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MAGNETISM IN γ -FeSi₂ NANOSTRUCTURES: A FIRST PRINCIPLES STUDY

Sahil Dhoka

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**MAGNETISM IN γ -FeSi₂ NANOSTRUCTURES: A FIRST
PRINCIPLES STUDY**

By

Sahil Dhoka

A THESIS

Submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

In Materials Science and Engineering

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This thesis has been approved in partial fulfillment of the requirements for the Degree of
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Abstract

First-principles calculations are performed on γ -FeSi₂ nanostructures grown on Si (111) and (001) substrate. An attempt to explain the origin of emergent magnetic properties of the metastable gamma phase of iron di-silicide (γ -FeSi₂) is made, which show ferromagnetic behavior on nanoscale, unlike its possible bulk form. Many papers try to explain this magnetism from factors like bulk, epitaxial strain, interface, surface, edges, and corners but doesn't provide an analytical study for these explanations. Density functional theory is used to analyze the magnetic effects of these factors. The results for the epitaxial structures show no magnetic behavior for the continuous thinfilm and nanoisland edge along [1 -1 0] directions grown on Si(111) substrate grown on Si(111) substrate. For the endotaxial structure grown on Si(001) substrate, two types of interface were analyzed i.e., silicon-terminated interface and iron-terminated interface. Significant magnetic moment is seen in both cases, but the contributing atoms for them are different.

Chapter 1

Introduction

1.1 Overview

Spintronics is a recently emerged field under solid-state physics. It exploits the spin properties of the electrons for its application in high-speed storage devices [7-9]. The coexistence of spin-orbit coupling, and magnetism have made transition metal silicide a potential candidate for their applications in spintronics. The main challenge for this is to induce spin-polarized current from a ferromagnetic material into a semiconductor. The challenge lies in tuning the interface between spin channel material and the ferromagnetic metal. But recent developments have shown the possibility of injecting spin-polarization into a semiconductor via transition metals [10]. Schottky Barrier Height affects the spin injection in a semiconductor, and the ability to tune the Schottky barrier makes transition metal silicides (TMS) one of the best options for spintronics and high-density magnetic recording media (e.g., bit-patterned recording) applications [9].

A silicide is a binary compound of silicon with a more electropositive element. Transition metal silicide (TMS) is a silicon compound with the electropositive element being a transition metal (TM). The mentioned applications of TMS would be only valid if their growth is feasible, i.e. they are both structurally and thermally stable. In the 20th century, most of the research done on silicides used powder metallurgical techniques for their growth [11]. High-quality crystalline growth has now become possible due to the development in bottom-up growth techniques like epitaxy. For a stable epitaxial growth of

a crystal, the lattice parameter should be in a close match to that of the substrate. Therefore, for the silicide to be epitaxially grown on a silicon substrate it must have a lattice parameter close to that of silicon. Also, the silicide formed should develop or sustain its magnetic nature for the potential applications. The three ferromagnets in the transition metal domains are Fe, Co, and Ni. These metals react with silicon to form many different thermodynamically stable equilibrium phases of various stoichiometry. Not all the equilibrium phases possess magnetic properties like their pure ferromagnetic metal. It is seen that for most of the phases observed, ferromagnetism is seen in phases which have an equal or higher atomic fraction of silicon in the compound [12]. In the past couple of decades, interest in binary iron silicide (FeSi_2) phases has significantly increased. The reported direct bandgap nature of $\beta\text{-FeSi}_2$ and its compatibility in silicon technology has drawn the attention of many researchers.

Most of the research done is focused on $\alpha\text{-FeSi}_2$ and $\beta\text{-FeSi}_2$ phases which are the only two stable bulk phases. These bulk phases have tetragonal and orthorhombic crystal structure which induces a significant amount of strain when deposited on the silicon substrate due to the lattice mismatch [13]. Recent discovery of $\gamma\text{-FeSi}_2$ and $s\text{-FeSi}_2$ which are metastable cubic phases grow with much smaller strain on silicon, which also have a cubic crystal [14]. The γ -phase have a better match with the silicon matrix and possess CaF_2 like lattice structure. The corresponding stable bulk phase is non-magnetic and the major difference in the two phases is the structure (fluorite for γ -phase and distorted fluorite for β -phase) [15]. Ferromagnetic material turns paramagnetic after a certain temperature called Curie temperature (T_c) and has a super para-magnetism (SPM) state under a certain

domain size called as the critical domain size. This is due to the increase of surface to volume ratio which increases the thermal influence on the materials. This is often seen in nanostructures where magnetic domains are not favored energetically, especially in single domain (single crystal) structures [5]. Tripathi *et al.* [16] observed ferromagnetic response of FeSi₂ nano-islands and nanowires. This phenomenon is often explained by researchers due to crystal discontinuity on surface, edges, or corners. But for small nanostructures, the islands mostly consist of a single domain. So, the possible cause for the magnetization would be from the structure itself i.e. from the core, interfacial edge (lattice mismatch), crystallite-surface or due to the surface edge. The thesis aims to figure out the factors contributing to the magnetism [17-20] i.e. interfacial [21], surficial and edge effects, for an ensemble of γ -FeSi₂ nanostructures. This thesis presents the first-principle modelling and magnetic calculations of γ -FeSi₂ bulk, epitaxial (i.e. thinfilm and nanoislands), and endotaxial (embedded diamond like) structures on Si (111) and Si (001) substrates. The calculations performed are used to investigate the emergent magnetic properties of the metastable phase. The calculations are performed using density functional theory (DFT) based software *Vienna Ab-initio Simulation Package (VASP)* and the visualization of the structures are done on a software by JP-Minerals - *Visualization for Electronic and Structural Analysis (VESTA)* [22].

