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RARE-EARTH SILICIDE NANOSTRUCTURE EPITAXIAL GROWTH AND CRYSTALLOGRAPHY

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RARE-EARTH SILICIDE NANOSTRUCTURE EPITAXIAL GROWTH AND CRYSTALLOGRAPHY

Ву

Gangfeng Ye

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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ABSTRACT

RARE-EARTH SILICIDE NANOSTRUCTURE EPITAXIAL GROWTH AND CRYSTALLOGRAPHY

By

Gangfeng Ye

This thesis focuses on rare-earth metal (RE) silicide nanostructures (nanowires and islands) epitaxially grown on Si(001) substrates. Gd, Dy and Tb are taken as prototypical silicide nanowire forming metals. Combined studies by scanning tunneling microscopy (STM) and transmission electron microscopy (TEM) reveal that RE silicide nanowires have the hexagonal crystal structure, and nano-islands have either orthorhombic or tetragonal structures. In the nanowires, there is a small lattice mismatch between the silicide and the silicon along the long axis, and a large mismatch across their widths. This observation confirms the commonly accepted growth mechanism that RE silicide nanowires are formed due to the anisotropic lattice mismatch between the silicide and the silicon.

Further analysis shows that the lattice parameters of the nanostructures do not significantly deviate from bulk silicide values. Hence, the strain between the silicide and the silicon due to lattice mismatch is accommodated by interfacial dislocations, which are observed. Furthermore, other strain accommodation mechanisms such as edge dislocations and stacking faults within the silicide, and nanostructure lattice tilting, are also observed.

Both the STM and TEM studies suggest the possibility of a phase transformation from the hexagonal to the orthorhombic/tetragonal phases (or nanowires to islands). The transformation appears to nucleate either at nanowire intersections or at the ends of isolated nanowires.

Sc silicide nanowire formation has also been studied. It is expected that Sc silicide nanowire growth will be distinct from the other RE metal silicides, since the anisotropy in the lattice mismatch between the hexagonal Sc silicide and the substrate is arranged in this way: the large lattice mismatch direction is along the a-axis and the small mismatch is along the c-axis, while, in case of other RE silicides, the large mismatch is along the c-axis and small mismatch is along the a-axis. TEM of the Sc nanowires shows that they are composed of two layers, with hexagonal Sc₃Si₅ at the silicide-silicon interface, and hexagonal Sc₅Si₃ on the top. The stabilization of the metal rich silicide phase is a unique feature of this system.

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Chapter 1 Introduction

Certain rare-earth (RE) metal silicides have been reported to self-assemble into nanowires on silicon [1-12]. These nanowires have some superior characteristics to those fabricated by conventional lithography techniques: they are small (5~8nm wide) and are single crystal with atomically flat surfaces. These nanowires have potential for application as nano-size interconnects. Furthermore, the RE silicides have very low Schottky barrier heights of 0.3~0.4 eV with n-type silicon [13, 14], which allows the silicides to form near perfect Ohmic contacts. Infrared detectors and photovoltaic devices can also be constructed due to the high barrier heights of 0.7~0.8 eV between the silicide and p-type silicon [14-16]. Because of this compatibility with the semiconductor fabrication process and the ability to form nanowires, the RE silicides have attracted significant interest.

However, the initial stages of silicide growth are very complicated. Other types of nanostructures, such as nano-size islands, also grow simultaneously with the nanowires, and several silicide phases with similar chemical stoichiometry may also contribute to the nanostructures formation. Hence, it is important to understand the fundamental issues surrounding nanostructure phases and growth mechanisms. This is the objective of the thesis. It is hoped that the results described here will help further the research and application of RE silicide nanowires.

A brief history of RE silicide nanostructures is given in this chapter, followed by the introduction of the current understanding of nanowire growth mechanisms that illustrate why RE silicides form nanowires on Si(001). Basic silicide crystallographic

information is given to support the fact that many RE silicides can form nanowires. At the end of this section, the current state of nanostructure research is reviewed.

1.1 Self-assembled rare-earth (RE) silicide nanowires

1.1.1 Discovery of self-assembled rare-earth (RE) silicide nanowires

DySi_{2-x} was the first RE silicide reported to form nanowires by self-assembly on Si(001) substrate, by Preinesberger *et al.* in 1998 [1]. This group demonstrated that, when deposited onto the Si(001) substrates at elevated temperature in a vacuum system, Dy reacted with Si to form a silicide, and the silicide grew into nanowires and/or islands under different growth conditions. One year later, the *New York Times* reported that a research group at Hewlett-Packard (HP) made a breakthrough in nanotechnology by growing 10 atom wide self-assembled Er silicide nanowires [17].

Chen *at al.* [2] and Nogami *et al.* [3] proposed that the RE silicide nanowires were formed because of the anisotropic lattice mismatch between the hexagonal form of the RE silicide and the silicon substrate [18]. They asserted that the silicide lattice parameter along one of the silicide axes matches that of Si, while there is a large lattice parameter difference between the silicide and the silicon along the perpendicular axis. Consequently, the silicide preferred to grow along the small lattice mismatch direction, resulting in the elongated nanostructures, or nanowires.

Besides Dy and Er silicides, many other RE silicides, such as Sm [5], Gd [4, 6, 7], Ho [3, 11, 19], Yb [12], Sc [4], and Y [20] silicides, were also reported to form nanowires on silicon substrates, as shown in Table 1.1. Note that Sc (#21 element in the periodic table) and Y (#39) are not the rare-earth metals, since lanthanides metals, La

(#57) through to Lu (#71), are considered to be typical rare earth metals. However, Sc and Y will also be included in the rare-earth metals in this thesis, since they are in the same Group III column as the lanthanides (see Table 1.1) in the periodic table, and their silicides have similar properties as the lanthanide metal silicides [18].

Table 1.1 Periodic tables of the elements. In the thesis, rare-earth metals (RE) refers as Lanthanides $(^{27}$ La through to 71 Lu), 21 Sc and 39 Y, as shaded in the periodic table; The RE which has been reported to be able to form nanowires are highlighted by bold font

² He	¹⁰ Ne	¹⁸ Ar	³⁶ Kr	⁵⁴ Xe	⁸⁶ Rn		
	$^{9}\mathrm{F}$	1 ⁷ CI	³⁵ Br	Iss	⁸⁵ At		
	°0	16S	³⁴ Se	⁵² Te	⁸⁴ Po		
	N	15P	33As	⁵¹ Sb	⁸³ Bi		
	°C	¹⁴ Si	³² Ge	⁵⁰ Sn	⁸² Pb		
	ξB	¹³ AI	³¹ Ga	⁴⁹ In	81TI		
			³⁰ Zn	⁴⁸ Cd	⁸⁰ Hg		
			²⁹ Cu	⁴⁷ Ag	nY ₆₄	¹¹¹ Rg	
			²⁸ Ni	⁴⁶ Pd	78Pt	¹¹⁰ Ds	
			27Co	⁴⁵ Rh	$^{\eta}\mathbf{Ir}$	¹⁰⁹ Mt	
			²⁶ Fe	⁴⁴ Ru	76Os	108Hs	
			²⁵ Mn	⁴³ Tc	75Re	¹⁰⁷ Bh	
			²⁴ Cr	⁴² Mo	W ⁴⁷	106Sg	
			²³ V	⁴¹ Nb	⁷³ Ta	¹⁰⁵ Db	
			²² Ti	⁴⁰ Zr	72Hf	$^{104}\mathrm{Rf}$	
			²¹ Sc	$\lambda_{6\epsilon}$	La	Ľ	
1	⁴ Be	¹² Mg	²⁰ Ca	³⁸ Sr	⁵⁶ Ba	⁸⁸ Ra	
H	³ Li	¹¹ Na	¹⁹ K	³⁷ Rb	55Cs	⁸⁷ Fr	

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E L	u 95	⁹³ Nn ⁹⁴ Pu ⁹⁵ A	⁹² U ⁹³ Np ⁹⁴ Pu ⁹⁵ A	⁹¹ Pa ⁹² U ⁹³ Np ⁹⁴ Pu ⁹⁵ A	⁹⁰ Th ⁹¹ Pa ⁹² U ⁹³ Np ⁹⁴ Pu ⁹⁵ A

1.1.2 Silicide nanowire formation: the role of anisotropic lattice mismatch

While many RE silicides form nanowires on Si(001), Gd silicide is considered as a prototypical example to demonstrate the nanowire formation due to the anisotropic lattice mismatch with Si(001) substrate.

The crystal structure of the hexagonal form of Gd silicide (GdSi_{1.6}) and a bulk terminated Si(001) plane are given in figure 1.1 [21]. The lattice parameters of the silicide are a=0.388 nm, and c=0.417 nm [18, 21], as indicated in the figure. The Si(001) surface has a periodicity of 0.384 nm along Si<110> directions. Hence, it is obvious that there is a large lattice mismatch (8.65%) between the c-axis of the silicide and the silicon. In contrast, the lattice mismatch between the a-axis of the silicide and the silicon is small (0.96%). Consequently, when the hexagonal Gd silicide is grown on Si(001), it is expected that the growth along the c-axis is restricted because of large lattice mismatch, while the silicide can grow freely along the a-axis (small mismatch direction). This results in the formation of nanostructures with large aspect ratios, or nanowires, with the long direction along the a-axis. A 100×100 nm size scanning tunneling microscopy (STM) image of GdSi_{1.6} nanowires grown on Si(001) is shown in figure 1.2. Note that the GdSi_{1.6} nanowires tend to cluster together, resulting in the formation of the nanowire bundles.

Many other RE silicides have been reported to form nanowires on Si(001). In these cases the silicides also have anisotropic lattice mismatches with respect to the Si substrates [18], suggesting that the mechanism of anisotropic lattice mismatch growth also applies more generally than the Gd silicide case.



Fig. 1.1 Fundamentals of how the hexagonal form of Gd silicide forms nanowires. (a) the hexagonal structure of the Gd silicide; (b) the Si(001) surface; (c) the formation of a nanowire: nanowire grows along the a-axis due to the small lattice mismatch, while there is a large lattice mismatch along the c-axis.



Fig. 1.2 STM image of Gd silicide nanowires grown on a Si(001) substrate. Nanowires tend to cluster to form nanowire bundles.

1.2 Background information on the RE silicides

Before going into depth concerning RE silicide nanostructures, it is important to gain an understanding of some of the fundamentals of the known bulk phases of the RE silicides. This section includes some phase diagrams, as well as crystallographic information such as crystal structures, lattice parameters, and lattice mismatches with respect to the Si(001) surface. Three major crystal structures, the hexagonal, orthorhombic, and tetragonal are discussed.

1.2.1 RE silicide phase diagrams

In this section, only the phase diagrams of Gd- and Sc-Si systems are presented (see figures 1.3 and 1.4) since the Gd and Sc silicide nanostructures are the primary subjects of the thesis. No comprehensive studies of the RE - silicon system have been carried out. Hence, the phase diagram information is very limited and results from different studies. Considerable uncertainty exists in these diagrams, as indicated by the large number of dotted solubility limits and poorly specified temperatures.

The Gd silicide phase diagram (figure 1.3) shows there are 7 phases. However, because only a small amount of the RE metals are evaporated onto Si substrates, and the substrate temperature is typically around 600°C (see Chapter 2.1), it is expected that silicides form on the Si rich side, where three phases with similar stoichiometry may be present. These phases are α GdSi_{2-x} (hexagonal AlB₂ type structure with 60~62% atomic percent of silicon and temperature < ~1000°C), α GdSi₂ (orthorhombic GdSi₂ type structure with 64~66.8% atomic percent of silicon and temperature < 400~500°C), and β GdSi₂ (tetragonal ThSi₂ type structure with 64~66.8% atomic percent of silicon and

temperature > $400 \sim 500^{\circ}$ C). Many RE-Si systems have similar phase diagrams as that of Gd with hexagonal, orthorhombic, and tetragonal phases being reported [22].

The Sc-Si system is relatively simpler, as shown in the figure 1.4. There are only three known phases, Sc_5Si_3 , ScSi, and Sc_3Si_5 . Among these phases, the formation of Sc_3Si_5 (or $ScSi_{1.6}$) is more favorable in a Si rich environment.



Fig. 1.3 Gd-Si phase diagram, after [22]. Shaded area in the diagram shows the possible phases in case of Si rich environment



Fig. 1.4 Sc-Si phase diagram, after [22]

1.2.2 Crystal structures, lattice parameters, and lattice mismatch

Similar with Gd-Si system, many other RE-Si systems have three phases near the same stoichiometry on the Si rich side of their phase diagrams [22]. These phases have the hexagonal, orthorhombic, and tetragonal structures.

These three phases are designated as RESi_{2-x} , with x=0 for the tetragonal structure, x=0.1~0.25 for the orthorhombic structure, and x=0.33 for the hexagonal structure. However, for convenience, all these silicides will be referred as RESi_2 for the remainder of this thesis, although the three crystal structures will continue to be distinguished. The hexagonal RESi_2 , which is able to form nanowires according to the anisotropic lattice mismatch growth model, has an AlB_2 type crystal structure and P6/mmm space group; the orthorhombic phase has a GdSi_2 type structure and space group of Imma; the tetragonal phase has a ThSi_2 structure and space group of I41amd. The crystallographic information of the three phases is summarized in Table 1.2.

The lattice parameters of these phases of variety of RE silicides are outlined in Table 1.3 [18], along with the lattice mismatches of the silicides with respect to Si<110> on Si(001), which has atomic spacing of 0.384 nm.

structure	prototype	space group	stoichiometry
hexagonal	AlB ₂	P6/mmm	RESi _{1.67}
orthorhombic	GdSi ₂	Imma	RESi _{1.75~1.9}
tetragonal	ThSi ₂	I4 ₁ amd	RESi ₂

Table 1.2 Crystallographic information of the hexagonal, orthorhombic, and tetragonal phases, after [18, 22]

Silicide	Structure	Lattice parameter (mismatch %)				
		a (nm) (%)	b (nm) (%)	c (nm) (%)		
Sc ₅ Si ₃	hexagonal Mn ₅ Si ₃	0.786 (101)		0.581 (51)		
ScSi	orthorhombic BCr	0.400 (4.1)	0.988	0.366 (-4.7)		
Sc ₃ Si ₅	hexagonal AlB ₂	0.366 (-4.7)		0.387 (+0.8)		
YSi _{2-x}	hexagonal AlB ₂	0.384 (+0.05)		0.414 (+7.9)		
	tetragonal ThSi ₂	0.404 (+5.2)		1.342		
	orthorhombic GdSi ₂	0.405 (+5.5)	0.395 (+3.0)	1.336		
LaSi _{2-x}	hexagonal AlB ₂					
	tetragonal ThSi ₂	0.430 (+12)		1.375		
	orthorhombic GdSi2	0.427 (+11)	0.418 (+8.9)	1.404		
CeSi _{2-x}	hexagonal AlB ₂					
	tetragonal ThSi ₂	0.419 (+9.2)		1.386		
	orthorhombic GdSi2	0.419 (+9.1)	0.413 (+7.6)	1.392		
PrSi _{2-x}	hexagonal AlB ₂					
	tetragonal ThSi ₂	0.422	(+9.9)	1.371		
	orthorhombic GdSi2	0.420 (+9.4)	0.416 (+8.3)	1.376		
NdSi _{2-x}	hexagonal AlB ₂	0.412	(+7.3)	0.444 (+16)		
	tetragonal ThSi ₂	0.411 (+7.1)		1.356		
	orthorhombic GdSi2	0.416 (+8.2)	0.412 (+7.4)	1.367		
PmSi _{2-x}						
SmSi _{2-x}	hexagonal AlB ₂	0.390 (+1.6)		0.421 (+9.6)		
	tetragonal ThSi ₂	0.408 (+6.3)		1.351		
	orthorhombic GdSi ₂	0.411 (+6.9)	0.404 (+5.1)	1.346		
	hexagonal AlB ₂					

Table 1.3 RE silicides lattice parameters and mismatches with respect to Si<110> on Si(001) (surface lattice period is 0.384 nm), after [18, 22]

~...

