

Energetics of ultrathin CoSi_2 film on a Si(001) surface

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2003 J. Phys.: Condens. Matter 15 67

(<http://iopscience.iop.org/0953-8984/15/2/307>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.119

The article was downloaded on 19/05/2010 at 06:27

Please note that [terms and conditions apply](#).

Energetics of ultrathin CoSi₂ film on a Si(001) surface

Byung Sub Kang¹, Suhk Kun Oh¹, Hee Jae Kang¹ and Ki Soo Sohn²

¹ Institute for Basic Science, Department of Physics, Chungbuk National University, Cheongju, 361-763, Korea

² Department of Physics, Kyungpook National University, Daegu 702-701, Korea

E-mail: kangbs@nscience.chungbuk.ac.kr

Received 13 August 2002, in final form 12 November 2002

Published 20 December 2002

Online at stacks.iop.org/JPhysCM/15/67

Abstract

We present a first-principles study on the structural stability of Co silicide phases and their magnetic properties for 1–2 monolayers (ML) of Co deposited on Si(001). The Co–Si interaction between the nearest neighbouring sites at the surface layer is strongly attractive. The formation of CoSi in the subsurface layer is energetically more favourable than that in a surface layer. The interdiffusion of a Co atom to the fourfold (tetrahedral) site is found to be energetically favourable. For surface alloy films of 1 and 2 ML Co on Si(001), there are no Co atoms at the surface due to the interdiffusion of Co atoms. The structural stability of the ‘fourfold Si surface’ model with the CoSi₂ phase is compared with that of the sixfold model. Our result for the surface and interface of a thin CoSi₂/Si(001) film is consistent with experimental and other theoretical data.

1. Introduction

Co disilicide has been considered to be one of the most attractive candidates for contact and interconnect materials in spite of problems such as the formation of pinholes and misoriented grains, and the difficulty of growing high-quality epitaxial CoSi₂(100) films [1–4]. The importance of investigation of the silicidation of Co has been emphasized from various viewpoints [5–10]. The formation sequence of Co silicide in Si wafers deposited with a Co overlayer upon thermal annealing was observed as $\text{Co} + \text{Si} \rightarrow \text{Co}_2\text{Si} \rightarrow \text{CoSi} \rightarrow \text{CoSi}_2$ [11–13]. Here we address the following questions: what are energetically the most favourable geometries of key phases during the deposition of Co atoms on Si? What dominant diffusing species occur on the surface and at the interface? Despite a lot of work done in this area the mechanism of reactions is not fully understood. Most experiments do not provide information at the atomic length scale. The exceptions are experiments treating very low coverages of Co on Si(001) [14, 15], and calculations investigating the detailed structure of thin Co film on Si [16, 17].

Microprocessors are already being manufactured for which the insulating oxide on a metal–oxide–semiconductor field-effect transistor gate is only 13 Å thick. This is of the order of ten atomic layers. At this length scale individual atoms are beginning to matter. So, in systems of few monolayers (ML) thick, we need more investigations to understand the formation process of Co silicides. This subject of energetics for the atomic length scale is very important for the development of next generation devices using high performance material. In order to obtain more precise understanding of the ground state properties during the early stage in the deposition of Co on the Si substrate, we carry out first-principles electronic structure calculations for 1–2 ML Co films on a Si(001) surface, which includes CoSi surface alloy films having the stoichiometries Co₂Si, CoSi and CoSi₂. Furthermore, we study the energetics for the structural model of a thin film with a CoSi₂ phase. Thereby, based on our calculated results, we can make predictions for the structural stability and atomic structure of thin films. We also discuss the magnetic properties of thin Co/Si(001) films. In section 2, we outline the method used in the numerical calculations. Our results and comparison with experimental data are described in section 3. In the final section, a summary is given.