1.2 Phases in iron di-silicide

Iron-Silicon binary system phases have a diverse application in electronic, optoelectronic, photonic, and spintronics field [1]. The phase diagram shown in figure 1.1 shows the iron-silicon binary system with some of their applications.

Figure 1.1: Iron-silicon binary system and their silicides with some functional properties for electronic, optoelectronics, photonics or spintronics [1].

The semiconducting phase of FeSi₂ has a band gap of 0.87 eV near room temperature (RT) i.e. at 300K. This is also favorable for optical fiber communication at 1.5μm wavelength. From the phase diagram FeSi₂ exists in two stable phases in bulk form, they are, metallic high temperature phase α -FeSi₂ (α -Fe₂Si₅ is present as α -FeSi₂ and ϵ -FeSi) above ~950°C and semiconducting β -FeSi₂ phase in ~ 500°C to ~900°C. The α -phase has a tetragonal crystal structure ($a = b = 2.684 \text{ \AA}$ and $c = 5.128 \text{ \AA}$) and the β -phase has an orthorhombic crystal structure ($a = 9.863 \text{ \AA}$, $b = 7.791 \text{ \AA}$, and $c = 7.833 \text{ \AA}$). Due to the advancement in bottom-up growth approach two metastable phases γ -phase and s-phase have been discovered. These phases have a cubic lattice structure which are only stable as thin epitaxial layers of thickness of a few nanometers. Due to the unstable nature and experimental difficulties, not much literature is there for these phases, especially for the s-phase. Information about the structures and properties of Fe-Si di-silicides is given in Table 1.1.

Table 2.1: *Stable and metastable (*) phases of iron di-silicide [6]*

Phase	Lattice Parameters(Å)	Lattice	Properties
α	$a=2.684, c=5.128$	Tetragonal P4/mmm	Metallic
β	$a=9.863, b=7.791, c=7.833$	Orthorhombic Cmca	Semiconducting
γ^*	$a=5.389$	Cubic (FCC) Fm3m	Metallic
s^*	$a=2.7$	Cubic (BCC) Pm3m	Metallic

The potential futuristic applications of the γ -phase phase have lured the researcher to study the phase despite the difficulties.

The γ -FeSi₂ structure has a fluorite structure like CaF₂. The fluorite like structures is also seen in other transition metal silicide like NiSi₂ and CoSi₂ [23-25], which are stable in the bulk form, unlike the γ -FeSi₂ phase. In the bulk form, orthorhombic structure of β -FeSi₂ is more stable and is often referred as the distorted fluorite structure. This stability can be understood by studying the electronic structure, which shows a high density of d-states (d-DOS), which leads to Jahn-Teller-like instability of fluorite FeSi₂. But when the phases are grown on a silicon substrate, there is additional instability due to the strain on the interface, which occurs because of the lattice mismatch of the two crystals. The lattice mismatch for the orthorhombic structure (β -FeSi₂) is quite high and puts a large amount of strain on the interface but for the cubic structure (γ -FeSi₂) the lattice mismatch is around 0.2% and thus increases the stability of the fluorite structure in the epitaxial. The stability of the system is maintained only for few nanometers ($\sim 50\text{\AA}$) after that the β -FeSi₂ bulk phase becomes more stable or rather, the γ -FeSi₂ becomes unstable and is transformed from cubic to orthorhombic structure.

Chapter 2

Theoretical Background & Computational Tools

2.1 Density Functional Theory (DFT)

2.1.1 Quantum Mechanics and the Schrödinger equation

The advancements of quantum mechanics in the 20th century and its confirmation done by experimental observations proved researchers its astonishing accuracy to predict various phenomena in the universe. Quantum mechanics can only be useful if one is able to solve the Schrödinger equation with significant accuracy. Schrödinger equation is a partial differential equation which describes the state of the quantum-mechanical system. A simple form of the Schrödinger equation is the time-independent nonrelativistic Schrödinger equation [16],

$$H\psi = E\psi \quad \dots \text{eq (2.1)}$$

Here, H is the Hamiltonian operator, and ψ is the eigenstates of the Hamiltonian. Eigenstates are the sets of the solution, ψ_n , for the eigenvalues of E_n , which is a real number. A Hamiltonian represents a physical system that is defined by the Schrödinger equation. For simple systems, e.g., Particle in a box or a harmonic oscillator, the Schrödinger equation can be solved exactly. But for most of the practical problems, the system is not as simple, and solving the Schrödinger equation exactly is almost impossible.

Consider an atom inside a crystal; to calculate the energy of the atom, one must define its state, and for that, the positions of its electrons and nucleus must be known. This energy

also depends on the positions of surrounding atoms, i.e., the positions of the surrounding electrons and nucleus. Therefore, change in position of the any electron of neighboring atom will affect the energy of the atom and thus the stability of the crystal. The complexity of the system can be reduced if we apply the Born-Oppenheimer approximation which separates the nuclei and electrons into two separate mathematical problems. The mass of the nuclei is extremely large compared to that of the electron. This implies that response to the change is much higher in electrons compared to that of the nuclei. In this manner one can first solve equation of motion of electrons considering the atomic nuclei positions fixed. This helps to find the states of the electrons for the system and the state which leads to the minimum energy of the system is called as the ground state.