0.429 (+12)

1.366

EuSi₂

tetragonal ThSi₂

orthorhombic $GdSi_2$

Table 1.3 (continued)

Silicide	Structure	Lattice parameter (mismatch %)			
		a (nm) (%)	b (nm) (%)	c (nm) (%)	
GdSi _{2-x}	hexagonal AlB ₂	0.388 (+1.0)		0.417 (+8.7)	
	tetragonal ThSi ₂	0.410 (+6.8)		1.361	
	orthorhombic GdSi ₂	0.409 (+6.5)	0.409 (+4.4)	1.344	
TbSi _{2-x}	hexagonal AlB ₂	0.385 (+0.18)		0.415 (+8.0)	
	tetragonal ThSi ₂				
	orthorhombic GdSi2	0.406 (+5.7)	0.397 (+3.4)	1.338	
DySi _{2-x}	hexagonal AlB ₂	0.383 (-0.2)		0.412 (+7.3)	
	tetragonal ThSi ₂	0.403	(+5.0)	1.338	
	orthorhombic GdSi ₂	0.404 (+5.2)	0.395 (+2.9)	1.334	
HoSi _{2-x}	hexagonal AlB ₂	0.382	(-0.6)	0.411 (+7.0)	
	tetragonal ThSi ₂	0.396 (+3.2)		1.330	
	orthorhombic GdSi2	0.403 (+5.0)	0.394 (+2.7)	1.330	
ErSi _{2-x}	hexagonal AlB ₂	0.380	(-1.3)	0.409 (+6.5)	
	tetragonal ThSi ₂	0.396	(+3.1)	1.326	
	orthorhombic GdSi2				
TmSi _{2-x}	hexagonal AlB ₂	0.377	(-1.9)	0.407 (+6.0)	
	tetragonal ThSi ₂				
	orthorhombic GdSi2				
YbSi _{2-x}	hexagonal AlB ₂	0.378	(-1.5)	0.410 (+6.7)	
	tetragonal ThSi ₂				
	orthorhombic GdSi2				
LuSi ₂	hexagonal AlB ₂	0.375	(-2.4)	0.405 (+5.4)	
	tetragonal ThSi ₂				
	orthorhombic GdSi2				

1.2.3 The relation between the three major RE silicide crystal structures: the hexagonal, orthorhombic, and tetragonal structures

One of the objectives of the thesis is to identify the crystal structure of the nanostructures. Hence, it is important to know the differences between the hexagonal, orthorhombic, and tetragonal phases. Furthermore, since it has been observed that one type of nanostructure may transform to another one, the relationship between the three phases is critical to help us understand the phase transformations.

It is important to understand that the orthorhombic structure is very similar to the tetragonal structure, with only some slight differences in lattice parameters [21, 23]. This makes it very difficult to distinguish these two phases using transmission electron microscopy (TEM) approaches. Hence, these two structures will be referred as orth/tet, for much of the thesis.

Crystal structures of the hexagonal and orth/tet phases, together with the projections along different axes, are shown in figure 1.5. It is evident that some of the projections are different with others, which allows the hexagonal and the orth/tet to be distinguished in TEM. The hexagonal structure displays 6-fold symmetry when projected along the c-axis (or [0001] axis), and rectangular symmetries when projected along the $[2\overline{1}\overline{1}0]$ axis (a-axis) and $[0\overline{1}10]$ axis (this axis will be referred as the t-axis or top projection), as indicated in the figure. For the orth/tet structure, projection along the c-axis ([001] axis) shows a square or close to square (due to different lattice parameters in the a- and b-axes of orthorhombic structure) symmetry. In the orth/tet structure projections along a- or b-axes, there is a half unit plane shift on every two (001) planes, as indicated in figure 1.5. The t-axis projection of the hexagonal structure appears similar

to the c-axis projection of the orth/tet structure. Hence, the a-axis and c-axis projections of the hexagonal structure, and the a- or b-axis projections of the orth/tet structure can be used to distinguish the hexagonal and orth/tet structures.

Although it is clear that the hexagonal crystal structure is different from the orth/tet structure, these structures are closely related to each other, sharing a common structural unit. This structural unit is defined as "a parallelepipedic polyhedron with eight silicon atoms as apexes, and a rare earth atom at the center" shown in figure 1.6 [21]. Note that each corner Si atom is shared by 4 structural units, hence, the corresponding stoichiometry of the silicide is RESi₂. The sizes of the structural units for different structures differ slightly, due to slight lattice parameter difference between these structures. When the hexagonal and orth/tet phases are expressed in terms of multiples of the common structural unit (see figure 1.6), it is clear that the difference between the hexagonal structure and the orth/tet structure is that the stacking order of the rectangular subunits are different, as indicated in figure 1.6 [21]. The hexagonal structure has a simple ABAB...stacking order, whereas in the orth/tet structure, successive layers are stacked with shifts alternatively along the a- and b- axis ([100] and [010] axes), resulting in a ABCDABCD...stacking order.



Fig. 1.5 The crystal structures of hexagonal, orthorhombic and tetragonal phases, together with the projections along different axes. Hexagonal and rectangular symmetries are seen for the hexagonal structure projections; there is a half-unit shift along on every two horizontal atom lines in the orthorhombic and tetragonal phases.



Fig. 1.6 The difference of the hexagonal and the orth/tet structures. These structures are distinguished by the stacking order of the structural units: the hexagonal structure is stacked consistently along the a-axis, while the orth/tet structure is stacked alternatively along the a- and b-axes.

1.3 Literature review of RE silicide nanostructures grown on silicon surfaces

Many researchers have focused on the epitaxial growth studies of the RE silicides nanostructures (nanowires and islands), trying to understand the nanostructure crystallography and the growth mechanisms. Other efforts have focused on the electrical properties and the electronic structure of these structures.

1.3.1 Epitaxial growth studies of RE silicide nanostructures

Most of the prior experimental observations suggested that the self-assembled RE silicide nanowires are hexagonal [2-7, 9, 11, 23-30], which is consistent with the assumption that the nanowires are formed due to the anisotropic lattice mismatch between the silicide and the silicon [2, 3]. It has also been hypothesized that the silicide islands with lower aspect ratios have the orth/tet crystal structure [9]. However, no experimental results have been able to explicitly confirm these suppositions due to the technical difficulty in characterizing the small structures with dimensions of 10~100nm.

A range of variables have been studied in relation to the growth of these nanostructures. Silicon substrates with different indices such as Si(001) [3-9, 11, 12, 20, 23, 24, 26-35], Si(110) [10], Si(111) [36-38], Si(113) [39], and Si(5 5 12) [39], have been used to grow RE silicide nanostructures. In addition, different RE silicides have been grown to examine the impact of the magnitude and the direction of the lattice mismatch on the nanowire growth. A common element among these studies is the conclusion that the RE silicides form nanowires due to their anisotropic lattice mismatch, although He *et al.* demonstrated that the Dy silicide nanowire formation on Si(110) is related to the lowenergy coherent interface instead of anisotropic lattice mismatch [10]. Another variation in epitaxy studies was to grow parallel nanowires on vicinal Si(001) substrates [6, 25, 32]. Vicinal Si(001) is cut several degrees away from Si(001) plane and, hence, has a single-domain surface (see more details of vicinal Si(001) in Appendix A), which allows all the RE silicide nanowires to be grown and aligned in one direction. Hence, these studies show that the nanowire growth direction can be somewhat controlled by adjusting the substrate environment.

Another variable which affects nanostructure growth is the substrate temperature, since it affects the surface diffusion, activation barriers, and phase stability. Many reports show that the nanowires of most of the RE silicides will disappear and convert into more compact island shapes after annealing for a period of time (10~60min) [1, 3, 4, 10, 11, 20, 23, 26-30, 40]. However, there has been no systematic study of the impact of the substrate temperature on the nanostructure growth in many of these systems.

Harrison *et al.* have reported a Gd silicide nanostructure distinct from either nanowires or 3D islands using real-time STM imaging at elevated temperatures [24]. The new nanostructures have an elongated morphology, with "U" shape cross section, and grows perpendicular to the regular silicide nanowires. The formation mechanism of this nanostructure is remained unknown. However, Harrison *et al.* suggest that these new structures are composed of orthorhombic GdSi₂ according to Gd-Si diagram analysis. It was observed that these new nanostructures grow at the expense of the hexagonal nanowires, suggesting that the orthorhombic phase is more thermodynamically favorable than the hexagonal nanowires. This may also be inferred from the high congruent melting temperature of the orth/tet phase (see figure 1.3). However, the STM approach
does not allow the identification of different crystal structures, leaving considerable uncertainty in Harrison *et al.* conclusions.

Ohbuchi *et al.* used low energy electron microscopy (LEEM) to study the evolution of Dy silicide nanostructures grown on Si(001) [40]. It was observed that the 2×7 surface reconstruction of the Dy silicide is metastable, and will convert to 2×4 with 600°C annealing. The nanowires were observed to disappear during higher temperature (700°C) annealing, where islands formed. Hence, islands, which have smaller aspect ratios and are suspected to have orthorhombic or tetragonal structures, are more thermally stable than hexagonal structure.

Huang *et al.* conducted some preliminary research to establish a perfect anisotropic lattice mismatch growth system [41], which means zero mismatch in one direction and large mismatch in the perpendicular direction between the silicide and the silicon. They investigated ternary RE silicide systems, such as $(Er_{1-x}Gd_x)Si_{1.6}$ and $(Er_{1-x}Sm_x)Si_{1.6}$ (x=0~1). X-ray diffraction was used to measure the lattice parameters of the ternary RE silicides with different compositions. They "experimentally observed that solid solutions of $(Er_{1-x}Gd_x)Si_{1.6}$ and $(Er_{1-x}Sm_x)Si_{1.6}$ exist over the entire composition range between the respective binary end members and that the a and c unit cell parameters vary linearly with the mole fraction of $ErSi_{1.6}$ ". Hence, the small lattice a-axis mismatch of $ErSi_{1.6}$ (-1.30%) can be cancelled by that of GdSi_{1.6} (0.96%) or SmSi_{1.6} (1.64%), by mixing the two RE silicide in a proper mole fraction. Use of such ternary phases may lead to perfect nanowire growth along the nanowire length direction (or the a-axis). However, this study involved only the synthesis of bulk samples, and no epitaxial growth of nanostructures was done.

1.3.2 RE silicide nanostructure electrical and electronic properties

Preinesberger *et al.* used angular resolved photoelectron spectroscopy to study Dy silicide nanowires grown on vicinal Si(001), on which most of the nanowires are aligned along one direction [32]. This study demonstrated that there are two states crossing the Fermi level along the nanowire length direction, which strongly indicates that these nanowires have one dimensional metallic character. Yeom *et al.* also used angle-resolved photoemission to study the electronic band structure of similar Gd silicide nanowires grown on vicinal Si(001) [25]. Their results also showed that the nanowires are one-dimensional metallic as well, by demonstrating two fractionally filled bands passing the Fermi level, with the electrons in these two bands behaving similar to free electrons.

Masakazu *et al.* developed a multiple-probe STM to study the electrical conductivity of the RE silicide nanowires.[42] In this STM, independent STM tips were used as the contacts for a single nanowire by touching both ends of a single nanowire simultaneously, enabling the electrical conductivity measurement of a nanowire. For ErSi₂ nanowires, "ballistic conduction was observed at lengths less than about 500 and 20 nm at room temperature".

Transport measurements have also been conducted to evaluate the nanowire electrical properties, although not many results are published yet. Bennett *et al.* (Arizona State Univeristy) started to measure the electron transport properties of Dy silicide nanowires on Si(001) to determine "fundamental properties such as carrier density and scattering lengths, both coherent and incoherent" by 4 points measurement with nanowire contacts fabricated by e-beam lithography. Ohbuchi *et al.* (Michigan State University) used *ex-situ* four-terminal measurements to measure a nanowire network on Si(001) at

4.2K. Nemanich *et al.* (North Carolina State University) are trying to use scanning tunneling spectroscopy (STS) to measure the Dy and Er silicide nanowire properties.None of the transport measurements have shown results significantly different from what would be expected for the conductivity of the bulk RE silicides.

1.4 Research Objective

The ultimate goal of studies of self-assembled RE silicides nanostructure is to find applications in nano-devices and nano-size interconnects. However, this requires a thorough understanding of the silicide nanostructure structural properties and evolution mechanisms during epitaxial growth.

Explicit experimental identification of the crystal structures of RE silicide nanostructures (both nanowires and islands) are of great importance and will be studied in this thesis. This study confirms the supposition that RE nanowires growth is based on the anisotropic lattice mismatch between the silicide and silicon, establishing a solid base for further research.

The relationships between the morphology and the nanostructure crystal structures have also been investigated. Accurate nanostructure lattice parameter measurements allow development of an understanding of the impact of the magnitude and direction of the lattice mismatches on the nanostructure morphology.

Based on the association between the morphology and crystal structures, phase transformation mechanisms are explored since they allow us to understand the observed nanostructure phase change from one crystal structure to another. This understanding enables further investigation on controlled RE silicide nanostructure growth, aiming at possible engineering applications.

Chapter 2 Experimental Procedures and Methods

This chapter introduces the experimental procedures and methods used in this thesis. The overall experiment procedure is given at the beginning. After this, RE silicide nanostructures grown by vacuum deposition is detailed, followed by the introduction of characterization methods, such as scanning tunneling microscopy (STM) and transmission electron microscopy (TEM). Specialized techniques in TEM such as scanning TEM (STEM), nano-beam diffraction (NBD), moiré fringes, and fast Fourier transformation (FFT) image analysis, are also introduced. At the end, both Si(001) and vicinal Si(001) are introduced since both of them were used as nanostructure growth substrates in this research.

2.1 General experimental flow

The basic experiment procedure proceeded as follows: silicide nanostructures were grown on pre-cleaned silicon substrates by physical vapor deposition (PVD) in an ultra-high vacuum (UHV) system. After the growth, the samples were transferred to an STM chamber, without exposure to the atmosphere, for morphology study. After this, samples were exposed to atmosphere and prepared into TEM samples through a series of procedures (see section 2.3.2.1). The last step was the TEM investigation.



Fig. 2.1 Flow chart of the experiment procedure

2.2 Epitaxial growth of RE silicide nanostructures

RE silicide nanostructures were self-assembled on Si(001) substrates by depositing RE metals onto the Si(001) at elevated temperature in an ultra-high vacuum (UHV) system, as illustrated in figure 2.2. These RE silicide nanostructures were studied by STM and TEM after their growth.

The vacuum chamber used for deposition was a commercialized Omicron STM-1 UHV system, with a base pressure of $\sim 2 \times 10^{-10}$ torr. In such a vacuum, a clean Si(001) surface could be maintained for at least several hours before a molecule layer of residual gases, such as H₂O, CO₂, and H₂, in the chamber covered the surface. Although the pressure might reach 1×10^{-8} torr during the metal evaporation, it quickly dropped to $\sim 10^{-10}$ torr scale shortly after the evaporation was finished. RE metals, with purities of 99.9%, were purchased from Alfa-Aesar. The metal coverage and the deposition rate were calibrated by quartz-crystal monitor. The coverage was determined by timed exposure to the metal source. In this thesis, the coverage of the metal is expressed in the unit of monolayer or ML

$$(1ML = \frac{1}{(a_{Si(001)})^2} = \frac{1}{(0.384nm)^2} = 6.78 \times 10^{18} \text{ atoms/m}^2)$$
. The Si(001)

used as substrates had nominal orientations within 0.1° and had resistivities of less than 10 Ohm-cm, regardless of n-type or p-type. Vicinal Si(001) were obtained from Virginia Semiconductor and were cut 4° towards Si<1 $\overline{10}$ > away from Si(001). The substrates were pre-cleaned before the RE metal deposition by washing in acetone and isopropyl alcohol in ambient atmosphere, followed by flashing at temperature from 975°C to 1175°C in UHV to remove the surface oxide. The temperature of the substrates was measured by an optical pyrometer.

As illustrated in figure 2.2, the RE metal was placed in a tungsten wire basket in the vacuum system, and was sublimed when the basket was heated by passing a current through it. As the substrate was held at a high temperature, typically 600 ~ 650°C, the metal spontaneously reacted with the silicon in the substrate to form a silicide upon arrival. After the evaporation was finished, the substrate might undergo annealing depending on experiment design. The samples were cooled down slowly after the annealing to avoid substrate cracking due to thermal expansion before STM morphology investigation. All STM imaging was done at room temperature.



