (5.3) provides the approximate values of n_f at different energies ranging from 0.7 to 1.0 eV, i.e., $n_f=n(E)$. Using the thickness of the FeSi₂ layer determined by cross-sectional TEM measurement, $d_f=55$ nm= 5.5×10^{-6} cm, the absorption spectra of FeSi₂ can readily be calculated by Equation (5.1).

5.4.2 Absorbance and absorption spectra

Figure 5.6 shows the photon energy dependence of absorbance for the FeSi₂/p-Si(100) samples at different RTA temperatures. For all the samples, the curves exhibit typical characteristics of increasing absorbance with photon energy. To extract the detailed information about the optical properties, it is necessary to translate the measured absorbance spectra into the absorption spectra. The absorption spectra of FeSi₂ were determined based on the framework of our proposed optical absorption model for the double-layer structure as previously described.

Figure 5.7 shows the plot of the square of the optical absorption coefficient α^2 against the photon energy over a range of 0.7-1.0 eV. For the β -FeSi₂ on the Si substrate annealed at 800 °C, the value of the absorption coefficient ($\sim 7\times 10^4$ cm⁻¹) is close to the order of 10^5 cm⁻¹ at 1.0 eV [see Figure 5.7(b)], which agrees well with the accepted values in the literatures [8, 27]. This good agreement supports our proposed optical absorption model. The exact treatment of the transmittance of the thin film/substrate system results in a set of equations that contains a number of transcendental functions that are impractical for calculation [130]. Nonetheless, by making several reasonable

assumptions, the analysis can be greatly simplified to arrive at an analytical solution for α_f .

As suggested clearly by Equation (5.1), the optical absorption coefficient can be expressed as a function of the film thickness and the reflection coefficients at various interfaces. In all cases, α should always be a positive quantity so that the absorbance A must satisfy the following relation:

$$A > \log_{10} \left[\frac{b(1-R')}{a} \right]. \quad (\text{Equation 5.4})$$

Using $n_f=5.6$ for β -FeSi₂ [28], a simple estimation by Equation (5.4) predicts that A must be greater than about 0.1410 to yield a positive α in the case of β -FeSi₂. These conditions were readily satisfied in our photo-absorption experiment as can be seen from the absorbance spectra in Figure 5.6. Hence, any measured absorbance value far below this estimated value will give a negative absorption coefficient that is physically impossible.

Figure 5.6. Absorbance as a function of photon energy in the range of 0.7-1.0 eV for FeSi₂ on *p*-Si(100) at different RTA temperatures.

Figure 5.7. Square of the absorption coefficient α^2 as a function of photon energy for FeSi₂ on p-Si(100) at different RTA temperatures: (a) ≤ 400 °C and (b) 500-800 °C.

5.4.3 Direct bandgap determination

The energy bandgap E_g of a semiconductor can be determined by the fundamental absorption, which manifests itself by a rapid rise in absorption. Theoretically, the optical absorption coefficient $\alpha(h\nu)$ at a given photon energy $E=h\nu$ (h is the Planck's constant and ν is the frequency) is proportional to the density of electrons in the initial state, the density of empty states in the final state, and the probability of the transition from the

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initial state to the final state. This process must be summed over all possible transitions between the states separated by an energy difference equal to $h\nu$. In the parabolic bands, it can be shown that the absorption coefficient for the allowed direct transitions takes the form [131]

$$\alpha(h\nu) = A'(h\nu - E_{gD})^{1/2}, \quad (\text{Equation 5.5})$$

where A' is a temperature-independent constant and E_{gD} is the direct bandgap energy in eV. The direct bandgap E_{gD} can therefore be extracted from the horizontal intercept of the plot of α^2 against $E=h\nu$. As shown in Figure 5.7, the α^2 spectra show a linear dependence on E over a significant energy range which can be fitted by Equation (5.5), indicating a direct transition in the FeSi_2 films. The direct bandgap E_{gD} of 0.86 eV was obtained for the $\beta\text{-FeSi}_2$ on the Si sample annealed at 800 °C, while E_{gD} values of 0.82-0.87 eV were extracted for other samples. The result of the optical absorption measurements also shows that the amorphous FeSi_2 films (i.e., the as-deposited film and the films RTA-annealed at ≤ 400 °C) are semiconducting in nature.

The variation in the direct bandgap E_{gD} of FeSi_2 with RTA temperature was shown in Figure 5.8. We start our analysis with the semiconducting $\beta\text{-FeSi}_2$ formed at 500 °C and above. For the $\beta\text{-FeSi}_2/p\text{-Si}(100)$, the bandgap of $\beta\text{-FeSi}_2$ was found to increase from ~0.85 eV at 500 °C to ~0.87 eV at 700 °C and then drop to ~0.86 eV at 800 °C. The small variation of the bandgap with annealing temperature is expected since different conditions of the thermal treatment generally result in the silicide film having varied structural orders and properties and even defects that will slightly affect the bandgap, despite the fact that they may produce the same required silicide phase. Nonetheless, for all the $\beta\text{-FeSi}_2$ films, the direct bandgap energy obtained consistently

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ranges from 0.85 to 0.87 eV. By comparison with Table 2.2 in Chapter 2, it can therefore be concluded that our results based on the study of sputter-deposited FeSi₂ are in good agreement with that reported in the literature.

Figure 5.8. Variation in the direct bandgap E_{gD} of FeSi₂ with RTA temperature.

Typically, a direct bandgap of 0.85-0.87 eV is believed to best represent β -FeSi₂ [12]. As shown clearly in Figure 5.8, our optical absorption study suggests that a direct bandgap value of 0.86 eV is most probable to characterize β -FeSi₂, which is in good consistency with the reported values. This corresponds to the β -FeSi₂ formed after RTA at 800 °C. For the amorphous FeSi₂ (α -FeSi₂) obtained at 400 °C and below, we surprisingly observed a direct transition from the α^2 versus photon energy plots [see Figure 5.7(a)], suggesting that the α -FeSi₂ is a direct bandgap semiconductor. This is unusual for an amorphous semiconductor; however, it had been previously reported about

the existence of α -FeSi₂ exhibiting a direct bandgap of 0.88 eV [132]. The extracted direct bandgap for α -FeSi₂ lies in the range of 0.82-0.84 eV as shown in Figure 5.8.

5.4.4 Subgap optical absorption

A significant absorption below the fundamental edge was observed in the absorption spectra as shown in Figure 5.7. Such subgap optical absorption should be caused by the transitions between the defect states associated with the point defects and one of the bands and could be correlated to the residual carrier concentration in FeSi₂. In theory, impurities can perturb the band edges via deformation potential, via coulomb interaction, and by forming a band of impurity states, thereby inducing tails in the conduction band and valence band states. Such impurities may involve substitutional atoms or point defects such as interstitials and vacancies. When present at high concentrations, the impurities states will form a band, the so-called impurity band, whose distribution tails into the forbidden bandgap [126]. This impurity band formation is a consequence of the overlapping of electron wavefunctions from the sufficiently close and interacting impurity atoms, analogous to the energy band formation in semiconductors, and the resulting effect of band tailing is responsible for the subgap optical absorption. The extent of the band tailing generally varies in accordance with the impurity concentration. This strong correlation between the band tailing and the impurity concentration was clearly seen in Figures 5.7(b) and 5.9, where we observed a broader low-energy tail (also known as the Urbach tail) for the FeSi₂ with a higher residual electron concentration. The residual carrier concentration does satisfactorily reflect the density of ionized point defects in FeSi₂ because carriers are generated as a result whether

Fe vacancies donate electrons to the conduction band or Si vacancies accept electrons from the valence band.

5.5 Electrical Properties

In this section, we study the transport properties of carriers in undoped or unintentionally doped β -FeSi₂, the I - V characteristics of β -FeSi₂/ p -Si heterojunction, and the energy band alignment of β -FeSi₂ on Si substrate. These properties provide the fundamental understanding of the electrical characteristics of β -FeSi₂ and related devices.

5.5.1 Carrier type, concentration, and mobility

Bare p -type Si(100) substrates with high resistivity ($\rho=5$ -25.2 k Ω -cm) were used in this study. Figure 5.9 shows the residual carrier concentration and Hall mobility as a function of RTA temperature. For the β -FeSi₂ on the Si samples annealed at ≥ 700 °C, the sign of the Hall coefficient R_H as obtained is consistently negative, suggesting that the conductivity is n -type and mainly due to the electrons in these samples. On the other hand, the R_H for the samples annealed at ≤ 600 °C could not be accurately determined because the carrier density was too large, for which we observed a conductivity-type variation in the samples upon RTA at ≤ 600 °C. Nevertheless, the results unambiguously indicate an n -type conductivity for the undoped β -FeSi₂ samples annealed at 700 °C and above, whose carrier concentration could be related to the donor levels associated with the Fe vacancies present in the Si-rich films as a result of the promoted Si diffusion into the film or Fe diffusion into the substrate upon thermal annealing. This appears plausible and shows very good agreement with the theoretical prediction in Chapter 4 (Section K. H. Tan

4.4.2) that Fe vacancies introduce donor-like defect levels below the conduction band resulting in *n*-type conductivity. The residual electron concentration of $\sim 4 \times 10^{17} \text{ cm}^{-3}$ and a mobility of $\sim 75 \text{ cm}^2/\text{Vs}$ were obtained in our undoped $\beta\text{-FeSi}_2$ sample annealed at 700 °C. It should be noted that the values obtained for the sample annealed at 800 °C should not reflect the actual carrier concentration and mobility in the sample due to the electrical contribution from the substrate at this temperature [see Chapter 6 (Section 6.4.2)].