Even the Born-Oppenheimer approximation simplifies the Schrödinger equation to a certain extent the equation remains enough complicated to be solved. The Hamilton consists of terms involving multiple electron-electron interactions, nuclei-nuclei interactions and electron-nuclei interactions. The Schrödinger equation in this case is given as [26],

$$\left[-\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N V(r_i) + \sum_{i=1}^N \sum_{j < i} U(r_i, r_j) \right] \psi = E\psi \dots \text{eq (2.2)}$$

Here, m is the mass of the electron. The first term in the bracket represents the kinetic energy of the electrons, the second term represents the electron-nuclei interaction and the last terms represents the electron-electron interactions. Ψ is the electronic wave function which itself is the function of the spatial co-ordinates of N electrons.

$$\psi = \psi(r_1, r_2, r_3 \dots r_N) \dots \text{eq (2.3)}$$

This wave function is often approximated as the product of individual electron wave function [26],

$$\psi = \psi_1(r)\psi_2(r) \dots \psi_N(r) \dots \text{eq (2.4)}$$

This reduces the degree of freedom of the wave function from N^3 to $3N$. This expression of the wave function is known as the Hartree product. Even though this approximation reduces the degrees of freedom significantly, it is simply not enough to practically solve the Schrödinger equation. A single molecule of CO_2 would require a 66-dimensional function (3 dimensions for each of the 22 electrons), and a nanocluster of 100 Pt atoms will require a function of more than 23,000 dimensions. Therefore, to further simplify the Schrödinger equation, more reasonable approximations must be introduced.

2.1.2 Inclusion of electron density.

The wave function from the Schrödinger equation cannot be directly observed. In principle, the quantity that can be measured is the probability of the electron being at a location. This probability is given by the product of complex conjugate of the wave function and the wave function [26].

$$P(r) = \psi^*(r)\psi(r) \dots \text{eq (2.5)}$$

ψ^* is the complex conjugate of wave function ψ , and $P(r)$ is the probability of finding the electron at r . In reality we cannot distinguish between two electrons and therefore its not practically possible to label electrons as $r_1, r_2, \dots r_N$. The more appropriate quantity to

represent the spatial position of electrons is the electron density $n(r)$. This can be expressed as [26],

$$n(r) = 2 \sum_i \psi_i^*(r) \psi_i(r) \dots \text{eq (2.6)}$$

Here, the summations is over all the wave functions which are occupied by the electron. $\psi_i(r)$ is the individual electron wave function located at a position r . The factor 2 is due to the fact that elections have up and down spins and Pauli's exclusion principle states that an individual electron wave function can only be occupied two different electrons provided they have different spins. The state of the system can now be represented by the density of electrons which is a physically observable quantity from the full wave function solution.

2.1.3 Fundamentals of DFT

Density Functional Theory (DFT) is based on two fundamental theorems proved by Kohn and Hohenberg and the derived equation by Kohn and Sham. The first theorem states that the ground state of *the ground state energy from Schrödinger equation is the functional of the electron density*. It says that the ground-state energy E of the system can be expresses in terms of the electron density function $E[n(r)]$ i.e. the ground-state energy is a functional of the electron density function. And thus, the theory gets the name as Density Functional Theory (DFT) This reduces the $3N$ degrees of freedom of the system to three spatial degrees of freedom.

Though the first theorem proves that the ground-state energy is a functional of the electron density, it doesn't give us any information about the functional itself. The second theorem

says that *the electron density that minimizes the density of the overall functional is the true electron density corresponding to the full solution of the Schrödinger equation.*

This now allows us to vary the electron density until the energy functional obtains a minimum value. This principle of varying the electron density to obtain the minimum energy functional is known as variational principle and is widely used to solve the Schrödinger equation.

The functional can be written in terms of a single electron wave function. Also, the energy can be seen as the contribution of the known and the unknown factors where, the unknown factors contribute all the other quantum mechanical effects which are missed. The energy functional can be expressed as [26],

$$E((\psi_i)) = E_{known}((\psi_i)) + E_{xc}((\psi_i)) \dots \text{eq (2.7)}$$

Here, E_{xc} is the unknown contribution to the energy functional and is known as the exchange-correlation functional. The known term is the contribution of electron kinetic energies, columbic interaction between electron and nuclei, interaction between electron pairs and interaction between nuclei pairs [26].

$$E_{known}((\psi_i)) = -\frac{\hbar^2}{m} \sum_i \int \psi_i^* \nabla^2 \psi_i d^3r + \int V(r) n(r) d^3r + \frac{e^2}{2} \iint \frac{n(r)n(r')}{|r-r'|} d^3r d^3r' + E_{ion} \dots \text{eq (2.8)}$$

The electron-electron interaction also includes the self-interaction as the total density includes all the electrons. This is one of the effects which is compensated in the exchange-correlation functional. Thus, the Kohn-Sham equations have the form [26],

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(r) + V_H(r) + V_{xc}(r) \right] \psi_i(r) = \varepsilon_i \psi_i(r) \dots \text{eq (2.9)}$$

Here, the first 3 terms in the bracket is the known functional and the last term is the exchange correlation functional. The main difference in equations 2.2 and 2.9 is the summation sign. The equation 2.9 is for single-electron wave function with only three spatial variables. The exchange V_{xc} can formally defines as the functional derivative of the exchange correlation energy [26].

$$V_{xc}(r) = \frac{\delta E_{xc}}{\delta n(r)} \dots \text{eq (2.10)}$$

This all circles up, meaning, to solve the Kohn-Sham equations one must have the electron density function and to get the electron density function one must know the single-electron wave functions, and to know the these one must solve the Kohn-Sham equations. And thus, the iterative nature of the solution comes to play. First one defines a trial electron density $n(r)$. Then the Kohn-Sham equations are solved using the trail electron density function and then the single-electron wave functions are obtained, $\psi_i(r)$. Now, the obtained wave functions are used to calculate the electron density, $n_{KS}(r)$, by using equation 2.6. If the obtained electron density equals the trial electron density, then the electron density is the ground state electron density of the system.