Fig. 2.2 Vacuum system setup for RE silicide deposition and STM characterization. RE metals are evaporated from heated tungsten wire basket and deposited onto Si(001) substrate at elevated temperature (600~650°C). The sample will be transferred to STM without air exposure for further morphology investigation.

2.3 Nanostructure characterization methods

2.3.1 Scanning tunneling microscopy (STM) and imaging

STM has been extensively used to obtain the atomic resolution images of the morphology and topography of RE silicide nanostructures, aiming at the determination of the nanostructure crystallography.

STM operation employs the principle of quantum mechanical phenomenon of electron tunneling. It is well documented that in a one-dimensional square barrier system, an electron with energy E_0 (lower than barrier height U_0) is able to tunnel through the barrier, as illustrated in figure 2.3(a), and the tunneling current penetrating the one-dimensional barrier is:

$$I \propto T = e^{-2\frac{\sqrt{2m(U_0 - E_0)}}{\hbar}L}$$
(2.1)

where T is the barrier transmission probability, L is the width of the barrier, U_0 is the barrier height, E_0 is the electron energy, m is the electron mass, and \hbar is the reduced Planck's constant (1.055×10⁻³⁴ Js).

The tip-sample setup in an STM is approximately a one-dimensional square barrier system, as shown in figure 2.3(b) and (c). Due to the bias between the tip and the sample, the Fermi energies of the tip and the sample differ. The electron density of states of the sample and tip within the different energy range, which is several eV typically, contribute to the tunneling current. The bent barrier due to the bias can be approximately treated as square barrier. Consequently, the tunneling current is exponential in the tipsample distance according to equation (2.1). Therefore, a significant tunneling current difference can be detected when the tip is over an atom or between the atoms, allowing spatial resolution at the atomic level to be achieved. The resolution of current STMs reaches 0.01 nm in the lateral directions, and 0.001 nm in the vertical direction, compared to the typical atom size of 0.3 nm.

The physical structure of an STM is shown in figure 2.4. A sharp metallic tip is placed on a XYZ piezoelectric scanner. Since piezoelectric materials deform predictably according to the applied electric field, a piezoelectric ceramics Z, together with a feedback system, is used to approach or retract the STM tip from the sample to keep the tip-sample distance in a proper range to collect tunneling current. Meanwhile, programmed voltage ramps applied to piezoelectric ceramics X and Y enable a scanner with integrated tip to scan over a selected area of the sample. A computer is used to control the motion of the piezoelectric ceramics and to reconstruct the morphology of the sample surface by collecting the tunneling signals vs. X/Y scanning positions.

STM have two working modes, constant current and constant height imaging modes. In the constant current mode, the piezoelectric ceramic Z adjusts the tip-sample distance to make sure that the tunneling current is constant. Hence the motion of the piezoelectric ceramic Z vs. XY scanning position allows the surface morphology information to be obtained. In the constant height mode, the piezoelectric ceramic Z does not move after approaching the tip to a proper tunneling position. The collected tunneling current varies at different area, and is used to reconstruct the sample morphology. All of the data in this thesis were acquired in the constant current mode.



Fig. 2.3 (a) shows a one dimensional square barrier system; (b) and (c) show the physical and electronic bands setup of the tip-sample system in an STM, which is also a one-dimensional barrier system



Fig. 2.4 Basic components of a scanning tunneling microscopy (STM)

2.3.2 Transmission Electron Microscopy (TEM) and imaging

Transmission electron microscopy (TEM) has been used for the characterization of the RE silicide nanostructures from both a morphological and a crystallographic point of view. This TEM work has incorporated functions such as scanning TEM (STEM), nano-beam diffraction (NBD), and energy dispersive X-ray spectroscopy (EDS or EDX).

In this section, the TEM sample preparation is first introduced, followed by the introduction of the techniques used in this study, including high resolution TEM (HRTEM), STEM, NBD, and moiré fringe imaging are discussed in detail.

2.3.2.1 Cross-section and plan view TEM samples preparation

Both cross sectional and plan view TEM samples were used in this study. Cross section TEM samples are sectioned perpendicular to an interface, allowing the nanostructures and substrate to be imaged side by side, as illustrated in figure 2.5. In contrast, plan view samples allow the TEM investigation with nanostructures superimposed on the substrate. Both cross sectional and plan view samples required the investigated areas to be thinner than 50 nm.

Cross sectional view TEM samples were prepared by following these steps [43]:

- Samples were cut into half, and then were glued face-to-face using G-1 epoxy (Gatan). The epoxy was cured by heating to 130°C for 10 minutes, using a hot plate.
- The samples were sliced into pieces, perpendicular to the interface, using an Accuton-5 diamond (Struers) microprocessor controlled wafering saw operated at 3000 rpm with 0.05mm/sec feeding speed. The slices ranged from 200 to 500 μm in thickness.

- 3. The slices were glued onto molybdenum (Mo) rings (Structure Probe) with G-1 epoxy (Gatan) by heating to 130°C for 10 minutes.
- 4. A sapphire plate (South Bay Technology) was glued to the other side of the Mo ring with mounting wax (Crystalbond) by heating to 130°C for 3 minutes.
- 5. The open side of the slice were ground and polished, using a series of (15, 6, 1, 0.5 μ m) diamond lapping films (Allied) until the slice thickness reached 50~100 μ m.
- 6. The area of interest was dimpled on the open side of the slice using a D500i Dimpler (VCR group). A 15.5 mm stainless steel dimpling wheels and 1 μm diamond slurry were used. The dimpling was finished when the thinnest area on the slice was ~15 μm.
- 7. The slice was removed from the sapphire plate by putting the slice assembly in the acetone for 2 hours to dissolve the mounting wax (Crystalbond).
- 8. The slice, together with the Mo ring, was ion-milled from either single or double sides in a precision ion polishing system (Gatan, M 691), until a small hole on the slice was obtained. The ion accelerating voltage is 4KV and milling angle was 3.5°.
- 9. The slice was cleaned by gently rinsing with ethanol, and dried in air.

These steps are illustrated in figure 2.5. The sample preparation procedure for plan view TEM samples is simpler and starts from step 3. The side with nanostructures should be faced towards the Molybdenum ring, and the samples were ground and polished from the other side of the sample. Similarly, during the ion-milling, only the milling on the side without nanostructures was allowed for plan-view samples. The procedure for plan view sample preparation is also shown in figure 2.5.



Fig. 2.5 The cross-section and plan view TEM sample preparation procedures.

2.3.2.2 TEM and incorporated functions

This section introduces several TEM techniques that were used to characterize RE silicide nanostructures in this study. These techniques included high resolution TEM (HRTEM), nano-beam diffraction (NBD), and moiré fringe imaging.

2.3.2.2.1 High resolution TEM (HRTEM)

HRTEM has been extensively used to obtain atomic resolution images of the RE silicide nanostructures and the morphology in relation to the substrates. The microscopes used were a JEOL JEM2200FS and a JEM2010F, each with field emission gun, operated at 200KV at Center for Advanced Microscopy, Michigan state University.

HRTEM images are phase contrast images. This contrast formation can be described in a quantitative way: the ability of a lens passing electrons is described as transfer function T, and was derived as (at the back focal plane of the lens) [44]:

$$T(\mathbf{u}) = 2A(\mathbf{u}) \left[\cos \chi(\mathbf{u}) + i \sin \chi(\mathbf{u})\right]$$
(2.2)

Where A is the aperture function, χ is the incident electron phase shift due to the sample, **u** is the lattice vector in the reciprocal space and i is the imaginary unit (i sin $\chi(\mathbf{u})$ stands for the damping effect). Plots of $\chi(\mathbf{u})$ vs. **u**, and T(**u**) vs. **u** are shown in figure 2.6. Large values of T(**u**) represents that the information with the specific **u** can be strongly transmitted. The best resolution that can be directly interpreted corresponds to the first zero point of T(**u**), or sin $\chi(\mathbf{u})$, which is called the Scherzer resolution, as indicated in figure 2.6. The transfer function could be optimized by balancing the effect resulting from spherical aberration against a particular defocus (Scherzer defocus) at

$$\Delta f_{\rm Scherzer} = -1.2\sqrt{C_s\lambda} \tag{2.3}$$

where C_s is the spherical aberration of the lens and λ is the electron wavelength. At this defocus condition, the electron beams have nearly constant transmission ability up to the Scherzer resolution, which is $0.66C_s^{1/4}\lambda^{3/4}$. This resolution is also referred as the instrumental resolution limit, corresponding to the best resolution can be expected. Both of JEOL JEM2200FS and JEM2010F, working at 200KV, have C_s of 0.5 mm, and hence, the theoretical point-to-point Scherzer resolution of 0.19 nm.

Due to the spatial coherence spread of the electron source and chromatic aberration, T(u) is damped, as shown in figure 2.6. It is evident that T(u) is not able to transfer any information with u larger than a specific value, which is referred as information limit, as indicated in the figure.

In this study, HRTEM image simulation is conducted by JEMS, developed by Pierre A. Stadelmann at Centre Interdisciplinaire de Microscopie Electronique.



Fig. 2.6 sin $\chi(\mathbf{u})$ vs. \mathbf{u} (without damping), and T(\mathbf{u}) vs. \mathbf{u} modified by damping envelope (dashed line); $\Delta f = -100$ nm, C_s = 2.2 nm.

2.3.2.2.2 Scanning TEM (STEM)

Scanning TEM (STEM), combined with energy dispersive spectroscopy (EDS), was used to obtain the high resolution species spatial distribution in the thesis. This technique allowed the determination if a nanostructure was oxidized due to the exposure to atmosphere in TEM sample preparation.

In a STEM, an electron probe is focused on the sample within a range of a few angstroms, and is scanned across the sample. As shown in figure 2.7, the transmitted electron beam, composed of electrons without interaction with the sample, is collected by a bright field (BF) detector. High angle scattering electrons are collected by dark field (DF) detectors. By scanning the electron probe laterally, step by step, over a selected area, sample images are obtained by relating the signals collected by detectors to the corresponding scanning position (X and Y). Combined with the species identification by energy analysis of the X-rays simultaneously generated from the probed point, STEM enables element mapping of a selected area with resolution ~0.1 nm.



Fig. 2.7 Schematic set-up for STEM imaging. Bright Field (BF) detector receives the transmission electrons at the center, while the dark field (DF) detector receives the high angular electrons.

2.3.2.2.3 Nano-beam electron diffraction (NBD)

Nano-beam electron diffraction (NBD) enables the collection of diffraction information from a very small area. In the crystallographic study the RE silicide nanostructures, NBD has been used to determine the epitaxial relationship between the silicide and silicon substrates.

In NBD, a third condenser lens (or the front pole piece of the objective lens) is used to form a spatially coherent electron beam with a diameter of ~50nm, which allows the illumination of very small areas [45]. Consequently, diffraction information is generated only from the illuminated area, typically a single nanostructure, without the assistance of apertures. Hence, NBD is a powerful tool enabling the investigation of individual nanostructures.

NBD is more valuable in studying the small objects with the size less than 100 nm. A comparison of NBD and the selected area diffraction (SAD) working set-up is shown in figure 2.8. SAD suffers from the significant information from areas surrounding the interested nanostructures, since a smallest selected area for a typical TEM is about 500 nm, while in NBD the smallest illumination size is ~50nm. Furthermore, due to the spherical aberration error and focusing error which is inherent in microscopes, the diffraction information may result from an area different from the selected area.



Fig. 2.8 Comparison of nano-beam diffraction (NBD) and the selected area diffraction (SAD). In NBD, electron illumination area on samples has a small diameter with width ~50nm. Hence, the diffraction information is from this area only. In the SAD, a large sample area is illuminated by incident electrons while the aperture excludes the diffraction information from non-interested area (which is also large). However, due to the inherent lens imperfectness, non-interested area may also contribute to the diffraction pattern in the SAD.

2.3.2.2.4 Moiré fringe imaging

Moiré fringe patterns were used to study the epitaxy of individual nanostructures due to their sensitivity to lattice mismatch between the moiré target (RE silicide nanostructures) and the moiré reference (silicon substrate) in this study [44].

Moiré fringes are formed by the interference between two patterns that have similar periodicities. Note that "similar periodicities" means three different situations. 1, translational moiré fringe: two patterns are parallel with each other with tiny difference in space frequencies; 2, rotational moiré fringe: two patterns have same space frequencies but not are aligned parallel; 3, mixed moiré fringe: both space frequencies and the orientation are different. These cases are shown in figure 2.9, with the reciprocal vectors representing the space frequencies and orientations shown below.

The geometry configuration between the silicide and the silicon sketched in figure 2.9(c) allows some relationships (equivalent with each other) between spacing of the mixed moiré fringe with other factors such rotation angle and lattice parameters to be derived:

$$D_{moire_fringe} = \frac{d_{silicide} d_{si} \cos(\alpha)}{d_{silicide} - d_{si} \cos(\theta)}$$
(2.4)

$$D_{moire_fringe} = \frac{d_{silicide}d_{Si}}{\sqrt{d_{silicide}^2 + d_{Si}^2 - 2d_{Si}d_{silicide}\cos(\theta)}}$$
(2.5)

$$D_{moire_fringe} = \frac{\sin(\alpha)}{\sin(\theta)} d_{silicide}$$
(2.6)

where $d_{silicide}$ and d_{Si} are the lattice periodicities of the silicide and the silicon viewed along Si[001], D_{moire_fringe} is the moiré fringe spacing, α is the rotation angle between the silicide moiré fringes and that of the silicon, and θ is the rotation angle between the silicide and silicon lattices.

In the experimental studies here d_{Si} is 0.192 nm (bulk silicon), and $d_{silicide}$, $D_{maine_{-fringe}}$, and the angle α can be measured accurately, calibrated by the silicon lattice, from the TEM images. Hence, the actual rotation angle θ between the silicide and the silicon can be calculated, which is very small and difficult to detect directly by TEM diffraction studies.



Fig. 2.9 (a) translational moiré fringe; (b) rotational moiré fringe; and (c) mixed moiré fringe. The vector A, B and M are the reciprocal periodicity vectors standing for the pattern A, pattern B, and moiré fringe.

2.4 Fast Fourier transform (FFT) and filter FFT imaging

Fast Fourier transform (FFT) has been used to measure the interplanar spacings of silicides in this study, and filtered FFT is used to increase the contrast of the moiré fringes versus the background. The FFT analysis softwares used in this study was Scion Image (Scion) and Digital Micrograph (Gatan).

FFT is able to extract spatial frequencies or periodicities of an arbitrary function. Figure 2.10 shows that the periodicity of a two-dimension, high-resolution TEM image of Si viewed along Si[110] is shown in the corresponding FFT pattern. The silicon FFT spots are use to calibrate the silicide lattice in this study.

Filtered FFT is to reconstructs an image from an FFT pattern, with non-interested periodicities information blocked. Hence, the contrast of the information with desired periodicities can be greatly enhanced in the image. Figure 2.11(a) shows an image of a vacuum system, and (b) is the corresponding FFT pattern. Figure 2.11(c) shows the same FFT pattern of (a) with the center information blocked (or filtered) by applying a high-pass mask. In this case, only the high periodicities information or fine structures of the image survives the reverse FFT and contributes to the image reconstruction, as shown in figure 2.11(e). In contrast, figure 2.11(d) shows the same FFT of (a) with high periodicities filtered by applying a low-pass mask. This allows the image reconstruction by reverse FFT with reduced intensity of high periodicity information, resulting in main characters significantly enhanced. This low-pass filtered FFT was used to remove the background noise from TEM images and enhance the main features.



Fig. 2.10 (a) High-resolution TEM image of Si, viewed along the Si[110]; (b) Corresponding FFT pattern of (a). Some of the Si planes are marked in the figures.



Fig. 2.11 (a) an arbitrary image; (b) FFT pattern of (a); (c) and (d) high-pass and low pass FFT patterns of (a); (e) and (f) high-pass and low-pass filtered FFT images. For high-pass filtered FFT image, only the fine structures are shown, while the low-pass filtered image deliver the main structures only.

Chapter 3 Gd silicide nanostructures grown on Si(001)

Gd is the 64^{th} element in the periodic table and is one of the rare-earth (RE) metals. Because the hexagonal form of Gd silicide (GdSi₂) has a lattice mismatch of 0.96% between the a-axis and Si<110> axes on Si(001) substrates, and a 6.8% mismatch between the c-axis and Si<110>, it has an anisotropic lattice mismatch with respect to Si(001), and is thus supposed to form nanowires.