Figure 5.9. Residual carrier concentration and Hall mobility as a function of RTA temperature for $\beta\text{-FeSi}_2/p\text{-Si}(100)$.

It is important to note that the mobility was found to be inversely proportional to the residual carrier concentration. The temperature dependence of the mobility due to ionized impurity scattering is given by [128]

$$\mu_I = A_{I0} \left(\frac{T^{3/2}}{N_I} \right), \quad (\text{Equation 5.6})$$

where A_0 is a prefactor, T is the temperature, and N_I is the concentration of ionized impurities. At a constant temperature, μ_I is inversely proportional to N_I as suggested by Equation (5.6). In the undoped β -FeSi₂, the scattering of carriers by ionized impurities (mainly point defects) could be the predominant mechanism, thereby giving the observed inverse relationship between the mobility and the residual carrier concentration. This result suggests that the improvement of the mobility in the sputter-deposited FeSi₂ could be achieved by minimizing the residual carrier concentration.

5.5.2 Diode measurements and characteristics

Figure 5.10 shows the I - V characteristics of β -FeSi₂/ p -Si heterojunction diodes with a circular diode area of $7.854 \times 10^{-3} \text{ cm}^2$ (i.e., 1 mm in diameter). For the as-deposited FeSi₂/ p -Si, the linearity of the I - V curve indicates that this diode exhibits resistor-like behavior. However, clear rectifying characteristics were obtained for the β -FeSi₂/ p -Si heterojunction diodes annealed at 600-800 °C. It was found that the current through the junction is substantially larger when the applied voltage on the silicide is negative. This shows that the as-formed β -FeSi₂ is n -type, which confirmed our electrical results based on the Hall effect measurements.

Under positive applied voltage or reverse bias, it can be seen that the reverse (leakage) current decreases with increasing annealing temperature, which could be due to the reduction of residual carrier concentration in the silicide. The lowest leakage current was obtained at 800 °C, with the forward current being two orders of magnitude larger than the reverse current, indicating good rectifying characteristics. An ideality factor of $n=1.48$ was extracted from the initial portion of the forward I - V characteristics. The

observed ideality factor suggests that there exists a considerable recombination current component in the diodes. The recombination current is probably due to the recombination in the depletion region via defect levels or at the interface via interface states as a result of mismatch in lattice parameters and difference in thermal expansion coefficients between β -FeSi₂ and Si.

Figure 5.10. I - V characteristics of β -FeSi₂/ p -Si heterojunction diodes.

5.6 Summary

The structural, optical, and electrical properties of sputter-deposited FeSi₂ and their evolution with RTA temperature have been studied. The semiconducting β -FeSi₂ could be formed by RTA at ≥ 500 °C, below which the silicide films remained completely amorphous. The β -FeSi₂ thin films were polycrystalline and fine-grained and the surface was generally flat and smooth. The grains were found to exhibit columnar structure as indicated by the TEM analysis. A direct bandgap behavior has been concluded for both

amorphous and polycrystalline semiconducting FeSi₂. It was found that the absorption coefficient of β -FeSi₂ was in the order of 10^5 cm^{-1} at 1.0 eV and a direct bandgap in the range of 0.82-0.87 eV was consistently obtained with a bandgap value of 0.86 eV being concluded to best characterize β -FeSi₂. The subgap optical absorption observed in the absorption spectra could be attributed to the band tailing and correlated with the residual carrier concentration. The electrical results unambiguously indicate *n*-type conductivity for the FeSi₂ on the *p*-Si, whose electrical junction was found to exhibit good rectifying characteristics at 800 °C.

CHAPTER 6

IMPURITY DOPING EFFECTS IN BETA-PHASE IRON DISILICIDE

6.1 Introduction

This chapter presents the electrical study on the impurity-doped β -FeSi₂ thin films formed by ion implantation technique via RTA. The distribution profiles of the implanted dopant ions are studied using a Gaussian distribution. The effects of B and As doping on the electrical properties of B- and As-doped β -FeSi₂ are investigated. In addition, the effects of Si doping in β -FeSi₂ are briefly discussed.

6.2 Experiment

Bare *p*-type Si(100) substrates with high resistivity ($\rho=5000$ -25200 Ω -cm) were used in this study. The formation of the silicide film was performed by direct sputter deposition from a stoichiometric iron disilicide target (purity=4N, 99.99%) similar to our previous study in Chapter 5. Prior to the silicide film deposition, sequential chemical cleaning consisting of standard RCA wet cleaning process and HF solution (4% by volume) were used to remove the organic and metal contaminants as well as the native oxide on the Si surface. A layer of 200 nm FeSi₂ was subsequently sputter-deposited at RT in a DC magnetron sputtering chamber with a base pressure of 3×10^{-7} Torr. B⁺, As⁺, and Si⁺ ion implantations were separately performed at energies of 40, 180, and 100 keV,

respectively, to introduce boron, arsenic, and silicon dopants into FeSi₂ films with different doses ranging from 1×10^{13} to 1×10^{15} ions/cm². During the ion implantations, the wafers were positioned at a tilt of 7° and a twist of 22° to suppress the ion channeling effect. The samples were then subjected to RTA in an N₂ ambient at temperatures of 500-800 °C for 60 s for electrical characterization and SIMS profiling.

6.3 Impurity Distribution Profiles

6.3.1 Stopping mechanisms

Table 6.1 shows the stopping power, projected range, and longitudinal straggling estimated by the SRIM simulation [103] for the B, As, and Si ions implanted into FeSi₂ at the respective energy. The longitudinal straggling refers to the statistical fluctuation along the direction of the projected range. For the B implanted into the silicide at 40 keV, the electronic stopping power was found to be much larger than the nuclear stopping power. This suggests that the incident B ions will come to a rest within the crystal lattice mainly through collisions with electrons in the substrate. On the other hand, for the As implanted into the silicide at 180 keV, the nuclear stopping power was found to be significantly larger than the electronic stopping power, suggesting that it is obviously the predominant stopping mechanism. Since the energy and momentum of the incident As ions are transferred to the nuclei of the substrate atom after collision in nuclear stopping, the collision cascades could potentially generate a relatively larger concentration of damage as a result of high lattice disorder. For the Si implanted into the FeSi₂ at 100 keV, both stopping mechanisms were found to be comparable to each other as expected.

Table 6.1. Stopping power, projected range, and longitudinal straggling for B, As, and Si ions implanted into FeSi₂ at energies of 40, 180, and 100 keV, respectively.

Impurity dopant	Ion energy (keV)	Electronic stopping $S_e(E)$ (keV/ μ m)	Nuclear stopping $S_n(E)$ (keV/ μ m)	Projected range R_p (nm)	Longitudinal straggling ΔR_p (nm)
B	40	310.38	84.99	80.50	38.70
As	180	465.92	2057.70	63.20	21.20
Si	100	536.36	492.29	76.40	31.90

6.3.2 Gaussian distribution profiles

The distribution profile of the implanted ions can be approximately described by a Gaussian distribution function given by [100]

$$n(x) = \frac{\Phi}{\sqrt{2\pi}\Delta R_p} \exp\left[-\frac{(x - R_p)^2}{2\Delta R_p^2}\right] \quad (\text{Equation 6.1})$$

where the symbols have their physical meanings defined in Equation (3.2) in Chapter 3 (Section 3.2.2). Using the values of projected range R_p and longitudinal straggling ΔR_p obtained by the SRIM simulation as shown in Table 6.1, the distribution profiles of B, As, and Si implanted into the FeSi₂ for a given implantation dose can be calculated by Equation (6.1). These results are shown in Figure 6.1. The peak ion concentration at $x=R_p$ was estimated to be in the order of 10^{18} - 10^{20} cm⁻³ corresponding to an implantation dose of 10^{13} - 10^{15} cm⁻². It should be noted that the Gaussian ion profiles are generally accurate for the as-implanted samples. However, these profiles may change due to the diffusion effect during post-implantation annealing depending on the duration of anneals and the diffusivity of impurity atoms in the silicide.

Figure 6.1. Gaussian distribution profiles of (a) B, (b) As, and (c) Si implanted into the FeSi₂ at energies of 40, 180, and 100 keV, respectively, at different doses.

6.4 Boron and Arsenic Doping

In Chapter 4 (Section 4.5), we have shown theoretically that boron and arsenic are effective acceptor and donor dopants for β -FeSi₂, respectively. This section studies the effects of B and As doping on the electrical properties of B- and As-doped β -FeSi₂. The influence of implantation defects on the doping efficiency is also discussed.

6.4.1 Carrier conductivity and modulation

Figures 6.2 and 6.3 show the carrier concentration and Hall mobility as a function of the dose for the B- and As-doped β -FeSi₂, respectively, at different RTA temperatures. For the B-doped β -FeSi₂, the sign of the Hall coefficient R_H as measured is consistently positive [see Figure 6.2(a)], indicating that the conductivity is p -type and mainly due to the holes. For the As-doped β -FeSi₂, we obtained a negative R_H for the samples annealed at ≥ 700 °C [see Figure 6.3(a)], suggesting that the conductivity is n -type and mainly due to the electrons in these samples. Such effect of B and As doping on the film conductivity agrees with our theoretical predictions and that reported for the cosputtered films [39]. It should be noted that the R_H for the samples annealed at ≤ 600 °C could not be accurately determined because the carrier density was too large. This is similar to the undoped β -FeSi₂ as shown in Figure 5.9, where we observed a conductivity-type variation in the samples upon RTA at ≤ 600 °C.