2.1.4 Exchange correlation functionals

To solve the Kohn-Sham equation one must know the exchange correlation functional. But we defined the exchange correlation functional as the contribution to the energy functional by all the unknown quantum mechanical factors. But from equation 2.10 we can define the simplest exchange correlation functional i.e. for the case of uniform electron density, $n(\mathbf{r})=\text{constant}$. Though this is not the case in real materials as the interesting material properties are due to the variations in electron density, it gives us an approximate solution to the Kohn-Sham equations. As this approximation uses the local density of electron this is called as the Local Density Approximation (LDA).

Various other functional has been developed and still the development of functionals which can solve the Kohn-Sham equations with minimum errors are important areas of active research. Another approximation which includes more physical information than the LDA and is commonly used is the generalized gradient approximation (GGA). As the nature of the included information can be different there are many GGA functionals developed. The LDA is only the functional of the local electron density whereas the GGA functional of the local as well as the gradient of the electron densities. This does not mean that GGA is a better approximation than LDA. There are several cases where LDA gives more reasonable results than GGA. The two most widely used GGA functionals are the Perdew-Wang functional (PW91) and Perdew-Burke-Ernzerhof functional (PBE). Use of GGA-PWE functionals have been done for the simulations performed for the thesis.

2.2 Computational tools

All the calculations are performed on Vienna Ab-initio Simulation Package (VASP) with projector augmented wave (PAW) pseudopotentials [27, 28]. The valence electron configuration $3d^64s^2$ is taken for the Fe atoms and the $3s^23p^2$ for the Si atoms. The calculations are based on density functional theory (DFT) in the generalized gradient approximation (GGA), where the exchange-correlation functional is chosen within the Perdew-Burke-Ernzerhof (PBE) parametrization. Throughout all calculations, the plane-wave cut-off energy was 500 eV, and the Gauss broadening with a smearing of 0.1 eV is used. The Brillouin-zone integration was performed on a different Monkhorst-Pack (MP) grid. All computation was done on Michigan Tech's shared high-performance computing infrastructure, *Superior*. Computing components, 85 CPU compute nodes - each having 32 CPU cores (Intel Xeon E5-2683 2.10 GHz) and 256 GB RAM - providing 91 TFLOPS. All the visualization and most of the construction of supercells is done on JP-Mineral's VESTA software.

Chapter 3

Results & Discussions

3.1 Bulk Structures.

3.1.1 Silicon, Iron and γ -FeSi₂ bulk structures

Silicon has a diamond like structure which belongs to $Fd\bar{3}m$ space group and has a face-centered cubic (FCC) Bravais lattice. Silicon is a non-magnetic material i.e., its spin moment (spin magnetic moment) is zero. The silicon diamond structure is shown in Figure 3.1.1. The lattice constant of the silicon structure is 5.431Å.

Figure 3.1.1: Ball and stick model of Si FCC structure. The axis *a*, *b* and *c* represent the (100), (010) and (001) plains respectively.

Iron has a body-centered (BCC) crystal structure at room temperature and belongs to $\text{Im}\bar{3}\text{m}$ space group. Iron is a ferromagnetic material and has a strong spin moment of $\sim 2.2 \mu_{\text{B}}$ in its bulk form. The BCC structure of iron is shown in figure 3.1.2

Figure 3.1.2: Ball and stick model of iron BCC crystal. The axis a , b and c represent the (100) , (010) and (001) plains respectively.

The $\gamma\text{-FeSi}_2$ structure is similar to that of the diamond structure of silicon and is the main reason for the epitaxial growth of the metastable phase on the silicon substrate. As mentioned in Chapter 1, $\gamma\text{-FeSi}_2$ crystallizes in the CaF_2 structure (space group $Fm\bar{3}m$), i.e., in a face centered-cubic (FCC) lattice with Fe atoms at the origin, and two Si atoms at positions $\pm \left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$ respectively. Each Si atom is tetrahedrally coordinated with four Fe atoms, and each Fe atom has eight Si nearest neighbors. One Fe atom in this crystal is

bonded to eight Si atoms i.e., Fe atoms has a co-ordination number of eight in this structure.

The structure for γ -FeSi₂ is shown in figure 3.1.3

Figure 3.1.3: Ball and stick model of γ -FeSi₂ where the golden ball represents the Fe atoms and the blue ball are the Si atoms. The axis *a*, *b* and *c* represent the (100), (010) and (001) plains respectively.

Each iron atom in the structure is surrounded by eight silicon atoms and thus in γ -phase the co-ordination number of iron is eight and the Fe-atoms are called 8-fold symmetric. The lattice constant for the possible bulk state of γ -FeSi₂ is calculated by curve fitting the free energies for a range of lattice parameters and taking the value corresponding to that of minimum energy. The K-space integration is carried using the MP grid, and the grid dimensions of 11x11x11 is used. Figure 3.1.2 shows the plot of Free energy versus the lattice parameter.

Figure 3.1.4: Plot of Free energy vs lattice constant. The lattice constant corresponding to the minimum energy is the equilibrium lattice constant.

The lattice constant obtained from the curve has the value of 5.392569Å. This value is the same as that of values reported in the literature. The lattice constant obtained here opens the possibility of seen magnetic properties due to the lattice parameter mismatch of γ -FeSi₂ and the Si-substrate. In the next two sections, experimentally observed structures are investigated using first principle modelling and simulations. The lattice constant is used to calculate the spin moment of the atoms. The average spin moment for the Fe atom from the bulk calculations is $\sim 0.17 \mu_B$, which is very weak. This weak spin moment observed in

the bulk form have made researchers to think about the reason behind the experimentally seen magnetism of its nanostructures.