Gd silicide nanostructures are studied by variety of methods in this chapter. Nanostructure surface structural and morphological information are collected by scanning tunneling microscopy (STM). Transmission electron microscopy (TEM) study provides the microscopic and crystallographic information. The primary result is that Gd silicide forms two classes of nanostructures: nanowires and islands. In addition, the crystal structure of the silicide is associated with the nanostructure morphologies, and an understanding of nanostructure evolution during growth and annealing is developed.

3.1 Experimental observations

3.1.1 STM observation of Gd silicide nanostructures

Figure 3.1 shows a typical STM image of Gd silicide nanostructures grown at 650°C on Si(001) with a metal coverage of 1.5ML and 20 min of post-deposition annealing at the growth temperature. In this image, the long, thin structures are nanowire bundles, composed of many single nanowires. The brighter (higher) nanostructures with smaller aspect ratios are islands. Typically, both nanowires and islands grow on Si(001) simultaneously under the regular evaporation procedure described in Chapter 2.1. However, higher coverage and longer annealing duration typically result in more islands.

Besides the nanostructures, there can be a wetting layer consisting of Gd induced 2x7 and 2x4 surface reconstruction covering the areas without nanowires and islands[24, 31, 35]. This wetting layer is not visible at the magnification shown in figure 3.1. This section focuses on Gd silicide nanowires and islands studied by STM.



Fig. 3.1 Morphologies of GdSi₂ nanostructures on Si(001) by scanning tunneling microscopy (STM). Both nanowires and islands are present.

3.1.1.1 Gd silicide nanowires

Figure 3.2 shows an STM image of Gd silicide nanowires, with 0.2ML Gd coverage grown at 600°C and no post-deposition annealing. This image shows that the Gd silicide nanowires always grow on a single Si terrace and do not cross the terrace edges. In some cases, terrace edges are observed to move, either expanding or yielding, to accommodate nanowire growth, as indicated in figure 3.2. The long axes of nanowires

run along Si< $1\overline{10}$ > directions. It should be pointed out that the islands, when present, often form at the intersections of the nanowires. This situation is usually observed on silicides samples with higher metal coverage, as shown in figure 3.3.



Fig. 3.2 GdSi₂ nanowires grown on Si(001) at 600°C with coverage of 0.2ML and no postdeposition annealing. A nanowire does not cross the terrace edge and always grows on single terraces. Si(001) terraces may yield and/or expand to accommodate nanowire



Fig. 3.3 GdSi₂ islands may form at the nanowire intersections. For this sample, Gd coverage is 0.9 ML, growth temperature is 600°C, and there is no post-deposition

In general, Gd silicide nanowires have large aspect ratios (>>10:1). Nanowires may reach up to several microns. The widths are quantized in multiples of the Si(001) surface periodicity ($a_{Si} = 0.384$ nm) and usually range between 2 ~ 6 a_{Si} . Nanowire heights are also quantized in steps of 0.35 ± 0.3 nm, which corresponds to one atomic layer of silicide. Single and double atomic layer nanowires are most common.

Gd silicide nanowires usually cluster to form nanowire bundles. Figure 3.4(a) shows an STM image of a nanowire bundle at high magnification. This figure also shows that the individual nanowires in bundles have different widths. Most of the nanowires in the bundles have constant widths along their length. An exception is shown in figure 3.4(b), demonstrating that nanowire width can also change. It is observed that the wider nanowires in nanowire bundles also tend to be the first to add an additional layer, as shown by the nanowires labeled a-d in figure 3.4(a). In most respects, the nanowire morphology is the same as that reported previously for Gd and other nanowire forming RE metals [2, 3, 6, 11, 23, 26].



Fig. 3.4 STM images of nanowire bundles. (a) shows that nanowires have quantized height of -0.35 ± 0.03 nm. The scattered bright features on the nanowire bundle are the second layer growth, which tends to happen on wider nanowires, marked as a-d. (b) shows that the width of nanowires can change.

3.1.1.2 Gd silicide islands

GdSi₂ islands are much wider (>10 nm) and higher (>5nm) than nanowires, and have smaller aspect ratios (< 1:10). Most islands are situated at the end of nanowires or at the nanowire junctions, as shown in figures 3.1 and 3.3, although islands can be isolated from nanowires.

The topography of a typical Gd silicide island is shown in figure 3.5. The inset shows a magnified view where a $c(2\times2)$ surface reconstruction is seen. This $c(2\times2)$ reconstruction is same as that previously reported for GdSi2 nanowires [25]. However, it is not possible to distinguish the orth/tet from the hexagonal silicide crystal by nanostructure top reconstruction, since these two structures have a common structural unit, as illustrated in figure 1.6.



Fig. 3.5 STM topography of a Gd silicide island. $c(2\times 2)$ topography reconstruction is observed

3.1.1.3 Gd silicide nanowire intersections

Neighboring terraces on Si(001) have perpendicular dimer row (see details in Appendix A). Since the substrate surface affects the nucleation, nanowires on neighboring terraces grow in perpendicular directions. Therefore, the nanowires from

neighboring terraces may intersect at terrace edges, as shown in figures 3.2 and 3.3.

Figure 3.6 presents typical examples of nanowire intersections. When two singlelayer nanowires (labeled as nanowire A and nanowire B) intersect, it is observed that there is a gap between the nanowires A and B, resulting from the registry of the atoms on different terraces. However, when a second layer is present as shown in figure 3.6(b), this gap is covered as the second layer of nanowire A (referred as A2) overgrows a portion of nanowire B (B2). When additional layers are added, the overgrowth of one nanowire on the other continues, as seen for the third and fourth nanowire layers in figure 3.6(c). Here, the third layer of nanowire A (A3) protrudes into nanowire B. However, the fourth layer of nanowire B (B4) grows on top of, but perpendicular to, A3 in turn. Thus, the growth of NW on NW appears to break down between the third and fourth layer of silicide, resulting in what appears to be interlocking layers.

At the same time, the strict quantization of silicide layer thickness breaks down when there are more than three silicide layers at the nanowire intersections. For the single-layer nanowires, the top surfaces of these two intersecting nanowires (A1, B1) differ by 0.14±0.02 nm, consistent with height of the Si terrace step. This is illustrated by the profile in figure 3.6(a). For double-layer nanowire intersections, the top of A2 is similarly 0.12±0.02 nm higher than B2. However, the profile in figure 3.6(c) shows that A3 and B3, although in perpendicular directions, are within 0.02 nm of each other. Also note that area B3 has no trenches separating this plateau into nanowires. Similarly no nanowire bundle trenches are observed for B4, which overgrows nanowire A. The compact, rectangular appearance of these upper layers is more akin to the larger silicide islands than to NWs.



Fig. 3.6 STM images of the nanowire intersections. In (a), a gap is observed between two single-layer intersecting nanowires; (b) is for double-layer intersecting nanowires, one nanowire is observed to overgrow the other; (c) is for multiple-layer nanowires, Small rectangular islands are formed at the nanowire intersection.

3.1.2 TEM observation of Gd silicide nanostructures

3.1.2.1 Cross-section TEM observation

Figure 3.7 shows a low magnification TEM image of a cross-section TEM sample of Gd silicide nanostructures. The nanostructures are located between the glue and Si substrate, as shown in this image. The Si<110> cross-sections place some nanostructures end on while others are nearly parallel with the foil, which allows the TEM study of the nanostructures in the two directions along the cross-section views.



Fig. 3.7 Low magnification cross-sectional TEM image of GdSi₂ nanostructures. The inset diagram shows how the islands are placed end on or parallel to the TEM foil.

Energy dispersive x-ray spectroscopy (EDS), combined with scanning transmission electron microscopy (STEM), was used to map the chemical composition distribution of TEM samples. A fine focused electron beam was scanned over a selected area including nanostructures as shown in figure 3.8, and the emitted X-rays were collected simultaneously for EDS analysis. EDS atomic mappings are also shown in figure 3.8. It is evident that Gd distribution matched the nanostructure locations in the image. Oxygen mapping suggests that the nanostructures are not fully oxidized since oxygen is distributed rather uniformly along the interface as would be consistent with the oxidation of the surface of the TEM sample.



Fig. 3.8 EDS mapping of $GdSi_2$ nanostructures in cross-sectional sample. The gadolinium (Gd) and oxygen (O) distributions of the area marked by the box in the image are listed on the right.

Cross-sectional TEM of the Gd silicide nanostructures revealed three types of atomic arrangement involving three variations in stacking of the closest packed plane, as shown in figure 3.9. The inset fast Fourier transform (FFT) patterns in the figure include information from both the Si substrate and the silicide nanostructure, allowing accurate silicide interplanar spacing measurements, calibrated against the spots from the silicon substrate lattice.

Figure 3.9(a) shows a nanostructure with a hexagonal arrangement of atoms, resulting from ABAB...stacking of the silicide planes. This stacking order is consistent with the projection of the hexagonal GdSi₂ along the c-axis, as shown in figure 1.5(a). The hexagonal silicide ($2\overline{110}$) planes run perpendicular to the Si/silicide interface, and have an interplanar spacing, measured from the FFT, of 0.19 nm (measurement error is about 0.005 nm), which corresponds to a lattice parameter of a=0.38 nm. This value is

very close to the Si(110) interplanar spacing of 0.384 nm and the bulk $GdSi_2$ lattice parameter of 0.388 nm. No visible interface strain or dislocations were found between the silicide and the substrate in this view.

The GdSi₂ nanostructure shown in figure 3.9(b) displays rectangular symmetry (AAA...stacking), which corresponds to the hexagonal structure viewed along the a-axis (figure 1.5(a)). For such nanostructures, the GdSi₂(0001) interplanar spacing obtained from the FFT is 0.41 ± 0.01 nm, close to the lattice parameter of the bulk hexagonal silicide c=0.417 nm. A Burgers circuit encompassing the interface shows that there are ~9 silicide planes when there are ~10 silicon planes. Hence, interfacial dislocations are present to accommodate the lattice mismatch.

Figure 3.9(c) shows a third lattice stacking variant (AABBAABB...stacking), with a half atom column shift observed on every other two horizontal atom rows. This stacking is consistent with the orth/tet crystal structure viewed along either the *a* or *b* axes (figure 1.5(b)). The lattice parameter a (or b) obtained from the FFT is 0.40 ± 0.01 nm, while the lattice parameters of bulk orthorhombic GdSi₂ are 0.401 nm and 0.409 nm (0.410 nm for tetragonal). The Burgers circuit in this figure shows that there are ~9.5 silicide planes on every ~10 silicon planes, indicating that interfacial dislocations exist between the silicide and the silicon.

According to the analysis above, the $GdSi_2$ nanostructures can take up either the hexagonal or orth/tet crystal structures. The measured lattice parameters of the $GdSi_2$ nanostructures do not deviate significantly from the bulk silicide values. Therefore, $GdSi_2$ nanostructures have similar lattice mismatches as those of bulk materials with respect to silicon.



Fig. 3.9 Cross-sectional high resolution TEM images of $GdSi_2$ nanostructures. (a) is identified as the hexagonal phase viewed along the c-axis, (b) is the hexagonal phase viewed along the a-axis, and (c) is the orthorhombic or tetragonal phase viewed along the a- or b-axis. Insets are the corresponding FFT patterns.

3.1.2.2 Plan view TEM observation

A typical plan view TEM image of Gd silicide nanostructures grown on a Si(001) substrate is shown in figure 3.10. Just as in the observations by STM in figure 3.1, both nanowires and islands are present in this image. In this section, moiré fringe analysis and nano-beam electron diffraction (NBD) patterns of single nanostructures are reported.



Fig. 3.10 Morphologies of $GdSi_2$ nanostructures on Si(001) by transmission electron microscopy (TEM). Both nanowires and islands are present.

3.1.2.2.1 Moiré fringes

If there is no rotation between the silicide and the substrate along the Si(001) axis,

the moiré fringe spacing formula (equation 2.3) can be simplified as:

$$D_{moire_fringe} = \frac{d_{GdSi2}d_{Si}}{|d_{Si} - d_{GdSi2}|} = \frac{d_{GdSi2}}{mismatch}$$
(3.1)

where $D_{moire_{frigge}}$ is the moiré fringe spacing, d_{GdSi2} is the interplanar spacing of Gd silicides, and d_{Si} is the interplanar spacing of Si(200) planes, which is 0.192 nm.

Table 3.1 lists the moiré fringe spacings for the hexagonal, orthorhombic, and tetragonal phases calculated using equation 3.1 (based on bulk silicide lattice parameters and no rotation). According to Table 3.1, the moiré fringe spacing of the hexagonal phase along the large mismatch direction (c-axis) is 2.4nm, while that of the same phase along the small mismatch direction (a-axis) is much larger at 20.1nm. Hence, the moiré fringe patterns from the hexagonal phase nanostructures should have very large aspect ratios, appearing stripe-like. This appearance is observed experimentally and is shown in figure 3.11(a), where fine, long fringes running from the bottom left to the upper right, run perpendicular to coarse, short fringes. In contrast, the moiré fringes for the orth/tet structure (having similar mismatch along the two perpendicular Si<110> directions) should have a much smaller aspect ratio and appear mesh-like. This type of fringe pattern is observed and shown in figure 3.11(b).

Although similar fringes may arise from an interfacial dislocation network within the GdSi₂, no such uniform arrangement of dislocations was observed in cross sectional TEM. In addition, the average dislocation spacings predicted from the lattice mismatch are also different from the measured fringe spacings. For example, along the c-axis of the hexagonal structure, there is a dislocation spacing

$$D_{dislocation} = \frac{d_{Silicide(200)}}{mismatch} = \frac{0.417nm}{8.7\%} = 4.8nm$$
, while the moiré fringe spacing is

$$D_{moire_fringe} = \frac{d_{Si(220)}d_{silicide(200)}}{d_{silicide(200)} - d_{Si(220)}} = \frac{0.192 \times 0.209}{0.209 - 0.192} = 2.40nm$$
, which is consistent with

the observed value of 2.1~2.6 nm, as listed in Table 3.1. Hence, both the experimental observation in cross-section TEM, and the measured fringe spacings suggest that the fringes are moiré fringes, instead of resulting from an interfacial dislocation network.
Table 3.1 Comparison of the calculated and measured moiré fringe spacings of $GdSi_2$ on Si(001). The calculated spacings are based on bulk lattice parameters and zero rotation between the silicide and the silicon.

structure	calculated fringe spacing (nm)			measured fringe spacing (nm)			
	а	b	с	а	b	с	
hexagonal	82		2.8	>90		2.4~3.2	
tetragonal	4.1	4.1		3.2~6.9			
orthorhombic	3.9	7.2					

In the FFTs in figure 3.11, Si<220>, GdSi₂, and the moiré fringe spots are evident. The real space spacings of the silicide and moiré fringes can be obtained from the corresponding FFT spots calibrated with Si<220> spots. Note that the FFT spot measurements were reproducible with an error of 0.5%, resulting in a cumulative measurement error of ~1%. The average spacing of the stripe-like fringes in figure 3.11(a) was determined to be 2.5 nm, while that along the long axis was 9.3 nm. Based on these measurements, the corresponding lattice parameters, calculated by equation 3.1, are 0.417 nm (8.7% lattice mismatch with silicon) and 0.393 nm (2.3% mismatch), respectively. These values are consistent with those measured through calibrated silicide lattice spots in FFT, which give lattice parameters, 0.419 and 0.393 nm, respectively. The moiré fringe spots in the FFTs of the NWs are elongated perpendicular to the nanowire long axis. This indicates that the lattice is non-uniformly strained along this direction (with local mismatch measured from the FFTs varying from 7.3% to 9.9%).