The conductivity modulation could be closely related to the occupation of the host lattice site by the impurity atoms, thereby donating electrons to the conduction band or accepting electrons from the valence band (creating excess holes) depending on whether the impurity atoms are donors or acceptors, respectively. For the B- and As-doped β -

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Figure 6.2. (a) Carrier concentration and (b) Hall mobility as a function of the dose for B-doped β -FeSi₂ at different RTA temperatures. Open symbol represents *p*-type conductivity in the carrier concentration versus dose plot.

Figure 6.3. (a) Carrier concentration and (b) Hall mobility as a function of the dose for As-doped β -FeSi₂ at different RTA temperatures. Solid and open symbols represent *n*-type and *p*-type conductivities, respectively, in the carrier concentration versus dose plot.

FeSi₂, the boron and arsenic impurities were shown to preferentially occupy the Si site in β -FeSi₂ from our theoretical results in Chapter 4 (Section 4.5.1). Therefore, they act as the active dopants for β -FeSi₂ when occupying the substitutional Si sites and should at least partially be responsible for the observed conductivity modulation analogous to their roles in Si.

It is important to realize that *p*-type inversion of the film conductivity was induced by B doping. This can be attributed to the compensation of the residual electron concentration of $\sim 4 \times 10^{17} \text{ cm}^{-3}$ (see Figure 5.9) present in the original sputter-deposited and RTA-annealed *n*-type β -FeSi₂ film. Here, we used the reliable value of the residual electron concentration at 700 °C since the significant contribution of the Si substrate can no longer be neglected at 800 °C and therefore its value does not reflect the true concentration and even mobility in the β -FeSi₂ film. It is intuitive that one would require sufficient concentration of B atoms for the compensation. As a first order estimation, we assumed Gaussian profiles for the implanted ions as described in Section 6.3.2. The peak ion concentration was determined to be in the order of 10^{18} - 10^{20} cm^{-3} corresponding to an implantation dose of 10^{13} - 10^{15} cm^{-2} . This clearly indicates that there are sufficient B atoms for inducing the *p*-type inversion.

6.4.2 Carrier concentration and mobility

It was observed from Figures 6.2 and 6.3 that the carrier concentration and mobility in the B- and As-implanted β -FeSi₂ samples do not change monotonically with the dopant dose. This could be related to the random implantation-induced damage, despite the fact that the exact physical mechanism is not fully understood. The lowest

carrier concentration of both B- and As-doped β -FeSi₂ was obtained at 800 °C where the highest mobility was also obtained. However, these values should not represent the actual carrier concentration and mobility in the impurity-doped β -FeSi₂ samples annealed at 800 °C due to the severe contribution of the Si substrate as previously mentioned, though their true values are still anticipated to be lower than that obtained at other temperatures, possibly in the order of 10^{17} cm^{-3} .

To further illustrate the effect of the substrate contribution, one can compare the value of the measured sheet resistance R_s with that of the Si substrate R_{Si} . The R_s can be obtained as the parallel combination of the R_f and R_{Si} given by

$$R_s = \frac{R_f R_{Si}}{R_f + R_{Si}} < R_f, \quad (\text{Equation 6.2})$$

where R_f represents the sheet resistance of the β -FeSi₂ film. Figure 6.4 shows the variation in the average sheet resistance of the undoped and impurity-doped β -FeSi₂ with the annealing temperature. It can be seen that the R_s at 800 °C ($\sim 1.4 \times 10^5 \text{ } \Omega/\text{sq.}$) and hence the R_f are comparable to the R_{Si} of $\sim 2 \times 10^5 \text{ } \Omega/\text{sq.}$, assuming an average resistivity of $\rho = 10000 \text{ } \Omega\text{-cm}$ and a thickness of 500 μm for the Si substrate. This shows that the contribution of the Si substrate is very significant at 800 °C.

In principle, it is required that R_{Si} must be much larger than R_f so that the ratio $R_{Si}/(R_f + R_{Si})$ or equivalently $(R_{Si} - R_s)/R_{Si}$ approaches unity to minimize the influence from the underlying substrate, thereby giving accurate measurement results about the film as suggested by Equation (6.2). This condition was reasonably satisfied in our samples annealed at 700 °C, whose R_s of $\sim 1.6 \times 10^4 \text{ } \Omega/\text{sq.}$ is one order of magnitude smaller than R_{Si} . It follows that the carrier concentration and mobility obtained from the Hall effect

measurements do satisfactorily reflect the exact values in the B- and As-doped β -FeSi₂ at 700 °C. The net hole concentration from 1.8×10^{17} to 5.0×10^{17} cm⁻³ and mobility from 115 to 55 cm²/Vs were achieved for the B-doped β -FeSi₂ samples (see Figure 6.2), whereas the net electron concentration from 2.6×10^{17} to 5.6×10^{17} cm⁻³ and mobility from 95 to 35 cm²/Vs were obtained for the As-doped β -FeSi₂ samples (see Figure 6.3). This carrier concentration in the order of 10^{17} cm⁻³ in our B- and As-doped β -FeSi₂ films is comparable to the reported values for the cosputtered films [39], and a mobility in the order of 100 cm²/Vs could be achieved.

Figure 6.4. Variation in the average sheet resistance of undoped and impurity-doped β -FeSi₂ with RTA temperature.

6.4.3 Doping efficiency

It is surprising to see that the carrier concentration in the B- and As-doped β -FeSi₂ samples does not strongly vary in accordance with the doping concentration corresponding to the implantation dose. In the case of complete activation of dopants and

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removal of implantation damage, one would expect the carrier concentration to increase in proportion to the doping density and as a result, strong *p*-type B-doped and *n*-type As-doped β -FeSi₂ films should be obtained. However, this strong correlation between carrier concentration and doping density was not seen and instead, the carrier concentration was found to consistently fall in a narrow tunable range of 10^{17} cm^{-3} (for RTA at 700 °C), although $1 \times 10^{15} \text{ cm}^{-2}$ dose As-implanted β -FeSi₂ sample does show a noticeably larger carrier concentration ($\sim 6 \times 10^{17} \text{ cm}^{-3}$) than the undoped and low dose implanted samples [$\sim (3-4) \times 10^{17} \text{ cm}^{-3}$] (see Figures 6.3 and 5.9). It is important to note that the $1 \times 10^{15} \text{ cm}^{-2}$ dose As-implanted β -FeSi₂ sample also exhibits a substantially lower mobility of $\sim 35 \text{ cm}^2/\text{Vs}$ as compared to $\sim 75-95 \text{ cm}^2/\text{Vs}$ of the undoped and low dose implanted samples, which is probably due to the higher implantation damage in the high dose implanted sample.

In order to examine whether the near constant carrier concentration with varying implantation dose is due to the massive escape (or loss) of implanted B and As atoms from the silicide films during the post-implantation annealing process (particularly for high dose implanted samples), SIMS profiling of B and As was performed on the as-implanted and post-implantation annealed samples and the results were illustrated in Figure 6.5. As shown clearly, the distribution of the as-implanted B and As atoms could well be described by a Gaussian profile in agreement with the normal distribution behavior of typical as-implanted atoms in solid materials. For the B-doped β -FeSi₂ samples, it was found that the B dopants were relatively uniformly distributed throughout the silicide layer without any traces of the massive loss of B atoms after RTA at 700 and 800 °C [see Figure 6.5(a)]. The rather uniform distribution of B indicates a high

diffusivity of B in β -FeSi₂ at these temperatures. On the other hand, no evidence of As loss upon RTA was also observed in the As-doped β -FeSi₂ samples since the As distribution profiles in the RTA-annealed samples remained almost exactly the same as that in the as-implanted sample [see Figure 6.5(b)], which also implies a low diffusivity of As in β -FeSi₂.

Figure 6.5. SIMS profiles of (a) B and (b) As dopants in as-implanted and RTA-annealed β -FeSi₂ for an implantation dose of $1 \times 10^{15} \text{ cm}^{-2}$.

It is important to note that the dopant concentrations of the B- and As-implanted and subsequently annealed FeSi₂ films are typically much larger than the carrier concentration in the corresponding silicide (i.e., holes in the B-implanted film and electrons in the As-implanted film). For example, the B concentration of $\sim 5 \times 10^{19} \text{ cm}^{-3}$ in the B-implanted FeSi₂ film (200 nm thick) at a dose of $1 \times 10^{15} \text{ cm}^{-2}$ is about two orders of magnitude higher than the hole concentration in the film ($\sim 1.8 \times 10^{17} \text{ cm}^{-3}$ at 700 °C) detected by the Hall effect measurements. Similar result was also seen for As implantation. These clearly indicate that most of the implanted B and As atoms are not activated after RTA, unlike *in situ* B or As doping of β -FeSi₂ prepared using facing-target cosputtering method where a hole concentration as high as $\sim 2 \times 10^{19} \text{ cm}^{-3}$ was obtained in the B-doped β -FeSi₂ [11].