3.2 Epitaxial Structures (Thinfilms and Nano-islands) on Si-(111) substrate

Most of research done on epitaxial iron di-silicide are for silicide which are grown on the silicon (111) surface. This is because of better lattice match of the Si (111) plane than other planes. The phase formation strongly depends on the growth conditions and the temperature. Many authors have shown several epitaxial phases on Si (111) surfaces by different growth techniques like, solid phase epitaxy (SPE) - i.e., a substrate is held at room temperature (RT) during Fe deposition, and subsequently annealed reactive deposition epitaxy (RDE) - i.e., a substrate is held at high temperature during Fe deposition and co-deposition of Si and Fe and other methods [29]. Section 3.2 and 3.3 investigates experimentally observed γ -FeSi₂ nano-islands by I. Goldfarb *et. al* [5] grown on Si-(111) and Si-(001) substrate.

The epitaxially grown thinfilms sustains the lattice constant of the substrate on which it is grown up-to few nanometers. The thinfilms and nano-islands structures modeled for calculations have a thickness of less than 2 nm and therefore, the lattice constant used for the epitaxial structures of γ -FeSi₂ is kept same as that Si-substrate which is 5.431Å. The structures are relaxed by allowing the γ -FeSi₂ layers and the top two Si- substrate layers to move freely.

3.2.1 Thinfilms

Before proceeding to the nano-wire calculations, magnetization is checked for the γ -FeSi₂ thinfilm. This can help to understand the difference in magnetic properties for a thinfilm which can be consider as an edgeless surface and a nanoisland/wire with edges. There are two possible cases for the epitaxial growth. The first, where the epitaxial growth is initiated by the iron atoms of the silicide structure which is known as the Fe-terminated interface and the second, where the growth is initiated by the silicon atoms of the silicide which is known as Si-terminated interface. Both structures are shown in the figure 3.2.2.

Figure 3.2.1: Ball and stick model of 2 layered epitaxial film of γ -FeSi₂ on Si (111) surface (a) Si-terminated interface (b) Fe-terminated interface. The golden ball represents the Fe atoms and the blue ball are the Si atoms.

The Si-terminated interface has maintained the co-ordination number for Fe atoms at the interface whereas, the Fe-terminated interface has a reduced co-ordination of 7 at the interface and thus have 7-fold symmetry. Calculations for both cases are done using the MP 11 x 11 x 1 grid. The calculations are performed until the force on the interface atoms

is less than 0.01 eV/Å. Each structure is modeled for two epitaxial layers of iron. The results show no magnetism for either of the structures. The Si-terminated interface is energetically favored over the Fe-terminated interface since the Fe-Si bond has is energetically more stable than the Si-Si bond. Therefore, all the further calculations of the epitaxial structures are performed for Si-terminated interface and also silicon terminated surface as the Si dangling bonds are more stable than the Fe ones. To confirm the obtained results, one more Fe layer is added, and the calculations are done for the Si-terminated interface. The 3-layered structure is shown in Figure 3.2.2

Figure 3.2.2: Ball and stick model of 3-layerd Si-terminated epitaxial film of γ -FeSi₂ on Si (111) surface.

The results remained same. No magnetism is seen even for the 3-layered Si-terminated structure. This implies, there is no magnetism for a film – an edge less structure. This is in accordance to the experimental observations. The free surface, interface and epitaxial strain do not contribute to magnetism of the thinfilm.

3.2.2 Nanoislands

The formations of γ -FeSi₂ nanoislands were reported in the paper by Dascalu *et. al* [2]. The islands were grown as γ -FeSi₂ (111) || Si (111) were formed with the top surface size of around 20 nanometers, the height of the island about 1.5 nanometers and the edge angles between 30° to 50°. The nanoislands and their measurements are shown in the figure 3.2.3

Figure 3.2.3: (a) scanning tunneling microscopy micrographs of the Fe @Si (111) SPE grown surface. (b) Line profiles from the ($\sqrt{3} \times \sqrt{3}$) island in (a) [2].

Growth of ferromagnetic γ -FeSi₂ and α -FeSi₂ are shown by I. Goldfarb *et. al* [5] and Dascalu *et. al*[3] respectively. Both the reference shows the growth of cubic iron di-silicide, FeSi₂(111) || Si (111), and their growth in (1-1 0) directions. Dascalu *et. al* [3] also shows the growth of the islands along (11-2) direction. The observed island by I. Goldfarb *et. al*[5] are shown in figure 3.2.3 and by Dascalu *et. al* [3] are shown in figure 3.2.4.

Figure 3.2.4: *Scanning tunneling microscopy micrograph of the final stage of the SPE experiment of α -FeSi₂ [3].*

Ab-initio calculations are performed for infinite nanoislands of γ -FeSi₂/ Si (111). Initially, calculation for $[1 -1 0]$ direction growth of nanoisland with angled edge of $\sim 55^\circ$ and $\sim 35^\circ$ on either side is performed. The K-space meshing is done using MP grid with dimensions of $1 \times 11 \times 1$. The modeled structure for this calculation is shown in Figure 3.2.5 along with the spin moment of contributing atoms. Calculations are also performed for monolayer and bilayer structures of nanoisland growth in $[1 -1 0]$ direction to check effect of the nanoisland height and step formation, this is shown in figure 3.2.6. Two cases are considered in the bilayer structure, step formation for either side of the edge. Further, calculations for nanoisland growth in $[1 1 -2]$ direction are performed, and the modeled structures and spin moments of atoms are shown in figure 3.2.7. The K-space meshing is done using MP grid with dimensions of $5 \times 1 \times 1$. Here, three different types of tapered edges are considered, $\sim 41^\circ$, $\sim 60^\circ$ and 90° . The structure is modeled considering unit cell of γ -FeSi₂ and Si having $[1 1 -2]$, $[1 -1 0]$ and $[111]$ as the a, b and c axis respectively.