The moiré fringes shown in figure 3.11(b) have a mesh-like appearance. The similar moiré fringe spacing in the two perpendicular Si<110> directions, measured as 3.8 and 4.0 nm, suggest that the island is tetragonal. In many other cases, the fringe spacing is more anisotropic. The fringes in the "L" shaped island in the figure 3.12 have

spacings of 3.0 and 4.4 nm on one leg, and 4.6 and 3.4 nm on the other leg, suggesting orthorhombic symmetry. However, at the junction of the legs, the moiré fringe spacing is 3.8 and 3.8 nm, suggesting tetragonal symmetry. In fact, as mentioned in section 1.2.3, the orthorhombic phase has same crystal structure as that of the tetragonal phase except slight difference in lattice parameters (orthorhombic: a= 0.409 nm and b= 0.401 nm; tetragonal: a=b=0.410 nm). Hence, these two phases can form coherent joints with the aaxis of orthorhombic phase matching with the a- or b-axis of tetragonal phase. In 40 islands sampled, the islands with more isotropic moiré fringes typically had aspect ratios of less than 1:2, while islands with larger aspect ratios typically displayed more asymmetric moiré fringes. This suggests that the somewhat more anisotropic lattice mismatch of the orthorhombic phase may lead to larger aspect ratio islands, while the lack of anisotropic lattice mismatch of the tetragonal phase will result in more symmetric islands.



Fig. 3.11 Plan view TEM shows both stripe-like and mesh-like moiré fringe patterns are present, as shown in (a) and (b), respectively. Insets are the high-resolution images. The corresponding FFT is displayed at the right side of the images. The insets in FFTs represent the magnified areas with contrast enhanced.



Fig. 3.12 A "L" shape nanostructure with the anisotropic moiré fringe spacings on both legs and isotropic spacings at the junction. The spacings are indicated.

The overall conclusion of the moiré data is that nanowires have the hexagonal crystal structure and islands have the orth/tet crystal structure. More than 95% of the stripe-like moiré fringe patterns were observed for nanowires. In the few cases where stripe-like fringes were observed on low aspect ratio nanostructures, these nanostructures might have corresponded to incompletely formed nanowires. More than 95% of the mesh-like patterns were found for islands, while the exceptions (mesh-like fringes are seen on an island with aspect ration larger than 10:1) are not understood at this point. An example of the exception is shown in the figure 3.13, showing a rare exception: a mesh pattern on an island with a greater than 10:1 aspect ratio. This might correspond to the

elongated islands that Harrison and Boland observed at higher annealing temperatures; in their paper, they assume that some of their elongated islands are the orthorhombic silicide phase. Under the experimental conditions used here (growth and annealing at up to 650°C), such islands are very rare.

In many cases, the moiré fringes gradually rotate along the length of the nanowires. Such a nanowire is shown in figure 3.14. With the observed local fringe rotations of 2.3°, 5.3°, and 9.5° as indicated in this figure, equations 2.5 allows the rotation of the silicide lattice with respect to the Si substrate to be calculated as 0.22°, 0.52° and 0.93°. Indeed, the moiré fringes for the nanowires display significant numbers of edge dislocations, each of which will correspond to a silicide lattice edge dislocation, as shown in the inset. Moiré fringe rotation and dislocations were also observed on the orth/tet islands, as shown in figure 3.15, although less severe than that observed in the hexagonal nanowires. This may be a result of a smaller mismatch (4.43%–6.77%) in the orth/tet than the large mismatch (8.65%) along the c-axis of hexagonal nanowires.



Fig. 3.13 Mesh-like moiré fringes found on elongated islands in some rare cases.



Fig. 3.14 Moiré fringe rotation with respect to the nanowire. The inset shows the FFT filtered image from the selected area, demonstrating the fringe dislocations.



Fig. 3.15 Moiré fringe rotation and dislocations are observed on an orth/tet island.

The moiré fringes also showed coexistence of the hexagonal and orth/tet silicide phases within nanostructures. This was observed in nanostructures with dumbbell shapes: long, thin stripe terminating with rectangular or square nanostructure on both ends. Such complex nanostructures are commonly observed, as shown in figure 3.16(a). Figure 3.16(b) shows a plan TEM image with one end of such complex. According to the moiré fringe analysis shown above, the rectangular or square nanostructures at the ends were identified as having the orth/tet structure, while the stripes between the ends were hexagonal. Considering the nanostructure density in the figure, the probability that a nanowire connects an island at each end during the nanowire growth is very low, and, further more, such dumbbell shape nanostructure complex are fairly common, as shown in figure 3.16(a). Therefore, the nature of the dumbbell shape nanostructures suggests the possibility that the hexagonal phase is able to transform to the orth/tet phase.



Fig. 3.16 Dumbbell shape complexes (long, thin strip terminated by rectangular nanostructures on both ends) are observed, as pointed by arrows in (a). (a) presents a low magnification AFM image, showing that such complexes are common; (b) is a TEM image showing one end of such complex with moiré fringes present. The end of the dumbbell complex has a mesh-like moiré fringe (orth/tet), while the strip has stripe-like moiré fringe (hexagonal).

3.1.2.2.2 Nano-beam electron diffraction (NBD)

This section presents the diffraction information collected from single nanowire and islands, by nano-beam electron diffraction (NBD).

Figures 3.17 (a) and (b) show a nanowire and an island, respectively, illuminated with a small diameter electron probe (~150nm). In these images, moiré fringes are clearly visible. Figures 3.17 (c) and (d) show the corresponding NBD patterns. Although these two NBD patterns resemble each other, a subtle difference of the diffraction spots is found, as indicated on the patterns. For the nanowire, the GdSi₂ diffraction spots perpendicular to the long axis sit inside of the silicon spots, (measured as a large lattice mismatch of 9.3% with respect to the silicon), while a much smaller mismatch is evident along the long axis. In contrast, an apparent mismatch exists in both Si<110> directions for the island, measured as 6.9% and 5.6%, respectively. All these mismatches are consistent with those between Si and bulk hexagonal or orth/tet phases (see Table 1.3) and are also consistent with the experimental results from moiré fringe analyses (section 3.1.2.2.1). Combined with the previous cross-sectional TEM observations that the lattice parameters of $GdSi_2$ nanostructures do not significantly deviate from the bulk materials, it can be concluded that nanowires form with the hexagonal phase, with the small lattice mismatch direction (a-axis) along the nanowire long axis, and the islands display orth/tet crystal structure.



Fig. 3.17 Comparison of the nano-beam electron diffraction (NBD) patterns of a nanowire and island. (a) and (b) show the nanowire and island studied, with moiré fringes evident; (c) and (d) shows the corresponding NDB patterns. The nanowire has anisotropic silicide diffraction dots while those from the island are isotropic.

3.1.3 Gd silicide controlled growth

In general, "the challenges for self-assembled silicide nanowires are the control of aspect ratio and location. [46] " However, in the case of RE silicide nanowire growth, more than one type of nanostructures, involved more than one polytype of the silicide, can grow on Si(001). Hence, another fundamental issue is the controlling of nanostructure categories, which are associated with the silicide phases. In this section, preliminary research result is presented on the control of island vs. nanowire growth.

It was found that the metal evaporation rate and coverage play important roles in determining the formation of different nanostructure types. Figure 3.18 shows the relationship between the area ratios of islands to nanowires and the metal evaporation rate. All of the GdSi₂ samples shown in figure 3.18 were prepared with substrate temperature 650°C and 20 minutes post-deposition annealing at the same temperature. The metal coverages of these samples range from 1.0ML to 1.6ML, as indicated. Clearly, evaporation rate and coverage play important roles in the selective growth nanostructure category: lower rates and coverage lead to nanowire dominance while higher rates and coverage result in island dominance.



Fig. 3.18 The impact of Gd deposition rate and coverage on the $GdSi_2$ nanostructures morphology formation.

The length of NWs grown on vicinal Si(001) can be controlled by adjusting growth temperature within a narrow range. Vicinal Si(001) was used as the substrate because GdSi₂ nanowires grow along the same direction [6, 25, 32], and the nanowire length will not be limited by the Si surface steps and intersections with other nanowires. Figure 3.19 shows three STM images of Gd silicide nanowire growth on vicinal Si(001) substrates at growth temperatures of 550°C, 600°C, and 650°C, all with 0.9ML Gd coverage, 20 minutes post-deposition annealing, and a deposition rate of 0.2 ML/min. The average nanowire lengths are 40nm, 120nm and >300nm, respectively. Therefore, NW length can be regulated by, and is a strong function of the growth temperature.



Fig. 3.19 STM images of GdSi₂ nanowires grown on vicinal Si(001) substrates at 550° C, 600° C, and 650° C, with 0.9ML coverage, 20 min post-deposition annealing, and deposition rate of 0.2 ML/min. The average nanowire length in these images are 40 nm, 120 nm, and >300 nm.

3.2 Discussions and conclusions

Based on the combined analysis of the STM images, the cross-sectional TEM images, the plan view moiré fringe images, and the NBD patterns, silicide crystal structures are assigned to different type of GdSi₂ nanostructures, followed by a discussion of the relationship between the lattice mismatch and the nanostructure morphology. Phase transformation within the nanostructures is also discussed and two transformation mechanisms are proposed. Conclusions are present in the last part of this section.

3.2.1 Relationship between the crystal structures and silicide nanostructures

Three distinct types of lattice image are found in the cross-sectional TEM data, which are consistent with the projections of the hexagonal and orth/tet crystal structures, as shown in figure 3.9. Hence, these observations show that these crystal structures coexist among the GdSi₂ nanostructure. However, the cross sectional data taken as a whole does not unambiguously relate the crystal structures of the nanostructures to their morphology, since the cross-sectional width of nanowires can fall in the same range as that of the islands, as is evident from plan view images.

Cross-sectional TEM studies also indicate that the silicide nanostructure lattice spacings do not deviate from those of bulk materials. Hence, the lattice mismatch configurations of different GdSi₂ phases still hold. This observation, together with the conclusion that only the hexagonal and orth/tet phases exist in GdSi₂ nanostructures, allows a quick way to distinguish the hexagonal from the orth/tet structure, by identifying the lattice mismatch between the GdSi₂ and silicon, which can be done in plan view TEM. The analysis of both plan view moiré fringes and NBD patterns demonstrate that GdSi₂

nanowires have anisotropic lattice mismatch, which corresponds to the hexagonal structure, while islands have a more isotropic lattice mismatch, which results in the orth/tet structure. Hence, a general conclusion can be drawn that GdSi₂ nanowires are hexagonal and islands are orth/tet.

3.2.2 Relationship between the lattice mismatch and the nanostructure morphology

Both the plan view moiré fringe images and the NBD patterns reveal that the small lattice mismatch axis of $GdSi_2$ nanowires is aligned along the a-axis, also along the nanowire long axis. Therefore, the nanowire morphology is consistent with the proposed nanowire growth mechanism resulting from the anisotropic lattice mismatch between the silicide and the silicon substrate. In contrast, the analysis reveals that the islands, which have lower aspect ratios, have more isotropic lattice mismatches.

The strain accommodation due to the lattice mismatch between the silicide and the silicon plays an important role in epitaxial growth. The observation that the nanostructure lattice spacings do not deviate significantly from bulk values implies that the silicide layers in the nanostructures are fully relaxed, and thus the mismatch is primarily accommodated at the interface through interfacial dislocations (see Burgers circuit analysis in figure 3.9).

Generally, interfacial dislocations will increase free energy, and hence, growth along the large mismatch direction is not energetically favorable. This is consistent with the observation that the dimension of the nanowires along the c-axis (8.7% lattice mismatch along this axis) is only several nanometers. In contrast, no visible dislocations or strain are observed between the a-axis in the nanowires and the silicon in cross section

TEM. So it is reasonable to believe that the growth along this direction is energetically preferred, which is consistent with observation that the nanowire lengths can reach up to several microns. This results in the anisotropic growth for hexagonal phase nanostructures, and consequently in the long, thin morphology of the nanowires.

The orth/tet phases have lattice mismatches of $4.4\% \sim 6.8\%$ in perpendicular directions, which are all larger than that along the a-axis, but smaller than along of the c-axis of the hexagonal structure. This moderate, more isotropic mismatch results in the orth/tet islands having much more isotropic shapes. However, the orthorhombic island growth is still somewhat anisotropic, with islands generally elongated along the smaller lattice mismatch direction (this phase has mismatch of 6.5% and 4.4% in the two Si<110> directions), while the tetragonal islands usually have a close-to-square morphology (6.8% mismatches in both the a- and b-axis).

Moiré fringe analysis suggests that some minimal lattice mismatch is accommodated by lattice rotation, strain and dislocations. A model, showing that lattice mismatch can be reduced by such lattice rotation, is illustrated in figure 3.20 and suggests that lattice rotation may result in the lattice strain and dislocations. Si(001) and $GdSi_2(01\overline{10})$ are shown in figures 3.20(a) and (b). Figure 3.20(c) shows the mismatches between the Si and silicide, when there is no rotation between them, along two perpendicular Si<110> directions. However, the mismatch magnitudes change when the silicide rotates along the Si[001] axis, as shown in figure 3.20(d): the mismatch along the large mismatch direction is reduced, while the mismatch along the small lattice mismatch direction may be reduced or enlarged depending on the rotation angle. The equilibrium rotation of the nanostructure lattice results from the balancing of the mismatches along

two Si<110> directions, which is closely related to the overall strain energy. However, a constant lattice rotation over a large distance is impossible, lattice strain and dislocations may be produced to release the strain energy accumulated by the rotation.

Overall, the magnitude and the direction of the lattice mismatch between the silicide and the silicon have a strong impact on the GdSi₂ nanostructure morphology.



Fig. 3.20 Silicide lattice rotation with respect to Si(001). (a) and (b) show the Si(001) and GdSi₂(010) surfaces; (c) shows the mismatches between the SI and silicide without rotation; (d) shows the mismatch changing when silicide lattice rotates.

3.2.3 Phase transformation within nanostructures

According to previous studies, nanowires typically form at the initial growth stage, with silicides islands forming later in the growth and annealing processes. It has been shown that high temperature annealing (700°C) results in the morphology being dominated by islands [40], consistent with the real-time observation that islands will grow at the expense of the nanowires [24]. Combined with the results of the present work that these islands have the orth/tet structure and the nanowires are hexagonal, these observations suggest that the hexagonal phase have a lower surface energy due to less overall lattice mismatch with silicon, but higher volume free energy than the orth/tet phase. Therefore, the orth/tet phases are more stable than the hexagonal al phases, at least when in contact with the Si substrate, which is also consistent with that the orth/tet have a higher congruent melting temperature than the hexagonal phase, as shown in figure 1.3. Hence, a phase transformation from hexagonal to orth/tet during growth and annealing is expected, and is also observed in the plan view TEM observation in figure 3.16. At the atomic level, this transformation may be achieved by shearing the structural units of the GdSi₂, as shown in figure 1.6, followed by slight lattice spacing relaxation.

The combined STM and TEM studies suggest two mechanisms for the phase transformation from the hexagonal to the orth/tet phase. First, nanowires from neighboring Si(001) terraces can form interlocking structures at nanowire junctions (shown in figure 3.6), leading to orth/tet islands formation. It is clear that at the nanowire intersections, some overgrowth can occur. Alternative overlapping of layers from two intersecting nanowires may result in the nanowire structural units around the nanowires

junctions being stacked similarly with that of the orth/tet phase (figure 1.6), as sketched in figure 3.21. Consequently, the hexagonal to orth/tet phase transformation could grow from these nuclei. Moreover, at the intersection, it would not be surprising if the average strain on a growing island is more isotropic since it is attached to nanowires of both orientations at its edges, and the effect of the anisotropies in the nanowires might average out.



Fig. 3.21 Nanowire intersection may lead to orth/tet nucleation. The structural units of the two intersecting nanowires (nanowire A and B) are always shifted consistently along the nanowire long axis (or the a-axis). Hence, at the intersection of two perpendicular nanowires, the structural units shifting direction may change due to the overlap of the nanowires, resulting in a stacking order similar to that of the orth/tet structures. The arrows stand for the structural unit shifting direction.

Another possible phase transformation mechanism from the hexagonal to orth/tet is that the stacking order change occurs spontaneously in the nanowires due to lattice imperfections, such as stacking faults and dislocations. Figure 3.9(b) shows a stacking fault lying perpendicular to the nanowire long axis and parallel to the interface, resulting in the two layers of local structural units above the stacking fault being sheared to the "C" and "D" positions, which result in the local stacking order taking up that of the orth/tet phase (see figure 1.6). Consequently, the presence of the stacking faults may be a precursor for the hexagonal phase to transform to the orth/tet phase. Stacking faults within nanowires have already been suggested as a mechanism for strain relief. Also, dislocations may dissociate into partial dislocation that can change the structural unit stacking via partial dislocation slip.