We identify several possible factors that could potentially contribute to the observed poor doping efficiencies of implanted B and As atoms in β -FeSi₂ films. First, while Si site was found to be energetically favorable, a possible random dopant occupation of both the Fe and Si sites should not be excluded, particularly considering the generation of larger numbers of both Fe and Si vacancies by implantation damage. The occupation of Fe sites by B or As could produce competing effects of doping, since B and As may also act as amphoteric dopants in β -FeSi₂, analogous to the role of Si dopant in GaAs although the occupation of Si sites by B and As is preferable from the thermodynamic point of view.

Second, dopant loss as a consequence of incomplete activation will inevitably affect the carrier concentration by reducing the amount of active dopants. The non-substitutional dopant atoms could exist in the form of interstitial impurities, clusters or

precipitates, and possibly grain boundary segregation, which are mostly electrically inactive.

Lastly, the possibility of the compensation of B and As doping by opposite type carrier generation sources (like unoccupied Fe and Si vacancies) created by ion implantation could not be ruled out. It has been suggested theoretically in Chapter 4 (Section 4.4) and shown experimentally [99] that Si vacancies introduce acceptor-like defect levels above the valence band, whereas Fe vacancies introduce donor-like defect levels below the conduction band. Nevertheless, in all circumstances, the underlying physical mechanism should be strongly related to the implantation-induced defects and subsequent activation annealing.

6.5 Silicon Doping

In Chapter 4 (Section 4.4), we have concluded that Fe-deficient (or Si-rich, $x > 2$) and Si-deficient (or Fe-rich, $x < 2$) β -FeSi_x films exhibit *n*-type and *p*-type conductivities, respectively. This result implies that conductivity modulation could also be achieved by varying the stoichiometric ratio of the silicide film. It is therefore interesting to perform this study for the case of β -FeSi₂.

We focus our investigation on the Si-rich β -FeSi₂ films fabricated by the method of Si⁺ ion implantation. Figure 6.6 shows the carrier concentration and Hall mobility as a function of the dose for the Si-doped β -FeSi₂ at different RTA temperatures. It can be seen that the Si-doped β -FeSi₂ exhibits *n*-type conductivity for the samples annealed at ≥ 700 °C, which agrees with our theoretical results.

Figure 6.6. (a) Carrier concentration and (b) Hall mobility as a function of the dose for Si-doped β -FeSi₂ at different RTA temperatures. Solid and open symbols represent n -type and p -type conductivities, respectively, in the carrier concentration versus dose plot.

The n -type electrical conductivity observed for the Si-doped β -FeSi₂ should be caused by the excess electrons donated to the conduction band of β -FeSi₂. These additional electrons could have originated from the donor levels associated with the excess Si (or Fe vacancies) present in the Si-doped β -FeSi₂ films. However, the carrier concentration was found to be in the order of 10¹⁶ cm⁻³ which appears to be unusually low, taking into consideration the high dopant concentration of the Si-implanted and subsequently annealed β -FeSi₂ films.

We strongly believe that the small carrier concentration detected in the Si-doped β -FeSi₂ is closely related to the implantation damage in the silicide. It is apparent that the implantation-induced defects also results in the p -type silicide film at low temperatures, although the underlying physical reason is still not fully understood. This was also seen

for the B- and As-implanted β -FeSi₂ shown in Figures 6.2 and 6.3, which we observed an *p*-type conductivity for the samples annealed at 500 °C. Nonetheless, the result showed the possibility of modulating the conductivity in non-stoichiometric β -FeSi₂.

6.6 Summary

The electrical properties of impurity-doped β -FeSi₂ thin films fabricated by ion implantation technique and the effects of impurity doping have been studied. The B- and As-doped β -FeSi₂ films were found to exhibit *p*-type and *n*-type electrical conductivities, respectively, which confirmed our theoretical predictions on the film conductivity. A carrier concentration in a tunable range of 10^{17} cm⁻³ and a mobility in the order of 100 cm²/Vs were consistently obtained for the B- and As-doped β -FeSi₂. The observed limited doping efficiencies of implanted B and As atoms in β -FeSi₂ films could be attributed to the implantation-induced defects and incomplete activation. It was further shown that the conductivity modulation could be achieved by changing the stoichiometric ratio of the silicide film.

CHAPTER 7

SEMICONDUCTING BETA-PHASE IRON DISILICIDE-BASED HETEROJUNCTION SOLAR CELL DEVICES

7.1 Introduction

This chapter presents the PV characteristics of *p*-type B-doped β -FeSi₂/*n*-type Si heterojunction thin film solar cells. The fabrication process and characterization of solar cells are described. The transmittance spectra and photocurrent generation of silicide are studied. The photocurrent enhancement and the impact of area effect on the performance parameters are also discussed. In addition, the output characteristics of solar cells and the effects of various physical parameters on the cell performance are investigated.

7.2 Solar Cell Fabrication and Characterization

The fabrication of solar cells involves the formation of electrical junctions and conducting electrodes. This section presents the fabrication process of *p*-type B-doped β -FeSi₂/*n*-type Si heterojunction solar cells and the device measurements.

7.2.1 Heterojunction formation

Bare *n*-type Si(100) wafers with resistivity of 6-10 Ω -cm were used as the starting substrates to fabricate the β -FeSi₂-based heterojunction solar cells. The wafers were sequentially cleaned using the standard RCA wet cleaning process and HF solution (4%

by volume) to remove organic and metal contaminants as well as native oxide on the Si surface. FeSi₂ films of different thicknesses (50, 100, and 200 nm) were subsequently sputter-deposited from a stoichiometric iron disilicide target (purity=4N, 99.99%) at RT in a DC magnetron sputtering chamber. B⁺ ion implantation was performed at selected energies for different FeSi₂ layers to introduce B acceptor impurities into FeSi₂ films with doses of 1×10^{13} and 1×10^{15} ions/cm². During the ion implantation, the wafers were positioned at a tilt of 7° and a twist of 22° to suppress the ion channeling effect. The samples were then subjected to RTA and forming gas annealing (FGA) in an N₂ and N₂/H₂ (5% H₂) ambient, respectively, at various temperatures and duration of anneals.

Table 7.1 shows the ion energy used for different silicide layers and the resulting projected range and longitudinal straggling obtained from the SRIM simulation. These ion energies were deliberately chosen such that the peak ion concentration is located at a depth corresponding to ~40% of the silicide thickness. Figure 7.1 shows the schematics illustrating the formation of *p*-type B-doped β-FeSi₂/*n*-type Si heterojunctions.

Table 7.1. Ion energy for different silicide layers and the corresponding projected range and longitudinal straggling. Peak ion concentration was calculated by Equation (6.1).

FeSi ₂ thickness (nm)	Ion energy (keV)	Projected range R_p (nm)	Longitudinal straggling ΔR_p (nm)	Peak ion concentration $n(R_p)$ (10^{18} and 10^{20} cm ⁻³)
50	10	21.7	14.7	2.71
100	20	42.0	24.5	1.63
200	40	80.5	38.7	1.03

Figure 7.1. Schematics illustrating the formation of p -type B-doped β -FeSi₂/ n -type Si heterojunctions.

7.2.2 Ohmic contact formation

Figure 7.2 shows the schematics illustrating the formation of ohmic contacts to p -type B-doped β -FeSi₂/ n -type Si heterojunctions. The ohmic contacts were fabricated after the formation of the p -type B-doped β -FeSi₂/ n -type Si heterojunctions as illustrated in Figure 7.1. Prior to the ohmic contact formation, the samples were chemically cleaned in HF solution (1% by volume) for 10 s to remove any oxide on the β -FeSi₂. A layer of 200 nm ITO was subsequently deposited at RT onto the silicide by RF magnetron sputtering. The ITO layer serves as an ohmic contact to the β -FeSi₂ layer as well as transparent

conducting electrode for the heterojunction solar cells. The back ohmic contact to the n -Si substrates was formed by sequentially sputter-depositing a layer of 50 nm Ti followed by a layer of 50 nm Al at RT. The resulting PV devices were shaped into a square geometry of area $1 \times 1 \text{ cm}^2$.

Figure 7.2. Schematics illustrating the formation of ohmic contacts to p -type B-doped β -FeSi₂/ n -type Si heterojunctions.

7.2.3 Device measurements

Figure 7.2(c) shows the final device structure of the fabricated p -type B-doped β -FeSi₂/ n -type Si heterojunction solar cells. These PV cells have a total active area of $1 \times 1 \text{ cm}^2$. The dark and illuminated I - V characteristics of the solar cells were measured using *K. H. Tan*

the method described in Chapter 3 (Section 3.5.3), with the AM1.5 illumination incident on the top electrode while the bottom electrode is grounded as reference. In addition, we performed small area measurements for the PV cells, where the cells were shaded by an opaque shadow mask with a square opening of $2.5 \times 2.5 \text{ mm}^2$ at the center during the measurements. In this measurement, the dark I - V characteristics are expected to remain essentially unaffected; however, the illuminated I - V characteristics will differ due to the difference in the effective area of illumination. The transmittance spectra of the silicide and ITO were measured on the respective films grown on quartz substrates with the same processing conditions as described in Sections 7.2.1 and 7.2.2.

7.3 Optical Transmission

The transmittance of the top electrode and different layers in a solar cell are important in determining the optical coupling (or loss) to the PV device structure. In this section, we investigate the transmittance spectra of silicide and ITO and discuss the contribution of silicide to the photocurrent generation.