Figure 3.2.5: γ -FeSi₂/Si (111) nanos island atomic structure and the calculated magnetic moments at the four edges. The substrate is considered till 6-Si layers.

The Fe atoms along the surface and 55° side are 7-fold symmetric whereas, on the 35° side are 6-fold symmetric. The overall magnetic moment of the structure is negligible. Not much can be answered regarding the magnetic nature observed in the experiments. So, the monolayer and bilayer analysis are performed. The slight magnetization is seen for the six-fold symmetric Fe atom at the interfacial edge ($0.15\mu_B$) and seven-fold symmetry Fe atom at the surface edge of the 55° angled side ($0.13\mu_B$).

Figure 3.2.6: γ -FeSi₂/Si (111) monolayer nanoisland relaxed for 6 atomic layer Si substrate

Table 3.2.1: Spin moments for Fe atoms of monolayer γ -FeSi₂/Si (111) nanoisland growth with 6-layered Si substrate in [1-10] direction.

Atom (Fe)	Spin moment (μ_B)
1	0.04
2	0.03
3	0.04
4	0.03
5	0.04
6	0.03
7	0.03
8	0.03
9	0.05
10	0.01
11	0.15

Data in figure 3.2.6 and table 3.2.1 shows magnetic moment observed for the edge atoms (Fe 1 & Fe 11) are almost same for the monolayer and the bottom most layer of the

nanoisland grown for the growth in $[1\ -1\ 0]$ direction. Magnetization for the other atoms is almost zero. The Fe11 atom shows small amount of spin moment, this may be due to the reduced symmetry from eight-fold to six-fold while for the other atoms its reduced from eight-fold to seven-fold. If the F11 atom was also made seven-fold symmetric the Si atom added to it will have 3 dangling bonds which not energetically favored over 2 Fe dangling bonds.

Figure 3.2.7: γ -FeSi₂/Si (111) bilayer stepped (left) nanoisland atomic structure for 6 atomic layer Si substrate.

Table 3.2.2: Spin moments for Fe atoms of bilayer stepped (left) γ -FeSi₂/Si (111) nanoisland growth with 6-layered Si substrate in [1-10] direction.

Atom (Fe)	Spin moment (μ_B)
1	0.40
5	-0.20
16	-0.01
17	0.12

Data in figure 3.2.7 and table 3.2.2 shows that the addition of one step on the 55° angled side does not affect the magnetism much. The overall magnetization for the structure still is negligible.

Figure 3.2.8: γ -FeSi₂/Si (111) bilayer stepped (right) nanoisland atomic for 6 atomic layer Si substrate.

Table 3.2.3: Spin moments for Fe atoms of bilayer stepped (left) γ -FeSi₂/Si (111) nanoisland growth with 6-layered Si substrate in [1-10] direction.

Atom (Fe)	Spin moment (μ_B)
1	-0.01
3	-0.02
13	-0.04
17	0.16

Data in figure 3.2.8 and table 3.2.3 shows that the addition of one step on the 35° angled side doesn't enhance magnetic moment in any of the atoms. The overall magnetization for the structure is again negligible.

Figure 3.2.9: γ -FeSi₂/Si (111) monolayer nanoisland atomic structure and the calculated magnetic moments for 7 atomic layer Si substrate in [1-10] direction.

The magnetization of the monolayer surface is tested for 7-layered Si substrate, 8-layered substrate and, 6-layer Si substrate with 7th layer of hydrogen atom. Slight magnetization is seen in the interface for substrate thickness is less than 6 Si layers. When the thickness of Si-substrate is further increased, magnetization of atoms at the interfacial edges diminishes and the results are consistent for more substrate having more than six Si layers. Therefore, the calculations performed after this are for structures having 7-layer Si substrate thickness.

From the results, growth of nanoisland in the $[1 \ -1 \ 0]$ direction shows negligible magnetic properties. This leads us to analyze the magnetic properties of nanoisland grown along the $[1 \ 1 \ -2]$ direction.

The density of atoms is high in the $(1 \ 1 \ -2)$ plane compared to $(1 \ -1 \ 0)$ plane. The supercell modeled for calculation of nanoisland growth in $[1 \ 1 \ -2]$ direction having 60° tapered edge is shown in figure 3.2.10. The obtained structure and spin moments is shown in figure 3.2.11.

Figure 3.2.10: γ -FeSi₂/Si (111) 60°-edged nanoisland modeled atomic structure on 7 atomic layer Si substrate in [11-2] direction.

Figure 3.2.11: γ -FeSi₂/Si (111) 60°-edged nanoisland relaxed atomic structure and calculated magnetic moments (μ_b) on 7 atomic layer Si substrate in [11-2] direction.

The relaxed structure shows the corner atoms have more displacement compared to that of other atoms. The 90° edge is energetically not favored but is only used to reduce the number of atoms and thus the computation time and power. The spin moment is highest for the corner atoms which also show highest displacement after relaxation and forms a curved surface (maybe to reduce the surface area of the atoms having fewer bonds). The

magnetization of $\sim 0.48 \mu_B$ is seen for the corner edge, which can be used to explain the observed magnetism in experiments. Further, the calculations are performed for the $\sim 41^\circ$ tapered

Figure 3.2.12: γ -FeSi₂/Si (111) 41° -edged nanoisland modeled atomic structure on 7 atomic layer Si substrate in $[11-2]$ direction.

Figure 3.2.13: γ -FeSi₂/Si (111) 41^0 -edged nanoisland modeled atomic structure and calculated magnetic moments on 7 atomic layer Si substrate in $[11-2]$ direction.