Finally, the morphology of the dumbbells shown in Figure 3.16 show that the phase transformation can occur at the ends of isolated nanowires. This tendency could be driven by free energy considerations if the exposure of the end facet of a hexagonal silicide nanowire is not preferred over the side fact of the orth/tet unit cell. Alternatively, it could be a kinetic barrier where the activation energy required to drive the atomic rearrangement in figure 3.21 is lower at these end faces. It is not possible to draw further conclusions at this point with the data available.

It is important to realize that the first phase transformation mechanism (orth/tet nucleation due to nanowire intersections) is more important than the second one (self-nucleation by lattice imperfects) during the nanostructure growth on flat surfaces. The fact that silicide growth on vicinal Si(001) results in nanowire dominance implies that

once nanowire intersections are largely eliminated, the second mechanism does not produce significant numbers of islands.

3.2.4 Conclusions

Cross-sectional TEM studies shows that Gd silicide nanostructures have either hexagonal or orthorhombic/tetragonal crystal structures and no significant lattice parameter deviation from those of bulk materials was observed. Further study through plan view TEM moiré fringe and nano-beam electron diffraction analysis reveals that islands (small aspect ratio) are orthorhombic or tetragonal, and nanowires (large aspect ratio) have hexagonal crystal structure. Hence, this study confirms that the Gd silicide nanowires are formed due to the anisotropic lattice mismatch with respect to the silicon substrate.

Phase transformation from the hexagonal to orthorhombic/tetragonal phase is observed within the silicide nanostructures. This transformation may originate from the orthorhombic/tetragonal nuclei developed at the nanowire intersections or from selfnucleation due to lattice imperfections in the nanostructures, or at the ends of NWs.

Low metal coverages and deposition rates were found to favor nanowire formation, and nanowire length was a strong function of growth temperature.

Chapter 4 Dy and Tb silicide nanostructures grown on Si(001)

In this section, studies of both Dy and Tb silicide nanostructures grown on Si(001) substrates are presented. The data presented in this section are used to reinforce the results and discussions presented in Chapter 3, in which Gd silicide nanostructures were investigated. The Dy silicide nanostructure study is presented first, including both STM and TEM data. For Tb silicide nanostructures, only plan view TEM with moiré fringe analysis was conducted.

4.1 Dy silicide nanostructures grown on Si(001)

Dy is the 66^{th} element in the periodical table and one of the RE metals. The hexagonal form of DySi₂ has lattice mismatch of 0.23% and 7.3% with respect to the Si<110> directions on Si(001). Hence, Dy silicide is expected to form nanowires on Si(001) according to the anisotropic lattice mismatch nanowire formation mechanism. Dy is in fact the prototypical nanowire forming RE metal, since it was used in the initial report of nanowire formation by Preinesberger et al [1]. There have been several STM studies of Dy silicide nanostructure formation on Si(001) [3, 5, 8, 9, 23, 25, 28, 35]. In this chapter, STM morphology information is correlated with both subsurface behavior and silicide crystallography probed by TEM.

4.1.1 Silicide nanostructure morphology by STM

A typical STM image of $DySi_2$ nanostructures grown on Si(001) substrates is shown in figure 4.1. In this image, both nanowires and islands are observed. It is clear that $DySi_2$ nanowires usually grow together to form nanowire bundles, as indicated in the figure. Typically, the widths of DySi₂ nanowires within the bundles range from $2a_{si}$ to $16a_{si}$ ($a_{si} = 0.384$ nm, see Chapter 2.5.1). The heights of the nanowires are multiples of one silicide layer, which is 0.33 nm, and the Dy silicide nanowires are one or two layers high. It is also observed that these Dy silicide nanowires do not cross the Si(001) terrace edges. The Dy silicide islands are higher (>2nm) than the nanowires, and have much smaller aspect ratios (<5:1) than are observed for nanowires (>>10:1). Most of the islands form at nanowire intersections, as shown in figure 4.1. Besides the silicide nanostructures, a wetting layer consisting of Dy induced 2×7 and 2×4 surface reconstruction may cover the areas without nanowires and islands [8, 9, 35]. All of these points are consistent with prior STM work [3, 8, 9, 28, 35].



Fig. 4.1 Morphologies of $DySi_2$ nanostructures on Si(001) by scanning tunneling microscopy (STM). Both nanowires (bundles) and islands are present.

4.1.2 Cross-sectional TEM observation

Figure 4.2 demonstrates the three observed lattice symmetries observed for DySi₂ nanostructures in cross-sectional high resolution TEM (HRTEM) studies, with corresponding fast Fourier transform (FFT) patterns shown as insets. The FFTs include information from both of the Si substrate and the silicide nanostructure. The information from the substrate has been used to calibrate the silicide lattice parameter.

Figure 4.2(a) shows a small portion of a nanostructure with total lateral crosssectional width larger than 0.5 μ m. A hexagonal arrangement of atoms is seen in the silicide, which is consistent with the c-axis projection of the hexagonal silicide phase [Fig, 1.5 (a)]. In this view, no there is no detectable lattice mismatch or observed dislocations between the silicide and the Si. The FFT analysis shows that the measured lattice parameter is a = 0.38 ± 0.01 nm, consistent with bulk silicide values. Burgers circuits taken across the interface of the island show that there is no enclosed lattice failure, indicating that interfacial dislocations (if are there any) are widely spaced. In fact, no dislocations at either the interface or within the silicide were seen for the entire observable length of this nanostructure (including portions not shown in this image).

Figure 4.2(b) shows the second type of symmetry observed in $DySi_2$ nanostructures, which is rectangular symmetry. This symmetry is consistent with the aaxis projection of the hexagonal structure [Figure 1.5(a)]. For this type of nanostructure, the measured lattice parameter from the FFT in the direction parallel to the Si(001) surface is c = 0.40~0.41 nm, with the range in values reflecting measurements from different islands with this crystal structure. Again, this measured value is consistent with the bulk materials values, as shown in Table 1.3. This lattice parameter corresponds to a

lattice mismatch of 4.2%~6.8% with respect to Si(001). It was also noticed that the

interface is irregular, with ledges between the silicon and the silicide.



Fig. 4.2 Cross-sectional HRTEM images of DySi₂ nanostructures. Insets are the corresponding FFT patterns. (a) Here the silicide has a hexagonal symmetry, consistent with the c-axis projection of the hexagonal structure; (b) Here the silicide has a rectangular symmetry, consistent with the a-axis projection of the hexagonal structure. The dashed Burgers circuit in (b) shows there are interfacial dislocations. The stacking fault is seen in the lower right portion of the image.

Both nanostructure tilting and dislocations are seen in figure 4.2. In this figure, the FFT pattern analysis shows that the entire island is tilted a small angle (<1°) with respect to the substrate. The Burgers circuit in the same figure shows that for 20 planes in the silicide normal to the interface, there are 22 planes in the silicon. This indicates a mismatch of approximately 9% (2/22), close to the theoretical mismatch 7.23%, as shown in table 1.3. Thus, the mismatch appears to be accommodated in this case through interfacial dislocations. These dislocations are not readily apparent without the aid of the Burgers circuit because they have widely relaxed cores. In addition to the interfacial dislocations, there is a stacking fault, protruding from an interfacial ledge, shown in figure 4.2.

In other hexagonal silicide islands, the mismatch may be accommodated in other ways. The nanostructure in figure 4.3 shows the a-axis projection of a hexagonal structure, and displays dislocations in the silicide in addition to the interfacial dislocations noted by the Burgers circuit. These dislocations in the silicide are associated with irregular subgrains that tilt 1~5 degrees away from the substrate normal direction, as indicated in the figure. These subgrains have widths up to 7nm. This tilting effect is sometimes so significant that it was often impossible to get a sharp lattice image of both the substrate and the silicide simultaneously in the cross-sectional TEM observation; in such cases it was necessary to tilt the sample a few degrees from the Si<110> towards the Si<100> in order to obtain sharp lattice images of the silicide, as reported earlier [10].



Fig. 4.3 Dislocations and subgrains tilting in the a-axis projection view of a hexagonal nanostructure. Dislocations are either within the silicide or at the interface. Marks "T" indicate the dislocations which are within the silicide and the dash Burgers circuit encloses an interfacial dislocation.

The third symmetry observed in cross-sectional HRTEM is shown in figure 4.4. In the silicide lattice image there is a half atom column shift between every two horizontal atom lines, which is consistent with the orth/tet structure [figure 1.5(b)]. For most (>90%) such orth/tet nanostructures, the lattice parameters parallel to the Si(001) varies from $a = 0.39 \sim 0.40$ nm and $c = 1.33 \sim 1.37$ nm. The range in measured values represents data from different nanostructures with a measurement error of ±0.01 nm. Lattice mismatches of the orth/tet DySi₂ nanostructures with the substrate along either aor b-axes varies from 1.6% to 4.2%, which is less than or equal to the values expected from the bulk silicide data, as shown in Table 1.3.

A milder way to release strain energy in orth/tet islands is observed. Much less lattice tilting and fewer dislocations were observed in the orth/tet islands compared to the a-axis projection of the hexagonal nanostructures with similar size. Some nanostructures even showed partial lattice tilting (this means only part of a nanostructure tilts), as indicated by FFTs in figure 4.4. The left FFT pattern in figure 4.4 is from the left part of the island and the c-axis of DySi₂ is almost parallel with Si[001]; the right FFT comes from the right part of the island which is tilted 1.7 degree away from the Si[001]. Islands with sizes less than 50 nm usually have a small tilting angle (<1°) and larger ones tilt more (up to 3.4°). Some orth/tet nanostructures also show an expansion in the lattice parameter in the c direction to accommodate compression along a- or b-axis.



Fig. 4.4 HRTEM image of an orthorhombic or tetragonal nanostructure. The FFTs are obtained from the perfect and distorted lattice areas, respectively. In the distorted lattice area, the $D_{\rm VS12}(001)$ tilt ~ 1.79 away from Si(001).

Overall, the Dy silicide nanostructures possessed either hexagonal or orth/tet crystal structure. However, the cross sectional data presented in this section is not able to unambiguously relate the crystal structures of the nanostructures to their morphology, since the cross-sectional width of nanowires can fall in the same range as that of the islands, as is evident from plan view images. Nanostructure tilting (including partial tilting) and dislocations (including interfacial dislocations and edge dislocations within nanostructures) have been observed. Measurements show that the lattice parameters of DySi₂ nanostructures are similar with those of bulk silicide values.

4.1.3 Plan view moiré fringe study

Table 4.1 shows calculated moiré fringe spacings of $DySi_2$, based on equation (3.1) and bulk silicide lattice parameters. As in the case of Gd, the hexagonal phase should show a striped pattern of fringes and the orth/tet phase should show a mesh pattern. Both the stripe-like and mesh-like fringe patterns have been observed in plan view TEM, and examples are shown in figure 4.5. Figure 4.5(a) shows a mesh-like pattern, with fringe spacings ranging from 3.2nm to 6.9nm, with the fringe spacing varying for different nanostructures. Stripe-like moiré fringes with lateral spacings of 2.4 \sim 3.2nm are evident in figure 5(b). The measurement error is \sim 20%. The measured moiré fringe spacings are also included in Table 4.1, and are consistent with the calculated values.

Table 4.1 A comparison of the calculated and measured moiré fringe spacings of $DySi_2$ on Si(001). The calculated spacings are based on bulk lattice parameters and zero rotation between the silicide and the silicon.

structure	calculated fringe spacing (nm)			measured fringe spacing (nm)		
	a	b	с	a	b	с
hexagonal	82		2.8	>90		2.4~3.2
tetragonal	4.1	4.1		22.60		
orthorhombic	3.9	7.2		5.2~0.9		

It was found that stripe-like moiré fringe patterns were typically observed on nanowires, and the mesh-like patterns were only found on islands. This observation indicates that the orth/tet phase may be associated with islands, while the hexagonal phase may be assigned to nanowires.

The bending of the moiré fringes, shown in figure 4.5, indicates non-uniform lattice strain in $DySi_2$ nanostructures, while edge dislocations in the moiré fringe give a one-to-one correspondence to edge dislocations in the silicide. The hexagonal nanowire in figure 4.5(a) shows mild fringe bending and only a few dislocations along the length. This is consistent with the small lattice mismatch (-0.23%) along the length of the elongated island, resulting in the limited stress accumulation during hexagonal nanowire growth. In contrast, the distorted appearance of the mesh patterns seen on the island in figure 4.5(b) indicates larger lattice distortion, and dislocation as well, which are also seen in cross sectional images of orth/tet islands, as shown in figure 4.3. These distortions occur because the lattice mismatch ($2.73\% \sim 5.21\%$) introduces significant strain near the interface, even if silicide layers in the remainder of the island are relaxed.

Two silicide phases can co-exist in an individual nanostructure. Figure 4.6 shows a nanostructure with both ends having the orth/tet structure and the part between the ends having the hexagonal structure. Since it is common to see this phenomenon during TEM observation, it may suggest the possibility of a transformation from the hexagonal to the orth/tet phase. Previous STM studies have shown that nanowires (hexagonal phase) are transformed to the larger islands (orth/tet phase) by extended post growth annealing. Therefore, nanowires with orth/tet islands on both ends are probably in the process of transforming from one phase to the other.



Fig 4.5 Plan view TEM reveals stripe-like moiré fringe pattern on nanowires, as shown in (a), and mesh-like moiré fringe patterns on rectangular DySi₂ islands, as shown in (b). This indicates that islands, with small aspect ratio, have an orthorhombic/tetragonal form and nanowires have a hexagonal form. Fringe bending and dislocations are observed.



Fig. 4.6 The co-existence of the orth/tet and hexagonal phases. Meshed fringes indicative of the orth/tet phase are seen on both ends, while strip in the center part indicating the hexagonal phase.

4.2 Tb silicide nanostructures grown on Si(001)

Tb is the RE metal between Dy and Gd. The hexagonal phase of TbSi₂ has 0.18% and 8.0% lattice mismatch with the 2 perpendicular Si<110> directions on Si(001), respectively, enabling TbSi₂ nanowire formation on Si(001) substrates. In particular, the lattice mismatch along a-axis is less than that for either Gd or Dy, which might promote nanowire formation. In this section, moiré fringe data and analysis of TbSi₂ nanostructures are presented.

Figure 4.7 shows a large scale TEM image of TbSi₂ grown on a Si(001) substrate. Both silicide nanowires and islands are present, as indicated in the figure. The nanowires have large aspect ratios, typically >>10:1 and islands have smaller aspect ratios <5:1. The observation that larger diffraction contrast is observed on islands than that on nanowires suggests that islands are thicker than nanowires. It is also observed that most of the islands are situated on the end of nanowires.



Fig. 4.7 Morphologies of $TbSi_2$ nanostructures on Si(001) by transmission electron microscopy (TEM). Both nanowires (bundles) and islands are present.

Using bulk silicide lattice data, the Tb silicide moiré fringe spacings on Si(001) can be calculated and are listed in Table 4.2. According to these calculated moiré fringe spacings, the hexagonal Tb silicide should have a stripe-like fringe pattern, and the orthorhombic Tb silicide should have a mesh-like pattern. Both of these two patterns are observed in plan view TEM investigation. Figure 4.8(a) shows a nanowire with stripe-like moiré fringes. Figure 4.8(b) demonstrates an island with mesh-like moiré fringes. The corresponding FFTs are shown on the right and are used to measure the TbSi₂ interplanar spacings calibrated by Si. The measured fringe spacings are consistent with the calculated spacings by equation 2.4 listed in Table 4.2, once again showing that the nanostructure silicide is fully relaxed to bulk lattice parameters.

Figure 4.9 shows the coexistence of the hexagonal and orth/tet phases within a nanostructure. Just as for Gd and Dy, rectangular islands of the orth/tet phase terminate elongated islands of the hex phase. All measured nanowires were not long enough to detect any fringes along their length, which reflects the very small lattice mismatch along this direction.