7.3.1 Transmittance spectra

In the p -type B-doped β -FeSi₂/ n -type Si(100) heterojunction solar cells, the ITO (Sn-doped In₂O₃, with $E_g=3.7 \text{ eV}$ and electron affinity $\chi=4.2$ to 4.5 eV) [73] top electrode essentially serves the roles as a large gap (window) material which does not appreciably absorb sunlight and an ohmic contact to silicide for carrying cell-developed current. Figure 7.3 shows the photon wavelength dependence of transmittance over a broad wavelength range of 300-1800 nm for the ITO on quartz. This wavelength range covers

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from DUV region to near-IR region of the solar irradiance spectrum shown in Figure 2.7. It can be seen that the ITO layer is generally optically transparent with a transmittance of greater than 72% over the entire measured wavelength range above 437 nm. Below 437 nm, the transmittance of the ITO/quartz was found to decrease sharply, which is due to the strong optical absorption of the quartz substrate in these wavelengths.

Figure 7.3. Transmittance as a function of photon wavelength in the range of 300-1800 nm for ITO on quartz.

At a wavelength of about 1440 nm which corresponds to the bandgap energy of β -FeSi₂, the transmittance of the ITO top electrode was found to be about 86%. Below this wavelength, the transmittance increases monotonically with photon energy to the peak value of ~98% at around 770 nm. This result suggests that most of the incoming photons with energy close to the bandgap of β -FeSi₂ can be coupled into the underlying β -FeSi₂/Si heterojunction. Such optical coupling is highly advantageous because these photons can be strongly absorbed and efficiently used by β -FeSi₂. Below 770 nm, the transmittance

decreases gradually to a minimum value of $\sim 78\%$ at 530 nm and then raises to $\sim 91\%$ at 437 nm. It can therefore be concluded that the ITO front electrode exhibit high optical transparency over the critical range of the photon wavelength of interest.

Figure 7.4 shows the transmittance as a function of photon wavelength in the range of 300-1800 nm for the 50 and 100 nm as-deposited and RTA-annealed FeSi_2 on quartz. As shown clearly, the transmittance of the 100 nm silicide film was generally lower than that of the 50 nm silicide film as expected, which is caused by the increased optical absorption and hence reduced light transmission in the physically thicker film. For the RTA-annealed $\beta\text{-FeSi}_2$ films, the transmittance of the film was found to remain almost unchanged upon RTA at different temperatures. This implies that the film transmittance could be relatively insensitive to the annealing temperature in the annealed samples.

Figure 7.4. Transmittance as a function of photon wavelength in the range of 300-1800 nm for 50 and 100 nm as-deposited and RTA-annealed FeSi_2 on quartz.

At a given silicide thickness, it was observed that the transmittance of the as-deposited (amorphous) films was noticeably smaller than that of the RTA-annealed films. In essence, amorphous materials can contain large densities of localized gap states. These can be intrinsic localized states arising from the statistical distribution of bond angles and inter-atomic distances, and/or extrinsic localized states arising from the defects (broken chemical bonds) and impurities (as in crystalline materials) [133]. Since the density of localized states is very high in amorphous materials, carrier transport via these gap states is possible and as a result, the absorption edge in amorphous materials is often broad, and the optical absorption at and above the fundamental absorption edge can be stronger for amorphous materials than for corresponding material. Consequently, the as-deposited (amorphous) film would expect to exhibit a lower transmittance than that of the annealed (polycrystalline) film.

7.3.2 Photocurrent generation of silicide

The photocurrent developed in the heterojunction solar cell generally consists of contributions from both the β -FeSi₂ and Si layers. In order to examine whether the β -FeSi₂ layer does effectively contribute to the photocurrent generation, a simple estimation can be performed based on the transmittance spectra of the silicide film as shown in Figure 7.4. Since the photons with energy less than the bandgap of Si do not possess sufficient energy to create EHPs in the device, these photons will be lost even they are being coupled into the underlying Si substrate. For a 50 nm thick and RTA-annealed β -FeSi₂ film, using the average value of transmittance of ~8% between 300 and 1108 nm (corresponding to the bandgap of Si) and assuming a short-circuit current density of ~40

mA/cm² typically expected from a highly efficient monocrystalline Si solar cell [134-136], the upper limit of J_{sc} resulted from the Si in the present heterojunction solar cell was estimated to be about 3.2 mA/cm². However, it should be highlighted that this value was estimated based on the extremely high J_{sc} of a highly efficient Si solar cell, which effectively utilizes different light trapping techniques such as surface texturing or AR coating to minimize the optical losses. Therefore, the actual J_{sc} generated by the Si should be much smaller than this optimal value, probably in the order of 1 mA/cm². Similar result could also be drawn for the RTA-annealed cells with a 100 nm thick β -FeSi₂, where a smaller J_{sc} contribution from the Si is expected due to the lower transmittance. Figure 7.10(a) indicates that the J_{sc} obtained for the RTA-annealed cells with a 50 nm thick β -FeSi₂ was typically about 3.5-4.5 mA/cm². By comparison, it can therefore be concluded that the β -FeSi₂ layer does appreciably contribute to the photocurrent generation in the heterojunction solar cell.

To further justify that β -FeSi₂ is producing photocurrent, we performed a simple but useful experiment which is described as follows. Figure 7.5 shows the schematics of the experimental setup, which utilizes a standard reference Si cell for PV measurements. Under AM1.5 illumination, the output reading of the reference Si cell was first taken as shown in Figure 7.5(a). Subsequently, the reference Si cell was fully shaded by an ITO/ β -FeSi₂/quartz film stack, and its output reading was again taken as shown in Figure 7.5(b). The ratio of the latter to the former (units are omitted) which is technically important was calculated, and the results are presented in Table 7.2 for different silicide thicknesses at various RTA temperatures. Note that the ITO (200 nm) and β -FeSi₂ layers on quartz are processed exactly identical to that described in Section 7.2.

Figure 7.5. PV measurements of (a) a reference Si cell and (b) the reference Si cell shaded by an ITO/ β -FeSi₂/quartz film stack with different silicide thicknesses. Output readings of the reference Si cell are taken in (a) and (b) and their ratios are determined.

Table 7.2. Ratios of the reference Si cell output taken in Figure 7.5(b) to (a) for different silicide thicknesses at various RTA temperatures.

β -FeSi ₂ thickness (nm)	700 °C	800 °C	850 °C
50	7.99% (33/413)	7.95% (33/415)	7.99% (33/413)
100	2.65% (11/415)	2.70% (11/407)	3.17% (13/410)

For a 50 nm thick and RTA-annealed β -FeSi₂ film, the maximum J_{sc} that can be generated from the underlying Si in the heterojunction solar cell was calculated to be $\sim 3.2 \text{ mA/cm}^2$ (i.e., 7.99% multiplied by $\sim 40 \text{ mA/cm}^2$), assuming a short-circuit current density of $\sim 40 \text{ mA/cm}^2$ from a highly efficient monocrystalline Si solar cell. This result strongly supports our conclusion deduced from the transmittance spectra as previously discussed. In reality, the Si substrate in our samples and its junction interface with β -

FeSi₂ as well as the back contact are not optimized (for carrier collection). Furthermore, the underlying Si also inevitably suffered from the diffused Fe contamination. Therefore, such analysis would represent the worst case condition for the photocurrent generation of silicide, which also evidently suggests that β -FeSi₂ is generating photocurrent.

7.4 Electrical Characteristics

The I - V characteristics are important in understanding the electrical performance of semiconductor electronic devices. In this section, we analyze the I - V characteristics of p -type B-doped β -FeSi₂/ n -type Si heterojunction solar cells and discuss the photocurrent enhancement and the impact of area effect on the performance parameters J_{sc} and V_{oc} .

7.4.1 Photocurrent enhancement

Figure 7.6 shows the dark and illuminated I - V characteristics of the 200 nm and $1 \times 10^{15} \text{ cm}^{-2}$ dose B-doped β -FeSi₂/ n -type Si(100) heterojunction solar cells obtained after RTA and FGA at 800 °C. It can be seen from the dark I - V characteristics that the current through the junction is substantially larger when the applied voltage on the silicide is positive. This shows that the B-doped β -FeSi₂ is p -type, which agrees with our results from the Hall effect measurements in Chapter 6 (Section 6.4.1).

Under illumination, it was found that the illuminated I - V curves were displaced from the dark I - V characteristics, indicating the presence of photoresponse. The observed photocurrent enhancement is very significant, particularly for the RTA-annealed sample, where we observed an improvement of about one order of magnitude under negative applied voltage or reverse bias, despite the fact that there was only a slight shift of the

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Figure 7.6. Dark and illuminated I - V characteristics of 200 nm and $1 \times 10^{15} \text{ cm}^{-2}$ dose B-doped β -FeSi₂/ n -type Si(100) heterojunction solar cells obtained after (a) RTA at 800 °C for 60 s and (b) FGA at 800 °C for 3 h. The cells have an active area of $1 \times 1 \text{ cm}^2$. The insets next to (a) and (b) show the respective J - V curves plotted in linear scale.

illuminated I - V curve towards the positive voltage direction, which translates into a small photovoltage. For the FGA-annealed sample, the photovoltage was noticeably larger in addition to the photocurrent enhancement. It was found that the photocurrent increases with increasing reverse bias voltage for both cells RTA- and FGA-annealed at 800 °C. This can clearly be seen from the linear I - V curves shown in the insets in Figure 7.6.