Again, after relaxation of the cell, the highest spin moment of $\sim 1.16 \mu_B$ is seen for the corner atom of the tapered edge. Also, the atoms near the curvature show considerable spin moments.

It can be clearly stated that the interface and bulk doesn't contribute to observed magnetization. Also, the nanoisland which is grown in $[1\ -1\ 0]$ direction does not show significant magnetism. The major magnetization seen is from the nanoisland growth in the $[1\ 1\ -2]$ direction. The highest spin moment is seen by the corner atoms of the top-most surface which tries to form a curvature when relaxed. This can be used to analyze the edges in nanoislands which are observed in experiments. The rise of magnetic moment is due to instability caused by reduced symmetry (from 8-fold to 7/6-fold) and uneven bond lengths due to atomic relaxation. The results obtained partially supports the hypothesis made in paper by I. Goldfarb *et. al.* [5] "Fe rim atoms generate the measured magnetic moments." The support is said to be partial because contribution of the magnetic moment is from the Fe rim atoms in the $[1\ 1\ -2]$ growth direction and not by growth in $[1\ -1\ 0]$ direction.

3.3 Endotaxial Structures (Diamond shaped nanoisland) on Si (001) substrate.

Apart from epitaxial growth on (111) Si plane, attempts were made to grow thinfilms of Si-(001) substrate. It is observed that along with the epitaxial growth of nanoislands and nanoislands, some of the atoms self-orient (SO) themselves and form embedded diamond-shaped structures known as endotaxial structures [30, 31]. The term "endotaxy" refers to the growth of precipitate phases in a bulk matrix, with coherent interfaces surrounding the precipitate. Interesting and useful structures can be formed by endotaxy, as in thermoelectric or magnetic systems. Endotaxy is similar to "allotaxy", a process in which crystals grow by annealing of implanted species[30]. Cobalt silicide endotaxial structure reported in the literature are shown in figure 3.3.1.

Figure 3.3.1: (a) Superimposed stereographic projection of CoSi₂ onto Si with zone axis (ZA): [110] and CoSi₂(001)//Si (001). (b) TEM cross-section image of a flat island with ZA: [110]. The angle of the interface, α , is measured for all interfaces and shown as a histogram plot in (c).[4].

Many experiments show the formation of endotaxial structures especially for CoSi₂ on the Si (001) substrate[4]. Iron di-silicide endotaxial structures are also observed experimentally. Most of the observed growth of these structures are reported as α -FeSi₂ phase on Si (011) substrate[6, 32]. But experimental observation of I. Goldfarb *et al.*[5] shows the formation of endotaxial structures of γ -FeSi₂ on Si (001) substrate. This is shown in figure 3.3.2.

Figure 3.3.2: The HR-TEM (phase contrast) cross-sectional images of the flat-top S1 and iron-silicide and the submerged part of the island [5].

Atomistic model is created for the diamond like embedded structure of $\gamma\text{-FeSi}_2 \parallel \text{Si} (001)$ similar to CoSi_2 structure shown in figure 3.3.1(a). The K-space meshing is done using MP grid with dimensions of $9 \times 1 \times 1$. Calculations are done for both the Si-terminated and Fe-terminated cases. The growth direction of the embedded nanoisland is $[110]$.

Figure 3.3.3(a): Modeled endotaxial Si-terminated structure of γ -FeSi₂/Si (001) nanoisland along [110] direction.

Figure 3.3.3(b): Relaxed endotaxial Si-terminated structure of γ -FeSi₂/Si (001) nanoisland along [110] direction.

Table 3.3.1: Spin moments for atoms of Si-terminated endotaxial structure γ -FeSi₂/Si (001) nanoisland grown along [110] direction.

Atom (Fe)	Spin moment (μ_B)
1	0.02
2	0.01
3	0.36
4	0.09
5	0.00
6	0.02
7	0.01
8	-0.01
9	0.34
10	0.01
11	0.34
12	0.01
13	0.00

For Si-terminated case, atoms along the [1-1-1] and [-11-1] interface are 7-fold symmetric and the Fe5 atom is 8-fold symmetric. For the Fe-terminated case the atoms along the interface are 6-fold symmetric and Fe4 (Fe-terminated) is only 5-fold symmetric. So, we can expect a higher surface contribution to magnetism in Fe-terminated case than the Si-terminated one.

Figure 3.3.4(a): Modeled endotaxial Fe-terminated structure of γ -FeSi₂/Si (001) nanoisland along [110] direction.

Figure 3.3.4(b): Relaxed endotaxial Fe-terminated structure of γ -FeSi₂/Si (001) nanoisland along [110] direction.

Table 3.3.2: Spin moments for atoms of Fe-terminated endotaxial structure γ -FeSi₂/Si (001) nanoisland grown along [110] direction.

Atom (Fe)	Spin moment (μ_B)
1	0.04
2	0.00
3	0.02
4	0.70
5	0.01
6	-0.04
7	0.00
8	0.10
9	-0.05
10	-0.02
11	-0.05
12	-0.02
13	0.10

The majority of magnetization seen in the Si-terminated endotaxial structure is from the core atoms. The magnetism seen in Fe-terminated structure is from the [110] direction edges along the γ -FeSi₂/Si (1-1-1) & Si (-1 1-1) interface. For the silicon terminated structure all the Fe atoms have 8-fold symmetry except the edge atoms (Fe8, Fe13) along the [110] direction, which are 7-fold symmetric which has six Si bonds in the iron silicide crystal and one bond to substrate Si. This may cause the edge to be squeeze as there are six bonds try to bring the edge inside and only one bond trying to pull it. This can cause compressive stress on the core atoms along the X axis direction and thus make them unstable enough to obtain high spin moment. If this is the case for a bigger model the magnetism will diminish as the stress would be distributed large number of atoms. For the

Fe-terminated structure the edge atoms (Fe8, Fe13 and Fe4) have 6-fold symmetry while the rest of the Fe atoms at the interface have 7-fold symmetry. The 6-fold symmetric atoms are more unstable especially the Fe4 atom which has the highest number of Si-bond with the silicon substrate and poses the highest spin moment. The second highest spin moment is seen in the other two 6-fold symmetric Fe atoms. This may explain the obtained spin moments of both the structures. As the structure is symmetrical, the magnetic moments are the same for the symmetrically oriented atoms.