Table 4.2 A comparison of the calculated and measured moiré fringe spacings of $TbSi_2$ on Si(001). The calculated spacings are based on bulk lattice parameters and zero rotation between the silicide and the silicon.

structure	calculated fringe spacing (nm)			measured fringe spacing (nm)		
	a	b	С	a	b	с
hexagonal	107		2.6	no fringes		2.4~2.7
orthorhombic	3.6	5.8		4.0~6.1		



Fig. 4.8 Plan view TEM shows both stripe-like and mesh-like moiré fringe patterns are present, as shown in (a) and (b), respectively. The corresponding FFT is displayed at the right side of the images. The insets in FFTs represent the magnified areas with contrast enhanced.



Fig. 4.9 Co-existence of the hexagonal and the orthorhombic phase in $TbSi_2$ nanostructure complex. (a) and (b) shows hexagonal nanowires with one and two end(s) having the orth/tct islands, respectively.

4.3 Conclusion

The hexagonal form of both Dy and Tb silicides have anisotropic lattice mismatches with Si(001), as shown in Table 1.3, and, hence, are expected to form nanowires on Si(001). However, Dy and Tb silicides form nanowires and islands simultaneously on Si(001) substrates. Cross-sectional TEM study of DySi₂ nanostructures shows that the hexagonal and orth/tet phases co-exist among these nanostructures. Further crystallographic analysis by plan view TEM moiré fringes confirms that DySi₂ nanowires have the hexagonal crystal structure and islands have the orth/tet structure. TbSi₂ moiré fringe analysis reinforces this conclusion by showing TbSi₂ nanowires are hexagonal and islands have orthorhombic crystal structure. Hence, the crystallographic study on Dy and Tb silicides confirms that nanowire growth due to anisotropic lattice mismatch with substrates is not restricted to the specific case of Gd, but applies in a wider range of RE metals, as would be expected.

Both of the Dy and Tb silicide moiré fringe studies suggest the possibility of phase transformation from the hexagonal to the orth/tet, which is also consistent with Gd silicide data.

Chapter 5 Sc silicides nanostructure growth on Si(001)

Scandium is the 21st element in the periodic table. In chemical terms, Sc behaves similarly to Y and La, and thus shares some properties with the RE metals. In particular, Y silicide has been used to model certain RE silicides. According to the Sc-Si system phase diagram shown in figure 1.4, Sc silicide forms three stable silicides, hexagonal Sc_5Si_3 , orthorhombic ScSi, and hexagonal Sc_3Si_5 . The lattice parameters of these silicides would be smaller than analogous RE silicides because of the relative position of Sc and the RE's in the periodic table. The lattice parameters of the Sc silicides are listed in Table 1.3. The interesting fact is that Sc_3Si_5 has a good match with Si along the silicide c-axis, while the lattice constant along the a-axis is much larger. This implies that an anisotropic lattice mismatch with respect to the Si(001) substrates could arise, just as for the hexagonal RE silicides, but in a manner that is perpendicular to them. Thus, the growth of Sc silicide nanostructures is of considerable interest, especially if it is possible to grow nanowires which are perpendicular to RE silicide nanowires. However, the fact that the mismatch perpendicular to the direction of good match is large and negative rather than positive for the RE silicides may have some effects on the growth behavior.

In this chapter, Sc silicide nanostructure morphology studied by STM is presented first, followed by cross-sectional HRTEM and plan view TEM moiré fringe analysis.

One experimental note: in all of the Sc studies, it was very difficult to get stable Sc evaporation rates, and also to calibrate the deposition rates with the resistively heated sublimation sources that were used. Therefore, in contrast to the Gd work, no Sc metal coverages are reported.
5.1 Experimental results

5.1.1 Nanostructure morphology by STM

Figure 5.1(a) shows an STM image of Sc silicide nanostructures grown on Si(001) at 600°C without post-deposition annealing. In contrast, figure 5.1(b) presents an STM image of a different sample with Sc silicide nanostructures grown under the same conditions but treated with an extra 30 minute annealing at 600°C. It is obvious that post-deposition annealing ripens the nanostructures, so that only a few, large nanowires remain after annealing. Furthermore, the diversity in island shape and size is greatly reduced.

The un-annealed growth will be discussed first. Three different categories of nanostructures were observed on samples without annealing, as shown in figures 5.1 and 5.2. These three types of nanostructures are referred as "triangular nanowires", "tabular islands", and "small nanowires", respectively. The first nanostructures, triangular nanowires, are shown in figure 5.1(b), and have a triangular cross section. The nanowires are observed in both un-annealed and annealed samples. However, those on annealed samples are wider, higher, and much longer than those in un-annealed samples. The triangular nanowires on un-annealed samples always grow attached to a tabular island.

The small nanowires, shown in figure 5.2(a), are typically 6 or $8a_{Si}$ wide [a_{Si} is the Si(001) surface periodicity, 0.384 nm], and up to 50 nm long. The small nanowires grow parallel with Si(001) dimer rows, which makes them different from NWs formed by RE metals, all of which grow perpendicular to the substrate dimer row direction. These small nanowires appear to disappear after post annealing.

The third nanostructures observed are tabular islands, having small aspect ratios (usually <5:1), but wider and longer than the small nanowires. In general, the tabular islands have a large flat base, on which three different types of organized protrusions can be seen: elongated features with flat top, the aforementioned NWs with triangular cross section, and arrays of dot shaped features, as shown in figures 5.2(a) and (b). The flat top elongated features seen in figure 5.2(b) appear very much like nanowire bundles seen for Gd (see figure 3.4). Note, however, that both flat top and triangular elongated features are perpendicular with the longer dimension of larger tabular islands.



Fig. 5.1 STM images of Sc silicide nanostructures grown on Si(001) substrates. (a) shows a Sc silicide sample as deposited; (b) shows a sample after 30 min post-deposition annealing. The line profile in the inset of (b) shows that the cross section of the nanowire has a triangular shape.



Fig. 5.2 STM images of different types of Sc silicide nanostructures present on substrates. In (a), a small nanowire and several tabular islands with dot protrusions are seen and; in (b), tabular islands with elongated features (with flat top and triangular cross sections) are observed. It is evident that the nanostructure density and the category have changed after the Sc silicide samples are annealed. After annealing, the great majority of nanostructures surviving post-deposition annealing are triangular nanowires, as shown in figures 5.1(b) and 5.3. At the same time, these triangular nanowires grow longer, wider, and higher compared to those on un-annealed samples, being typically hundreds of nm long. Figure 5.3(a) shows that Sc nanowires may grow into Si(001) terraces by exhausting Si from terraces. A few tabular islands remain after annealing as shown in the larger scale AFM image in figure 5.3(b). All surviving tabular islands also have small raised ridges on them that appear to be the same features seen in figure 5.2(b).



Fig. 5.3 (a) and (b) show STM and AFM images of Sc silicide nanostructures present on substrates after post-annealing. Most of the surviving nanostructures are triangular nanowires, while a few tabular islands are also present.

A histogram analysis of the Sc silicide nanostructure heights for both as-deposited and annealed Sc silicide samples is shown in figure 5.4. Note that the heights of tabular islands were measured by ignoring ridged or dot like the protrusions on the top. In figure 5.4(a), which was obtained from samples without annealing, three distinct peaks are observed below the height of 0.5 nm, as marked as P1 - P3 in the figure. The heights of these three peaks correspond to 0.16, 0.30, and 0.44 nm above the surrounding substrate, respectively, with measurement error of 0.02 nm. In the range with heights larger than 0.5 nm, no simple rules are evident for the height distribution. The peaks in the height distribution have some correspondence with nanostructure type. The small nanowires have heights of about 0.16 nm, while the tabular islands are either 0.30 or 0.44 nm high. Most of the triangular nanowires are higher than 0.5 nm in both the as-deposited and annealed Sc samples. The triangular nanowires grow even higher after annealing. The sparse data in the histogram in the post annealed sample reflects the fact that there is a very low density of these features on the surface.



Fig. 5.4 Height histograms of Sc silicide samples. (a) shows a histogram from unannealed samples, showing that three peaks (marked as P1 through to P3) are present. P1 corresponds to the height, 0.16 nm, of small nanowires; P2 and P3 corresponds to the heights, 0.30 and 0.44 nm, of tabular islands; the height higher than ~0.5 nm are from triangular nanowires. (b) shows a histogram from annealed samples. Only triangular nanowires are present and their heights are larger than 0.8 nm.

5.1.2 Crystallography study by TEM

Just as for the Gd work, it was difficult to obtain TEM contrast in plan view or good cross sections for very thin silicide nanostructures due the oxidation, thus the TEM studies focused mainly on annealed triangular nanowires which the STM data show have heights in excess of 3 nm.

5.1.2.1 Cross-sectional TEM

The areal density of triangular nanowire was low, as shown in figures 5.1(b) and 5.3. Therefore, the possibility of finding a nanowire sectioned along its length in the limited thin area of a TEM foil is very small. Hence, it is expected most of the nanowires observed will be in cross section (sectioned perpendicular to their length).

Overall, three different lattice stacking variants were observed in the Sc silicide nanostructure cross sections. Figure 5.5 shows a high resolution TEM image of cross section of a Sc silicide nanowire. This image shows the first observed stacking variant, along with the corresponding FFT pattern. Note that the nanowire has a triangular cross section, consistent with the STM morphology shown in figure 5.1(b). The corresponding FFT spots (marked with circles) show 6-fold symmetry. In addition, the measured interplanar spacings of the marked FFT spots are all 0.32 ± 0.01 nm, which is consistent with Sc₃Si₅{0110} interplanar spacings. Hence, the Sc₃Si₅ phase (AlB₂ prototype, hexagonal) is assigned to this nanowire, with the c-axis parallel with, and the a-axis perpendicular to the nanowire long axis. It should be pointed out that the nanowires with such stacking variant were rare (1 out of 10 examined nanowires).



Fig. 5.5 A cross-sectional HRTEM image, and corresponding FFT pattern, of a Sc silicide triangular nanowire. This nanowire is composed by Sc_3Si_5 (hexagonal, AlB₂ prototype).

Most nanowires (7 out of 10 examined nanowires) show a more complicated internal structure consisting of two layers with different lattice structures, with the upper portion corresponding to the second, distinct type of lattice stacking variant observed. Two different nanowires are shown in figure 5.6 in order to reinforce the interesting structure of these nanowires. The bottom layer is about 2~3 atomic layers high (0.5~1 nm), while the upper layer has a triangular cross section and is typically higher than 2 nm. Both layers have lattices with distinct appearances.

The FFT s of the two images are same, hence, only one of them is shown in the figure. The FFT of such nanowires are complicated, as shown in figure 5.6. However, the FFT spots can be divided into three sets. The first set is from silicon, some of which are indexed in the figure; the second set of spots are marked by small circles and labeled with letters. These spots have a hexagonal symmetry, and the measured interplanar spacings of these marked spots are all 0.38 ± 0.01 nm, suggesting once again the Sc₃Si₅ phase (AlB₂ prototype) with the a-axis perpendicular to the nanowire long axis; the remaining silicide FFT spots, which are marked with triangles and labeled as numbers 1 through to 5, have interplanar spacings of 0.34, 0.54, 0.56, 0.28, and 0.54 nm, respectively, all with error of ± 0.01 nm. These measured spacings are consistent with interplanar spacings of Sc_5Si_3 (0110), (1012), (0001), (0002), and (1012). Hence, this phase is identified as Sc_5Si_3 (Mn_5Si_3 prototype) with the a-axis parallel with the nanowire long direction. Therefore, the FFT analysis shows that there are two phases present in these triangular nanowires. The inset in the figure 5.6(b) shows that, at the interface between Sc_3Si_5 (bottom layer) and Sc_5Si_3 (upper layer), there are 9 atom columns in the

bottom layer while there are only 6 atom columns in the upper layer, resulting in interfacial dislocations and lattice distortion, both of which are evident in figure 5.6(b).

By comparing the measured interplanar spacings in the FFTs to those in the high resolution TEM images, it is clear that the upper layer of the nanowires in figure 5.6 has the Sc_5Si_3 phase, and the buffer layer is Sc_3Si_5 . The crystal structure of Sc_3Si_5 is shown in figure 1.5(a), and that of Sc_5Si_3 is shown in figure 5.7. Figure 5.7(c) shows that in Sc_5Si_3 the Sc atom spacing along the a-axis is 0.786 nm, which is almost double that of the Si(001) surface lattice periodicity, 0.384 nm, or double of the c-axis of Sc_3Si_5 structure, 0.387 nm.







Fig. 5.7 Crystal structure of Sc_5Si_3 and the projections along different axes: c-axis ([0001]), a-axis ([$2\overline{110}$]), and [$0\overline{110}$] axis.

Figure 5.8 (a) and (b) show simulated HRTEM images of both Sc_5Si_3 (viewed along the a-axis or [2110]) and Si (viewed along [110] axis), while (c) shows a simulated HRTEM image of Sc_5Si_3 viewed along 3° tilted away from [2110] towards [1120], and (d) shows a simulated HRTEM image of Si viewed along 3° tilted away from [110] towards [001].

The appearances of the upper layer of silicide and the substrate Si in figure 5.6(a) are consistent with in the simulations in figures 5.8(a) and (b). The simulated HRTEM image of the Sc silicide has a stripe-like appearance when silicide is tilted 3° away towards [$11\overline{20}$], and Si have a rectangular symmetry when tilted 3° towards [001]. These simulated images with 3° tilting are consistent with those in figure 5.6(b). Hence, the difference in appearance of the silicide lattices between the two nanowires shown in figure 5.6 may result from the effect of tilting, and can originate from a same crystal structure. Note that the bottom layer has a sharp image when the sample is tilted 3°, as shown in figure 5.6(b), and is blurred when the sample is oriented directly to the Si[110] zone, as shown in figure 5.6(a). This suggests that the bottom layer may be tilted with respect to the Si(001) substrates and the Sc₅Si₃ in the upper layer.



Fig. 5.8 HRTEM simulation images of Sc₃Si₃ and Si. (a) and (b) show simulation images of Sc₃Si₃ (viewed along the a-axis or [$2\overline{110}$]) and Si (viewed along [110] axis); (c) shows a simulation image of Sc₃Si₃ viewed along 3° away from [$2\overline{110}$] towards [$11\overline{20}$]; (d) shows a simulation image of Si viewed along 3° away from [110] towards [001]. The simulation was done by setting the defocus as 50 nm, and thickness as 14 nm.

The third lattice stacking variant observed is shown in figure 5.9. This nanostructure has a flat top, and is 2~3 atomic layers thick and about 5 nm wide. Two such nanostructures are observed out of 10 studied nanostructures in cross-sectional TEM, which is somewhat consistent with the tabular island density on Si, as shown in figure 5.3. The interplanar spacings were measured directly from the image and calibrated by the Si, because there is not enough silicide planes to obtain a reasonable FFT pattern due to small size of the nanostructure. The planes perpendicular to the interface have a spacing of 0.38 \pm 0.02 nm, and those parallel with the interface have a spacing of 0.42 \pm 0.03 nm. It is also seen that the left part of the nanostructure appears to have hexagonal symmetry, while the right part shows a rectangular symmetry. Therefore, it is difficult to assign any crystal structure to this nanostructure based on the available measurements.



Fig. 5.9 A cross-sectional TEM image of a Sc silicide nanostructure with flat top.

5.1.2.2 Plan view TEM: moiré fringes

Figure 5.10(a) shows a low magnification plan view TEM image of Sc silicide nanowires grown on Si(001), while (b) and (c) show two different observed moiré fringe patterns. Note that only a small portion of the Sc silicide nanostructures, display moiré fringes, which is very different behavior than for Gd, Dy, and Tb silicide nanostructures.

It should be pointed out that the thickness of silicon in the thin areas of TEM samples is about 10~50 nm, while the thicknesses of the silicide layers in nanostructures are less than 3 nm. Hence, the interference between the silicides and the silicon, instead of that between the different silicide layers, dominates the formation of moiré fringes. Furthermore, the lattice distortion, which is evident in the cross sectional HRTEM images, may also disable the formation of uniform moiré fringes. Therefore, only the moiré fringes formed between the silicon and the silicides are taken into account in this section.