Similar photocurrent increase with the reverse bias (not shown) was also seen for other RTA- and FGA-annealed cells measured on the $1 \times 1 \text{ cm}^2$ samples.

In principle, the illuminated characteristics of a PV cell are essentially the dark characteristics shifted by a constant amount equal to the light-generated current as pointed out in Chapter 2 (Section 2.3.3.2). The observed photocurrent increase with increasing reverse bias could be attributed to the increased junction depletion width under reverse bias. The increase in depletion width enhances the collection of photo-generated carriers, and hence the photocurrent increases as suggested by Equation (2.5).

7.4.2 Impact on short-circuit current

In the measurements performed on the $1 \times 1 \text{ cm}^2$ cell samples, there would be a loss of the photo-generated carriers at the electrodes (mainly transparent ITO electrode) that would otherwise contribute to the photocurrent under reverse bias. This was largely caused by the parasitic voltage drop due to a high film resistance, which can potentially reduce the effective voltage across the heterojunction or even possibly forward-bias the junction. Such problem can be alleviated by utilizing a highly conductive electrode (like high quality ITO) which minimizes the parasitic voltage drops, or alternatively a small area device or measurement, which also avoids the effect of the edges of the devices. Figure 7.7 shows the dark and illuminated J - V characteristics obtained from the small area measurements for the same devices corresponding to that in Figure 7.6. By comparison, it can be concluded that the photocurrent is relatively larger and hence the J_{sc} improves for both RTA- and FGA-annealed cells due to the enhanced collection of the photo-generated minority carriers.

Figure 7.7. Dark and illuminated J - V characteristics obtained from the small area ($2.5 \times 2.5 \text{ mm}^2$) measurements for the same devices corresponding to that in Figure 7.6.

7.4.3 Impact on open-circuit voltage

In the small area measurements, it should be noted that the effective area of illumination ($2.5 \times 2.5 \text{ mm}^2$) would significantly differ from the actual device area ($1 \times 1 \text{ cm}^2$). Theoretically, V_{oc} increases logarithmically with the ratio of light-generated current I_L to the diode saturation current I_0 given by

$$V_{oc} = \frac{kT}{e} \ln \left(\frac{I_L}{I_0} + 1 \right) \quad (\text{Equation 7.1})$$

where I_L is proportional to the area of illumination as shown in Equation (2.5). Since the illuminated area now becomes much smaller than the diode area, the measured V_{oc} would expect to reduce as suggested by Equation (7.1). Such impact on V_{oc} can clearly be seen by comparing Figures 7.6 and 7.7, where we consistently obtained a smaller V_{oc} from the small area measurements on the same device.

7.5 Photovoltaic Characteristics

This section characterizes the PV performance of the p -type B-doped β -FeSi₂/ n -type Si heterojunction solar cells whose output characteristics were obtained from the small area measurements. The effects of various physical parameters on the performance of the cells are also discussed.

7.5.1 Illuminated J - V characteristics

Figure 7.8 shows the dark and illuminated J - V characteristics of the 50 nm and $1 \times 10^{15} \text{ cm}^{-2}$ dose B-doped β -FeSi₂/ n -type Si(100) heterojunction solar cells obtained after RTA at 800 °C. Similar J - V characteristics were also observed for other RTA- and FGA-annealed cells, whose general features are discussed as follows.

Under positive applied voltage or forward bias, it can be seen that the illuminated characteristics remained almost exactly the same as the dark characteristics. This can be easily understood since at forward bias, the forward current is significantly larger than the light-generated current, which is a strong function of depletion width as suggested by Equation (2.5). The small junction depletion region at forward bias implies a small active region for current collection for a PV cell, thereby hindering the photocurrent generation.

Such limitation to collect the photo-generated minority carriers is even more severe at high forward bias where the depletion region will become so narrow that it could be ineffective for charge separation.

Figure 7.8. (a) Dark and illuminated J - V characteristics of 50 nm and $1 \times 10^{15} \text{ cm}^{-2}$ dose B-doped $\beta\text{-FeSi}_2/n$ -type Si(100) heterojunction solar cells obtained after RTA at 800 °C. (b) J - V characteristics in the fourth quadrant showing the PV output.

On the other hand, strong photocurrent enhancement was realized under reverse bias, where an almost constant shift of the illuminated characteristics were also observed, indicating the suppression of photocurrent degradation in small area measurements. Under reverse bias, the reverse leakage current is generally very small (ideally negligible), while the light-generated current is strongly enhanced due to the much larger junction depletion width [see Equation (2.5)] and hence the active region for current collection. As a result, strong photocurrent was typically generated at this condition.

Under illumination, it was evident that the cell exhibits the PV response, which manifests itself by the J - V characteristics in the fourth quadrant. Figure 7.8(b) clearly shows the PV output, from which the performance parameters of the cell can be extracted according to their definitions given in Chapter 2 (Section 2.3.3.3). In particular, it should be noted that the range of bias from 0 to V_{oc} represents the operating regime of the solar cell, in which the cell produces power. Moreover, it is important and meaningful to compare the photocurrent at a particular (reverse) bias voltage for different PV cells in addition to the J_{sc} .

Figure 7.9 shows the dark and illuminated J - V characteristics of the $1 \times 10^{15} \text{ cm}^{-2}$ dose B-doped β -FeSi₂/ n -type Si(100) heterojunction solar cells obtained via RTA at 700, 800, and 850 °C for different silicide thickness. The PV response was generally detected in all samples, except for the cell annealed at 700 °C with a 200 nm thick β -FeSi₂. For all the RTA-annealed cells with different silicide thickness, a high ratio of the illuminated current to the dark current (i.e., photosensitivity) under the reverse bias was observed. The largest photosensitivity was obtained for the cells with a 50 nm thick β -FeSi₂, in which the β -FeSi₂ layer contributes significantly to the photocurrent generation. The

maximum J_{sc} of about 4.31 mA/cm^2 was attained for the 50 nm thick $\beta\text{-FeSi}_2$ cell annealed at 700°C .

Figure 7.9. Dark and illuminated J - V characteristics of $1 \times 10^{15} \text{ cm}^{-2}$ dose B-doped $\beta\text{-FeSi}_2/n\text{-type Si}(100)$ heterojunction solar cells obtained with a RTA at 700, 800, and 850°C for different silicide thicknesses: (a)-(c) 50 nm, (d)-(f) 100 nm, and (g)-(i) 200 nm.

The V_{oc} which corresponds to the junction built-in potential is the maximum voltage available from a solar cell. The maximum V_{oc} of about 296 mV was achieved for the cells with a 50 nm thick $\beta\text{-FeSi}_2$ annealed at 800 and 850°C . This value is lower than that (450 mV) reported for the most efficient (3.7%) $n\text{-type } \beta\text{-FeSi}_2/p\text{-type Si}(111)$

heterojunction solar cell [43], but is higher than the values obtained for the n -type β -FeSi₂/ p -type Si (176 mV) [82] and n -type nanocrystalline FeSi₂/ p -type Si heterojunctions (<200 mV) [137] prepared by FTS method.

The obtained V_{oc} is mainly affected by the recombination processes in the solar cell. The Fe atoms diffused into the depletion region and the underlying Si could act as trap centers for the photo-generated carriers, which eventually degrade and limit the V_{oc} . Moreover, the interface states arising from the mismatch in the lattice parameters between β -FeSi₂ and Si could provide additional recombination sites that further reduce not only V_{oc} but also J_{sc} . For all samples, the FF was found to be in the range of 24-31%. The small FF should be caused by the high series resistance present in the device structure.

Tables 7.3-7.5 show the photocurrent density at a bias voltage of -1.0 V and the performance parameters (J_{sc} , V_{oc} , and FF) as well as conversion efficiency extracted for the heterojunction solar cells shown in Figure 7.9. The reasonable efficiency was found to be in the range of 0.27-0.35% for the cells with a 50 nm thick β -FeSi₂ layer. While these efficiencies are relatively low compared with the reported efficient cell employing an epitaxial β -FeSi₂ thin template for the growth of high quality β -FeSi₂ film on Si [43], it does in principle demonstrate the application potential of this novel material (β -FeSi₂) for PV energy conversion. The high photosensitivity at the reverse bias also indicates that the present B-doped β -FeSi₂/ n -type Si heterojunction can potentially be used as photodiodes in the photoconductive mode for near-IR light detection.

Table 7.3. Photocurrent density at a bias voltage of -1.0 V, performance parameters, and conversion efficiency of $1 \times 10^{15} \text{ cm}^{-2}$ dose B-doped $\beta\text{-FeSi}_2/n\text{-type Si}(100)$ heterojunction solar cells RTA-annealed at 700 °C for different silicide thicknesses.

$\beta\text{-FeSi}_2$ thickness (nm)	J_{ph} at -1.0 V (mA/cm ²)	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)	η (%)
50	5.40	4.31	291	24	0.30
100	1.97	1.43	238	25	0.09
200	1.55	...	...	...	...

Table 7.4. Photocurrent density at a bias voltage of -1.0 V, performance parameters, and conversion efficiency of $1 \times 10^{15} \text{ cm}^{-2}$ dose B-doped $\beta\text{-FeSi}_2/n\text{-type Si}(100)$ heterojunction solar cells RTA-annealed at 800 °C for different silicide thicknesses.