The K-space meshing used throughout the calculations for epitaxial as well as the endotaxial nanoislands is in the form of $A \times 1 \times 1$ which is usually taken for calculations of one-dimensional structures. The usual form of meshing used for nanostructures on two-dimensional films is $A \times A \times 1$. Where A is an integer greater than 1 and it allows fine meshing along the structure's periodically repeated axis. This was chosen after comparing the results of some of the nanostructures (monolayer nanoisland along $[1 -1 0]$ direction and 41^0 - tapered nanoisland along $[11-2]$ direction) by considering both cases of K-space meshing. The results obtained from both cases remained almost the same. The consideration of reduced k-space mesh dimension significantly reduces the computation time and computational power. Since, most of the calculations involving around 70 atoms in the system require more than 3 weeks on 16 core system, for one-dimensional meshing, the consideration of two-dimensional meshing will take more than 4 weeks. For this reason, all the nanoisland calculations were performed using the one-dimensional meshing of K-Space.

Chapter 4

Conclusion & Future work

In conclusion, the experimentally observed magnetism of γ -FeSi₂ nanostructures do not have a single answer. The magnetism which is not seen in bulk form and the continuous thinfilm (edgeless structure) form is emerged in their nanostructures cannot be solely explained by interfacial or edge or bulk contributions. But we can safely say that the magnetism observed is not due to the epitaxial strain. For nanoisland edge along [1 1 -2] direction the results show high spin moments of atoms near the tapered side (41⁰ and 60⁰) in the (1 1 -2) plane and no magnetism from the interface. For the nanoisland edge along [110] direction, magnetism observed from the tapered side and interface is negligible and thus there is no magnetism. For the endotaxial structures, the Fe-terminated structure shows high spin moments along the interfacial edges along the [1-10] direction while the Si-terminated edges show high spin moments for atoms in the core (bulk atoms). The magnetism seen is due to the contribution of reduced co-ordination and local environment. Also, substrate thickness should be chosen carefully as the smaller thickness can show magnetism at the interface, as seen for the 6-layer Si substrate. For the structures in this thesis, the substrate thickness of the seven Si layers was enough. The modeled structures are small compared to the observed; this is due to the computational limit of DFT. Practically DFT can only be used for systems containing less than 300 atoms, and more the atoms higher is the computation time and higher the computational power. The addition of one extra atom can exponentially increase the computation time. Thus, different calculation approaches should be made for bigger structures.

The magnetic properties strongly depend on the tapered angle of the islands. A similar study can be performed to investigate the effects of a taper angle on the magnetism of the edge. The optimal angle for the highest magnetism and stability can thus be used to make nanoisland with better magnetic properties. There are many other nanostructures observed in the literature that can still be analyzed using DFT. Here, the epitaxial analysis is performed for only nanoislands edge along [1-10] and [11-2] direction, but other direction analysis can also be done. A similar model can be made for bigger endotaxial structures as the current model is comparatively small compared to the observed one and only used ~90 atoms. The limits of DFT is around 300 atoms. Other micromagnetic modelling techniques for continuum could be performed for bigger structures. Further, consideration of dipole-dipole interaction between two or more nanoisland can be done.

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Appendix

1. Unit cell orientation using VESTA

1. Use the simplest unit cell co-ordinate to model it. Here we use the iron silicon unit cell having $[100]$, $[010]$ and $[001]$ as the x, y and z axis respectively.

Figure A1: Simple unit cell as $[100]$, $[010]$ and $[001]$ as the a, b and c axis respectively.

2. Next make unit cell planes visible in the orientation you want to see (The directions along which the new orientation is periodically repeated). In this case we will have (110) , $(1-10)$ and (001) planes i.e. the a, b and c axis for the new orientation are $[110]$, $[1-10]$ and $[001]$ respectively.

Figure A2: *Planes for new orientation along the direction the new cell will be repeated.*

Here red, blue and yellow represents (110), (1-10) and (001) planes respectively.

3. Increase the boundaries in the a, b, c atleast 3 times and make the bonds invisible.

Figure A3: *Extended boundaries along a, b and c axis.*

4. Orient the structure approximately along one of the planes such that the other two planes look like lines perpendicular to each other. Then find the periodicity of the structure along the other two planes.

Figure A4: *Orienting along the desired planes.*

Make Parallel plane to the previous ones like in Figure A4 such that you create a unit cell (box) from the planes. Then remove all the atoms except the one in the box and on its edges. This will be the look of the newly oriented unit cell.

Figure A5: *Determining the periodicity along the new directions.*

5. Now using the co-ordinates of the atoms left we can get the rotation matrix and basis vector for our new structure (chose one atom and find the shift of origin and then get the basis vector for it).

Figure A6: *Newly oriented unit cell having $[110]$, $[1-10]$ and $[001]$ directions as a , b and c axis respectively.*

The case considered here is quite simple, but this technique can be used to model complex unit cells. Here, we can easily verify by using the 45° rotation for the current direction.

6. Heterogenous structures can be created by simultaneously modelling 2 structures in 2 tabs (using same scales) and then extracting the atomic position information from the individual model and combining them in one file.

Figure A6: *Heterogenous model.*

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