In figure 5.10(b), the moiré fringes are perpendicular to the nanowire long axis with fringe spacings varying from 8.0 to 8.5 nm (corresponding to a silicide lattice parameter of $0.787 \sim 0.786$ nm), which is consistent with the spacing along resulting from the Sc₅Si₃ a-axis (0.7861 nm), as shown in Table 5.1. In contrast, the moiré fringes in figure 5.10(c) are parallel with the nanowires. Here, the fringe spacing is 4.5~5.6 nm, corresponding to an interplanar spacing of $0.368 \sim 0.371$ nm. These values are consistent with the Sc₃Si₅ c-axis (0.366 nm), as shown in Table 5.2. This moiré fringe analysis suggests that Sc₅Si₃ phase (with a-axis parallel with the nanowire long axis) and Sc₃Si₅ phase (with c-axis parallel with the long axis) are present in Sc silicide nanowires, which is consistent with the conclusion obtained from cross-sectional TEM data in Chapter 5.1.2.1. Table 5.1 Comparison of the calculated and measured moiré fringe spacings of Sc_5Si_3 (hexagonal phase) with respect to Si(001). The reported and calculated lattice parameters of the silicide are also listed.

	bulk lattice parameters (nm)	calculated moiré fringe spacings with Si(001) (nm)	measured moiré fringe spacings (nm)	calculated lattice parameters from measured results (nm)
a	0.7861	8.3	8.0~8.5	0.787~0.786
c	0.5812	<0.6	N/A	N/A

Table 5.2 Comparison of the calculated and measured moiré fringe spacings of Sc_3Si_5 (hexagonal phase) with respect to Si(001). The reported and calculated lattice parameters of the silicide are also listed.

	bulk lattice parameters (nm)	calculated moiré fringe spacings with Si(001) (nm)	measured moiré fringe spacings (nm)	calculated lattice parameters from measured results (nm)
a	0.366	3.9	4.5~5.6	0.368~0.371
c	0.387	<0.8	N/A	N/A

Although the moiré fringes show different features, the FFTs of the two nanowires in figure 5.10(b) and (c) are essentially the same except the spot intensity. Taking the nanowire in figure 5.10(c) as a prototypical example, the FFT pattern is shown figure 5.11(a). The nanowire in the figure has the Sc_3Si_5 crystal structure according to the moiré fringe analysis, and the FFT spots of the phase are also observed in the FFT, as marked in the figure 5.11(a). However, extra spots are also observed, as indicated in the figure. These spots have an identical symmetry with those shown in figure 5.12(b), which shows a FFT pattern obtained from a simulated Sc_5Si_3 HRTEM image along the [0110] axis. In addition, the measured interplanar spacings from these spots are also consistent with the values of bulk Sc_5Si_3 , as shown in Table 1.3. Hence, this data suggests that both Sc_3Si_5 and Sc_5Si_3 phases exist within single nanowires, which is consistent with the cross-section TEM data.



Fig. 5.10 (a) shows a low magnification TEM image of Sc silicide triangular nanowires grown on Si(001) substrates; (b) and (c) show two types of moiré fringes observed, with fringe spacings of 8.0–8.5 nm and 4.5–5.6 nm, respectively. Note that the moiré fringes in (b) are perpendicular to the nanowire long axis while those in (c) are parallel with long axis.



Fig. 5.11 (a) shows the FFT pattern of the nanowire in figure 5.8(a); (b) shows an FFT of a simulated high resolution TEM image of Sc₅Si₃ structure viewed along the [0110] axis. Some of the FFT spots in (a), marked by small circles, are consistent with those in (b), and assigned to Sc₅Si₃ phase. The rest of the FFT spots (Si spots excluded) in (a), marked by triangles, are assigned to Sc₅Si₅ phase.

5.2 Discussion and conclusion

STM morphology studies show that there are three different type of Sc silicide nanostructures present on Si(001) substrates, triangular nanowires, small nanowires, and tabular islands. All three types can be found on samples before post-deposition annealing. The small nanowires are 0.16 nm high, and the tabular islands are either 0.30 or 0.44 nm high, while the heights of triangular nanowires are larger than 0.5 nm. Once the samples are annealed, all the small nanowires and most of the tabular islands convert into larger and much longer triangular nanowires, with a small fraction of much smaller tabular islands.

Plan view TEM reveals that the triangular nanowires are composed of two phases, and cross-sectional TEM data clearly show that most triangular nanowires have two silicide layers with different phases: Sc_3Si_5 layer located at the Si-silicide interface, with a-axis perpendicular to the nanowire long axis, and a Sc_5Si_3 layer on top, with a-axis parallel with the long axis. This is consistent with the observation that most of the nanowires do not have moiré fringes in plan view TEM observations, since the electron beam transmits three different materials (two silicides and silicon) in this case, and, hence, the resulting image contrast are expected to be different from the moiré fringes caused by two overlapping materials with similar lattices. In addition, the dislocation and the lattice distortion seen at the interface between two silicide layers also contribute to the image contrast different from moiré fringes.

The cross section TEM data suggest that the triangular nanowires may develop on top of tabular islands. The size and the morphology suggest that the nanostructure in figure 5.9 is a tabular island. This nanostructure share common features with the bottom

layer of triangular nanowires shown in figure 5.6: both of them are 2~3 atomic layer thick, ~5 nm wide, and similar interplanar spacings. In addition, the STM image [figures 5.2(b)] and AFM image [figure 5.3(b)] shows that triangular nanowires can grow on top of tabular islands. All these observations may imply that triangular nanowires form on tabular islands.

The mechanism of the co-existence of the two phases in single nanowires needs more investigation. However, the phase diagram of Sc-Si system shown in figure 1.4 suggests that Sc_3Si_5 is preferred in a Si-rich environment, which is true since only a small amount of Sc was deposited on the Si substrates. In addition, it is expected that the Sc_3Si_5 phase form nanowires with the c-axis along the nanowire long axis, since this phase has an anisotropic lattice mismatch with respect to Si(001), with 0.78% mismatch along the c-axis and 4.7% mismatch along the a-axis. On the other hand, the phase diagram (figure 1.4) also shows that the Sc_5Si_3 phase has a higher melting temperature than Sc_3Si_5 . Hence, the Sc_5Si_3 phase is more energetically favorable, and may nucleate during annealing. The fact that the two silicide phases have between them one pair of lattice constants that match well in a 2:1 ratio may also facilitate the growth of one phase on the other. The balance of these two competing factors may result in the co-existence of two phases in single nanowires.

Chapter 6 Conclusion and suggestions for future work

6.1 Conclusion

This study has investigated the crystallography and epitaxial growth of several rare-earth metal (Gd, Dy, Tb, and Sc) silicides grown on Si(001) substrates by TEM and STM. It has been confirmed that the hexagonal form Gd, Dy, and Tb silicides grow into nanowires on Si(001) due to their anisotropic lattice mismatches with respect to substrates, and the orthorhombic or tetragonal phases of the silicides form nano-size islands due to their more isotropic lattice mismatch with the substrate. It was found that the lattice parameters of the silicide nanostructures do not significantly deviate from the bulk material values, suggesting that the nanostructures are almost fully relaxed. However, significant strains at the interface between the silicides and the silicon, and slight strain within the nanostructures are observed. Interfacial dislocations and lattice distortion may be introduced to relieve these strains, respectively. In addition, both STM and TEM studies suggest that phase transformation from the hexagonal to the orthorhombic or tetragonal phase may occur within single silicide nanostructures.

The Sc silicide nanostructure growth is more complicated than Gd, Dy, and Tb silicides, due to different anisotropic lattice mismatch system: Sc₃Si₅ has a good match with Si along the silicide c-axis, while the lattice constant along the a-axis is much larger, which is opposite to the Gd, Dy, and Tb silicides (small mismatch along the a-axis and large mismatch along the c-axis). However, the Sc silicide triangular nanowires, which form by post-deposition annealing, were found to have two silicide layers with different phases, and grow with length along the small lattice mismatch direction of the silicide,

 Sc_3Si_5 , in the bottom layer. Hence, the anisotropic lattice mismatch still plays a role in nanostructure morphology.

6.2 Growth control

The growth control of RE silicide nanowires and nano-size islands is attracting significant interest since the size of these nanostructures is below what the conventional fabrication techniques can reach. Hence, these structures have great potential for nano-devices and interconnects. However, fabrication of such devices and interconnects requires a thorough understanding of the nanostructure growth. The term "growth control" here means control of the nanostructure location and aspect ratio. Due to the nature of self-assembly, the silicide nanostructure growth on Si(001) depends highly on the substrate surface. Hence, the growth control may be achieved by finding ways to customize the substrate to accommodate the nanostructure growth. A good example is to grow Gd on vicinal Si(001): highly parallel Gd silicide nanowires are obtained due to the single domain surfaces of vicinal Si(001) (see more details for single domain surfaces in Appendix A).

At this point, no reports have been given on control of the location of the silicide nanostructures. Hence, it is valuable to study the nanostructure nucleation process, which leads to an understanding of the fundamental issues of how do silicides nucleate and what factors can affect the nucleation. Based on this understanding, customized substrate surfaces might be fabricated, allowing the nanostructure to be grown only on selected areas to build nano-components or interconnects for nano-devices.

The aspect ratios of the RE silicide nanowires may also be controlled by customized substrates. It has been shown that the nanowires do not cross the Si(001) terraces, which essentially can be interpreted as a barrier. Therefore, by fabricating barriers with designed patterns, possibly using lithography deposition, on substrates before the nanowire formation, the aspect ratios of the RE silicide nanowires might be controlled.

It is also important to understand the phase transformations that have been observed to occur within the nanostructures. Although two possible transformation mechanisms for the RE silicide nanostructures were proposed in Chapter 3, no explicit experimental observation on a real-time base has been carried out. Low energy electron microscopy (LEEM) or photoemission electron microscopy (PEEM) studies may be required to develop a better understanding of these transformations. A good understanding of the transformation may help to facilitate single phase nanostructure growth. Single phase nanostructures should, in general, increase the electrical and magnetic stability, over that of multiple phase nanostructures, which are of great importance in product applications.

6.3 Electrical and magnetic property evaluation of nanowires and islands

The electrical and magnetic properties of RE silicide nanowires and nano-size islands are of great interest. Without a clear understanding of these properties, applications of these nanostructures are not possible.

Although single Gd and Dy silicide nanowires have been confirmed to be metallic, no comprehensive study of the nanowire electrical properties has been done. By

depositing contacts on both ends of a nanowire, transport property measurement on single nanowires may be facilitated, leading to an understanding of related electrical properties. However, it is challenging to fabricate contacts, even using e-beam lithography methods, since the locations of self-assembled nanowires are still unpredictable. Knowledge of the magnetic properties of nanostructures is also of interest, as such structures may have potential for high-density data storage and logic applications

It has been elucidated that Sc silicide triangular nanowires are composed of two layers with different phases. Hence, this nanowire assembly is a self-assembled heteroepitaxial structure ($Sc_5Si_3 / Sc_3Si_5 / Si$). The overall properties of this complicated structure have not been evaluated, but may be very interesting since the stacking of three different materials/phases with nanometer sizes may produce novel properties.

APPENDIX A Si(001) and vicinal Si(001) surfaces

In this thesis, RE silicides nanostructures were always grown on Si(001) substrates, which included both Si(001) and single domain vicinal Si(001). Both of the surfaces of the regular and single domain vicinal Si(001) are introduced in this section on behalf of the further discussion in the thesis.

A.1 Si(001) surface

Bulk silicon has a diamond crystal structure, with lattice parameter of 0.543 nm and the space group of Fd3m, shown in figure A.1(a). If there is no surface reconstruction, Si(001) surface has a four-fold symmetry and a surface periodicity of $0.384 \text{ nm} (0.543 \times \frac{\sqrt{2}}{2} = 0.384 \text{ nm})$ along both Si<110> directions, as shown in figure A.1(b). However, the surface reconstruction drives neighboring Si atoms on Si(001) surface to form dimers, which reduce the surface energy by eliminating half of the dangling bonds [47], as shown in figure A.1(c). The formation of dimers results in the 2×1 surface reconstruction.

It should be pointed out that the dimer rows from one single Si(001) plane are all parallel with each other. This results in an anisotropic, 2-fold symmetric, surface, which will affect the growth direction of RE silicide nanowires. However, the dimers rotate 90° at every single height atomic step on the surface. This is the result of the diamond bulk crystal structure of silicon, where atoms on the a Si(001) plane have a different bonding orientation with that of the Si atoms from the next plane above or below, as sketched in figure A.2(a). This is confirmed by the STM observation of Si(001) surfaces, as shown in figure A.2(b). In the STM image, it is evident that the Si(001) surface is composed of two types of terraces with terrace height of 0.13 nm, which is consistent with the Si(001) interplanar spacing of 0.13nm, and the dimer rows on one terrace are perpendicular to those on the next terraces.

It was reported that the surface Si atoms on Si(001) have one partially occupied π orbital, and one occupied π^* -orbital, located at the center of a dimer.[*] When the sample is positively biased with respect to the tip (which is always held at virtual ground), tunneling electrons flow from the tip to the π -orbital. Hence, two maxima per dimer (corresponding to the dangling bonds at the ends of the dimer) are observed in STM images, as shown in figure A.3(a). When the sample is negatively biased, tunneling electrons go from the π^* -orbital to the tip, resulting in one maxima at the center of the dimer, as shown in figure A.3(b). These two imaging modes are called empty states (sample positively biased), and filled states (sample negatively biased), respectively. Because both of the modes are able to identify the dimer rows direction, mostly filled states will be shown in this thesis.



Fig. A.1 (a) silicon unit cell; (b) surface periodicity of Si(001) without surface reconstruction; (c): dimer formation on Si(001) due to the surface reconstruction, resulting in the 2×1 reconstruction.



Fig. A.2 Dimmer rows on neighboring Si(001) terraces are perpendicular with each other (a) schematic model (b) STM image.



Fig. A.3 STM images of Si(001) dimers at (a) empty states and (b) filled states. On the right of the STM images are the imaging models of dimers. 2×1 reconstruction is observed in both STM images, as marked by rectangular boxes.

A.2 Single domain vicinal Si(001) surface

Besides Si(001) substrates, single-domain vicinal Si(001) substrates are also used for the growth of RE silicides nanostructures. Their difference is that the surface of Si(001) is parallel with Si(001), while vicinal Si(001) is obtained by cutting silicon along Si(001) but a few degrees towards Si<1 $\overline{1}$ 0>.

More terraces and reduced terrace width are expected since the vicinal Si(001) surface is tilted compared to the Si(001). When the tilt angle is in excess of about 3.5°, then the parallel steps on the surface pair up, and the array of parallel double height steps results in a single domain surface. It is energetically favorable to have the Si dimer rows running perpendicular to the step direction on the terraces between the steps. An STM image of the vicinal Si(001) is shown in figure A4, indicating that there is mostly one terrace domain present on the surface. This allows us to grow well aligned RE silicide nanowires on a large scale, which make it possible to use some large probe spectroscopes (e.g. X-ray) to study the nanowires [25, 32].



Fig. A.4 empty states STM image of 4° vicinal Si(001) surface.

APPENDIX B List of publications

- Gangfeng Ye, Martin A. Crimp and Jun Nogami "Self-Assembled GdSi₂ Nanostructures Grown on Si(001) Studied by TEM and STM", Materials Research Society (MRS) Symposium Proceedings (2005 Fall), 901E 0901-Ra13-05
- Jiaming Zhang, Gangfeng Ye, R. Loloee, Martin A. Crimp and Jun Nogami "HRTEM and EELS Studies of GdSi₂ Nanostructures Grown by Self-Assembly", Materials Research Society (MRS) Symposium Proceedings (2005 Fall), 901E 0901-Ra22-39-Rb22-39
- 3. Gangfeng Ye, Jun Nogami and Martin A. Crimp "Dysprosium disilicide nanostructures on Silicon(001) studied by scanning tunneling microscopy and transmission electron microscopy", Thin Solid Films (2006), 497(1-2), 48-52
- 4. Gangfeng Ye, Martin A. Crimp and Jun Nogami "Crystallography study of dysprosium silicide nanostructures grown on Silicon(001)" (submitted)
- 5. Gangfeng Ye, Jun Nogami and Martin A. Crimp "Self-Assembled Gd Silicide Nanostructures Grown on Si(001)" (submitted)
- 6. Gangfeng Ye, Jun Nogami and Martin A. Crimp "Epitaxial growth and crystallography of Sc Silicide Nanowires Self-Assembled on Si(001)" (in preparation)

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