$\beta\text{-FeSi}_2$ thickness (nm)	J_{ph} at -1.0 V (mA/cm ²)	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)	η (%)
50	5.38	3.57	296	26	0.27
100	1.71	0.56	209	25	0.03
200	1.91	0.47	32	...	...

Table 7.5. Photocurrent density at a bias voltage of -1.0 V, performance parameters, and conversion efficiency of $1 \times 10^{15} \text{ cm}^{-2}$ dose B-doped $\beta\text{-FeSi}_2/n\text{-type Si}(100)$ heterojunction solar cells RTA-annealed at 850 °C for different silicide thicknesses.

$\beta\text{-FeSi}_2$ thickness (nm)	J_{ph} at -1.0 V (mA/cm ²)	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)	η (%)
50	4.53	3.85	296	31	0.35
100	2.20	1.03	212	25	0.06
200	0.45	0.28	126	30	0.01

7.5.2 Effects of silicide thickness

Figure 7.10 shows the J_{sc} , V_{oc} , and J_{ph} at a bias voltage of -1.0 V as a function of silicide thickness for the $1 \times 10^{15} \text{ cm}^{-2}$ dose B-doped $\beta\text{-FeSi}_2/n\text{-type Si}(100)$ heterojunction solar cells at different RTA temperatures. It was found that both J_{sc} and V_{oc} increase with decreasing silicide thickness. Theoretically, the light-generated current density J_L is determined by the carrier generation rate $G(x)$ and collection probability $CP(x)$ according to [76]

$$J_L = e \int_0^W G(x) CP(x) dx \quad (\text{Equation 7.2})$$

where W is the device thickness. The $CP(x)$ is a spatially dependent parameter that describes the probability that a photo-generated minority carrier absorbed in a certain region of the device will be collected, thus contributing to the light-generated current. In particular, the $CP(x)$ of carriers generated in the depletion region is unity and away from the depletion region edge, the $CP(x)$ decreases exponentially with a characteristic decay constant equal to the minority carrier diffusion length.

Since the $\beta\text{-FeSi}_2$ has an extremely high absorption coefficient of $\sim 10^5 \text{ cm}^{-1}$ at 1.0 eV [see Chapter 5 (Section 5.4.2)] which corresponds to an absorption depth of about 100 nm, most of the incoming photons will be absorbed in the region near the surface (mainly in the $\beta\text{-FeSi}_2$ layer). However, this is precisely where the collection probability is low. Such deficiency can be minimized if the junction is close to the surface (shallower junction). Consequently, the collection of carriers can be enhanced with decreasing $\beta\text{-FeSi}_2$ thickness and therefore the J_L increases as suggested by Equation (7.2). This increases the J_{sc} and generally J_{ph} as shown in Figure 7.10(c). The increase in V_{oc} can be

clearly interpreted by Equation (7.1), which states that V_{oc} increases logarithmically with J_L at a given saturation current density. Since the saturation current density [see Equation (2.4)] remained essentially unchanged with varying β -FeSi₂ thickness, V_{oc} would expect to increase.

Figure 7.10. (a) Short-circuit current density J_{sc} , (b) open-circuit voltage V_{oc} , and (c) photocurrent density J_{ph} at a bias voltage of -1.0 V as a function of silicide thickness for $1 \times 10^{15} \text{ cm}^{-2}$ dose B-doped β -FeSi₂/ n -type Si(100) heterojunction solar cells at different RTA temperatures.

J_{sc} and V_{oc} were found to attain their largest values at a thickness of 50 nm, beyond which they decrease. Similar result was also seen for the conversion efficiency as

shown in Tables 7.3-7.5. This result suggests that the diffusion length of the minority carriers in our B-doped β -FeSi₂ solar cells should be at ~50 nm.

7.5.3 Effects of thermal annealing

Figure 7.11 shows the dark and illuminated J - V characteristics of the 200 nm and $1 \times 10^{15} \text{ cm}^{-2}$ dose B-doped β -FeSi₂/ n -type Si(100) heterojunction solar cells obtained after FGA at 700 and 800 °C for different duration of anneals. Please note that Figure 7.11(b) is identical to Figure 7.7(b) and it is presented here for comparison. By comparing Figures 7.11(a) and (b) to the RTA-annealed cells at the same thickness shown in Figures 7.9(g) and (h), it was found that the J - V characteristics of the FGA-annealed cells in the dark exhibit a larger reverse leakage current at the same temperature. This could be attributed to the enhanced Fe or dopant diffusion into the underlying Si substrate during the longer FGA duration. However, it is surprising to see from Figures 7.11(c) and (d) that with longer annealing time of 8 h, the FGA-annealed samples showed a relatively low reverse leakage current, which should be closely related to the annealing dependent crystallinity of β -FeSi₂ and density of recombination centers at the heterojunction.

Under illumination, the J - V characteristics of the FGA-annealed cells were found to exhibit similar features as that observed in Figure 7.8. By comparing Figure 7.11 with Figures 7.9(g) and (h), it can be seen that the FGA-annealed samples generally showed a slightly better PV response than the RTA-annealed cells with a consistent improvement in both J_{sc} and V_{oc} at the same temperature, except for the cell annealed at 800 °C for 8 h which exhibits a smaller J_{sc} of about 0.19 mA/cm². It was found that the FGA samples annealed for 8 h also exhibit a relatively low photocurrent which is probably due to the

Figure 7.11. Dark and illuminated J - V characteristics of 200 nm and $1 \times 10^{15} \text{ cm}^{-2}$ dose B-doped β -FeSi₂/ n -type Si(100) heterojunction solar cells obtained after FGA at (a) 700 °C for 3 h, (b) 800 °C for 3 h, (c) 700 °C for 8 h, and (d) 800 °C for 8 h.

Table 7.6. Photocurrent density at a bias voltage of -1.0 V, performance parameters, and conversion efficiency of 200 nm and $1 \times 10^{15} \text{ cm}^{-2}$ dose B-doped β -FeSi₂/ n -type Si(100) heterojunction solar cells obtained using FGA.

FGA condition	J_{ph} at -1.0 V (mA/cm ²)	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)	η (%)
700 °C/3 h	1.85	...	...	...	...
800 °C/3 h	1.81	0.67	158	31	0.03
700 °C/8 h	0.37	0.21	95	31	0.01
800 °C/8 h	0.35	0.19	147	31	0.01

severe Fe diffusion into the Si. Table 7.6 shows the photocurrent density at a bias voltage of -1.0 V and the performance parameters as well as conversion efficiency extracted for the FGA-annealed heterojunction solar cells.

7.5.4 Effects of implantation dose

Figure 7.12 shows the dark and illuminated J - V characteristics of the 50 nm and $1 \times 10^{13} \text{ cm}^{-2}$ dose B-doped β -FeSi₂/ n -type Si(100) heterojunction solar cells obtained using RTA. By comparing Figure 7.12 with Figures 7.9(a)-(c) for the $1 \times 10^{15} \text{ cm}^{-2}$ doped RTA-annealed cells at the same thickness, it was found that the J - V characteristics of the $1 \times 10^{15} \text{ cm}^{-2}$ doped RTA-annealed cells in the dark exhibit a lower reverse leakage current than the $1 \times 10^{13} \text{ cm}^{-2}$ doped samples at all annealing temperatures. This is unusual since one would expect that with larger dose the reverse leakage current in the samples should be higher due to the higher implantation damage in the silicide. However, this correlation between the reverse leakage current and the dopant dose was not observed, for which the physical origin remains unknown.

Under illumination, it was found that the $1 \times 10^{13} \text{ cm}^{-2}$ doped RTA-annealed cells also exhibit a clear photoresponse at reverse bias similar to the $1 \times 10^{15} \text{ cm}^{-2}$ doped samples. However, the observed PV response was very weak, which should be caused by the poor collection of the optically generated minority carriers in these samples. By comparison, it can be concluded that the $1 \times 10^{15} \text{ cm}^{-2}$ doped RTA-annealed cells showed an overall better PV performance than the $1 \times 10^{13} \text{ cm}^{-2}$ doped samples.

Figure 7.12. Dark and illuminated J - V characteristics of 50 nm and $1 \times 10^{13} \text{ cm}^{-2}$ dose B-doped β -FeSi₂/ n -type Si(100) heterojunction solar cells obtained using RTA: (a) 700 °C, (b) 800 °C, and (c) 850 °C.

7.6 Summary

The semiconducting β -FeSi₂-based thin film solar cells have been successfully fabricated on the Si platform, with a demonstration of the p -type B-doped β -FeSi₂/ n -type Si(100) heterojunction solar cells whose PV characteristics and the effects of various physical parameters on the cell performance were investigated. The PV response and a strong photocurrent at reverse bias were generally observed in the RTA-annealed cells with different silicide thickness. The J_{sc} and V_{oc} were found to increase with decreasing β -FeSi₂ thickness due to the enhanced carrier collection in a shallow junction. A J_{sc} in the

range of 3.5-4.5 mA/cm² and a V_{oc} of about 296 mV could be achieved with a 50 nm thick β -FeSi₂, in which the β -FeSi₂ layer contributes significantly to the photocurrent generation. The FGA-annealed samples were found to exhibit slightly better PV response than the RTA-annealed cells, but with a much higher leakage current. It was further shown that the overall performance of the RTA-annealed cells was improved with higher B dopant concentration. While the present efficiency of 0.27-0.35% could be relatively low, it does in principle demonstrate the application potential of this novel β -FeSi₂ material for PV energy conversion.

CHAPTER 8

CONCLUSION AND RECOMMENDATIONS

8.1 Conclusion

We have performed both theoretical and experimental study of β -FeSi₂ and investigated its potential for thin film PV applications. The theoretical study was performed by first-principles calculations based on the DFT while the experimental study involves the formation and structural, optical, and electrical characterization of sputtered and processed β -FeSi₂ as well as demonstration of semiconducting β -FeSi₂-based thin film solar cells on Si platform.

First-principles calculations revealed the existence of both direct and indirect transitions in β -FeSi₂ and confirmed its semiconducting property. The presence of Fe or Si vacancies was found to introduce energy levels in the forbidden gap and affect the electrical conductivity of β -FeSi₂ depending on the types of vacancy defects, with Fe vacancies produce donor-like defect states below the conduction band while Si vacancies produce acceptor-like defect states above the valence band. The B and As were shown to be shallow impurities in β -FeSi₂ and therefore could be effective dopants for β -FeSi₂. In particular, *p*-type and *n*-type conductivities were suggested for the B- and As-doped β -FeSi₂, respectively. The impurity doping was found to induce structural relaxation via lattice distortion, with As doping causing elongation of the As-Si bonds and contraction of the As-Fe bonds while B doping resulting in both inward and outward relaxations of the neighboring Si and Fe host atoms.

Structural analysis conducted on the sputter-deposited and RTA-annealed FeSi₂ films confirmed that the semiconducting β -FeSi₂ could be formed by RTA at temperatures ≥ 500 °C, below which the silicide films remained completely amorphous. The β -FeSi₂ thin films were polycrystalline and fine-grained with a columnar grain structure. A direct bandgap behavior has been concluded for both amorphous and polycrystalline semiconducting FeSi₂. It was found that the absorption coefficient of β -FeSi₂ was in the order of 10^5 cm⁻¹ at 1.0 eV and a direct bandgap of 0.86 eV was concluded to best characterize β -FeSi₂. The subgap optical absorption observed in the absorption spectra could be attributed to the band tailing and correlated with the residual carrier concentration. The electrical results indicate heavily doped and *n*-type conductivity for the FeSi₂ on *p*-Si substrate, whose electrical junction was found to exhibit good rectifying characteristics at 800 °C.

Electrical study concluded that the conductivity modulation for doping control in β -FeSi₂ could be achieved by B and As doping. The B- and As-doped β -FeSi₂ films were found to exhibit *p*-type and *n*-type conductivities, respectively, which confirmed the theoretical predictions. A carrier concentration in a tunable range of 10^{17} cm⁻³ and a mobility in the order of 100 cm²/Vs were obtained. Using this knowledge, *p*-type B-doped β -FeSi₂/*n*-Si heterojunction thin film solar cells were fabricated. The PV response and a strong photocurrent at reverse bias were observed in the RTA-annealed cells with different silicide thickness. The J_{sc} and V_{oc} were found to increase with decreasing β -FeSi₂ thickness due to the enhanced carrier collection in a shallow junction, and a J_{sc} value of ~ 3.5 - 4.5 mA/cm² and a V_{oc} of ~ 296 mV could be achieved with a 50 nm thick β -

FeSi₂. While the present efficiency of 0.27-0.35% could be relatively low, it does in principle demonstrate the application potential of β -FeSi₂ for PV energy conversion.

In conclusion, a low power conversion efficiency was typically obtained for the present β -FeSi₂/Si devices, which is due to the non-optimized device structure and poor material and junction qualities that result in significant optical losses and degraded carrier collection. Despite the abundance of Fe and Si, this Kankyo semiconductor is far from ready for PV applications.

8.2 Recommendations for Future Research

Several research topics related to β -FeSi₂ should be studied to further extend this project. Some of the possible directions for future investigations are given as follows:

1. Quantum efficiency measurements can be carried out to further investigate the PV properties of β -FeSi₂/Si heterojunction solar cells. Cell response, such as front and rear surface recombination, to different photon wavelengths can be thoroughly understood. This can certainly provide useful insight in optimizing the cell design or architecture to enhance the PV performance.
2. Different annealing processes should be investigated for the formation of atomically abrupt β -FeSi₂/Si heterojunction with minimal Fe or dopant diffusion at the interface. In particular, laser annealing which is capable of forming a highly activated ultra-shallow junction can be explored in conjunction with RTA or FGA for the simultaneous formation of semiconducting β -FeSi₂ and achievement of good interface quality and dopant activation.

3. Although the β -FeSi₂-based thin film solar cells have been demonstrated on the Si platform, the fabrication of β -FeSi₂-based thin film solar cells on other low cost platforms such as plastic and glass substrates or stainless steel sheets should be explored. This is critically important to fully develop the potential capabilities of β -FeSi₂ for future generation thin film PV applications.

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1. K. H. Tan, D. Z. Chi, and K. L. Pey, "Optical and electrical characterization of sputter-deposited FeSi₂ and its evolution with annealing temperature," *Journal of Applied Physics*, vol. 104, p. 064117, 2008.
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APPENDIX A

SIMPLIFIED OPTICAL ABSORPTION MODEL OF A THIN FILM/SUBSTRATE DOUBLE-LAYER SYSTEM

In the following theoretical formulation, we shall derive the simplified model for the thin film/substrate double-layer structure. The FeSi₂/Si system was used in the derivation. However, it should be stressed that in principle the resulting model is generally applicable to other thin film silicide materials and is valid for both homojunctions and heterojunctions.

Considering the Si substrate without the FeSi₂ film shown in Figure A.1(a), the light transmitted through the Si substrate I_o can be expressed by

$$I_o = I_i G (1 - R_{Si})^2 \exp(-\alpha_{Si} d_{Si}), \quad (\text{Equation A.1})$$

where I_i is the normal incident light, α_{Si} is the absorption coefficient of Si, d_{Si} is the thickness, and R_{Si} is the reflection coefficient at the Si/air interface. The exponential term $\exp(-\alpha_{Si} d_{Si})$ in Equation (A.1) represents the typical characteristic exponential decay of light traveling in a lossy medium. Here, we assumed that (1) the effect of multiple internal reflections in the Si layer is negligible and (2) the scattering of light can occur at the non-planar bottom boundary. A loss factor, $G < 1$, is introduced to account for the light loss following these assumptions. It follows that the transmittance of the Si substrate T_{sub} is given by

$$T_{sub} = \frac{I_o}{I_i} = G (1 - R_{Si})^2 \exp(-\alpha_{Si} d_{Si}). \quad (\text{Equation A.2})$$

Figure A.1. (a) Si substrate as a reference for a double-layer structure. (b) Schematic diagram of a double-layer structure consisting of FeSi₂ thin film on a Si substrate.

When the FeSi₂ film is present on top of the Si substrate [see Figure A.1(b)], the total light transmitted through the FeSi₂/Si double-layer is given by

$$I_t = I_i \frac{(1 - R_f)(1 - R_{int})\exp(-\alpha_f d_f)}{1 - R_f R_{int} \exp(-2\alpha_f d_f)} \times G(1 - R_{Si})\exp(-\alpha_{Si} d_{Si}), \quad (\text{Equation A.3})$$

where α_f is the absorption coefficient of FeSi₂ film, d_f is the thickness, and R_f and R_{int} are the reflection coefficients at the FeSi₂/air and FeSi₂/Si interfaces, respectively. The first term in Equation (A.3) represents the light traversing the FeSi₂/Si interface and the second term refers to the transmitted light from the Si layer. Here, we took into account the effect of multiple internal reflections in the thin film silicide layer and assumed that (1) the silicide film is homogeneous and (2) the silicide film/Si interface is optically flat

such that the light impinging on this boundary will not be scattered off. Hence the total transmittance for the double-layer structure T_f is given by

$$T_f = \frac{I_t}{I_i} = \frac{(1 - R_f)(1 - R_{\text{int}})\exp(-\alpha_f d_f)}{1 - R_f R_{\text{int}} \exp(-2\alpha_f d_f)} \times G(1 - R_{Si})\exp(-\alpha_{Si} d_{Si}). \quad (\text{Equation A.4})$$

Normalizing the T_f by the T_{sub} , we obtain the ratio of I_t to I_o as

$$\frac{I_t}{I_o} = \frac{(1 - R_f)(1 - R_{\text{int}})\exp(-\alpha_f d_f)}{(1 - R_{Si})[1 - R_f R_{\text{int}} \exp(-2\alpha_f d_f)]} = 10^{-A}. \quad (\text{Equation A.5})$$

The logarithm of the inverse of this ratio is the absorbance A measured in photo-absorption experiment. Equation (A.5) relates the optical absorption coefficient α_f of the FeSi₂ film to the experimentally measured absorbance A and can be solved analytically for α_f . We eventually obtain the following relationship between α_f and A for the thin film/substrate double-layer system

$$\alpha_f = \frac{1}{d_f} \ln \left(\frac{2bR_f R_{\text{int}} \times 10^{-A}}{\sqrt{a^2 + 4b^2 R_f R_{\text{int}} \times 10^{-2A}} - a} \right), \quad (\text{Equation A.6})$$

where

$$a = (1 - R_f)(1 - R_{\text{int}}), \quad (\text{Equation A.7})$$

$$b = (1 - R_{Si}). \quad (\text{Equation A.8})$$