2. Computational method

The atomic structure of Co/Si(001) is modelled by a periodically repeated slab (=substrate + film) with a (2×2) surface cell. It consists of 13 and 15 layers in the cases of 1 and 2 ML Co, respectively, separated by seven layers of vacuum. We use a full-potential linear muffin-tin orbital (FPLMTO) method which makes no shape approximation for the crystal potential. Detailed information about the FPLMTO method can be seen in the recent articles [18–20]. The linear muffin-tin orbital (LMTO) basis in the vacuum regions consists of sets of appropriate s, p and d states. The crystal is divided into regions inside the atomic sphere and the interstitial region. The ‘full’ charge density including all nonspherical terms is evaluated by Fourier transformation in the interstitial region. The basis functions in the interstitial region are expanded by the smoothed Hankel functions [19]. The basis functions of Si and Co for the s, p and d electrons are generated with cut-off energy of $E_{cut} = 204.00, 296.48$ and 432.48 eV, respectively. The Co 3p electrons are treated as a semicore orbital and we do not use the frozen overlapped core approximation. Spin–orbit interactions are not included. The valence electrons are treated semi-relativistically with the local density approximation, using the exchange–correlation potential of Janak *et al* [21] within the generalized gradient approximation (GGA).

The k -space integrations are performed with the tetrahedron method. The linear tetrahedron method including the corrections of Blöchl *et al* [22] is chosen to improve the convergence of the electronic structure and total energy with respect to the number of k points. Using 45 k points corresponding to a $16 \times 16 \times 1$ grid insures that the total energy and magnetic moment are converged to better than 1 meV/cell and $0.01 \mu_B/\text{atom}$, respectively. In addition, $16 \times 16 \times 112$ mesh points in real space are used for calculating integrals of the potential over the interstitial region.

3. Results and discussion

The calculated equilibrium lattice constant for the bulk Si is 5.401 Å, which is used to set the lattice coordinates of the supercell. This value is slightly smaller than the experimental one of 5.428 Å. The supercell used in the calculations is sufficient to determine the atomic structures of surface alloy films with intermixing of Co and Si atoms in a few surface layers.

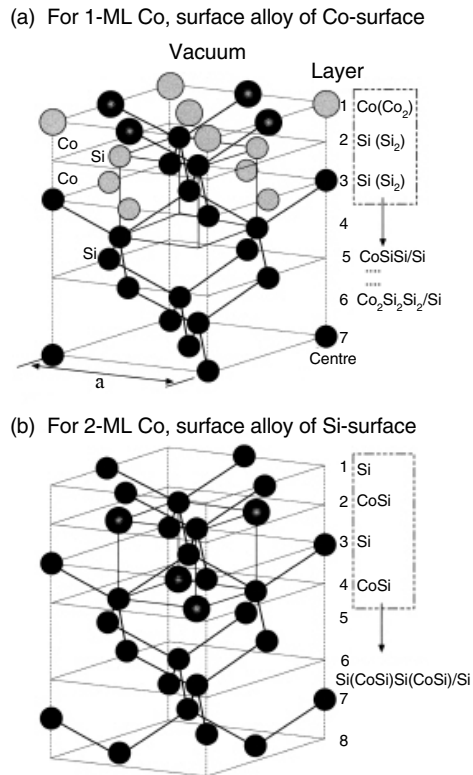


Figure 1. Structural model for two different terminated surfaces with 1 and 2 ML Co deposited on Si(001). (a) The layered Co–Si–Si or Co₂–Si₂–Si₂ atomic structure of the Co surface with 1 ML Co, (b) the layered Si–CoSi–Si–CoSi structure of the Si surface with 2 ML Co (right-hand boxes). Other layered structures of 2 ML Co are listed in table 2. For 1 ML Co, they are excluded from the table. The representation of Si₂ or Co₂ in square brackets means the lattice structure which includes grey small or big filled circles, which consists of twice as many atoms in each atomic layer. The solid line represents a diamond lattice. The light solid line represents the structure of a half lattice constant.

3.1. Structural model of thin Co/Si(001) film

We take the atomic structures of three different terminated surfaces in the cases of 1–2 ML Co deposited on Si(001). We consider the lattice structures consisting of a Co-terminated surface (Co surface), a Si-terminated surface (Si surface) and a CoSi-terminated surface (CoSi surface). They have the layered Co–Si–Si, or Si–Co–Si or CoSi–Si–Si (i.e., the top three layers) structure for 1 ML Co and the layered Co–Si–Co–Si, Si–Co–Si–Co or CoSi–Si–CoSi–Si (i.e., the top four layers) structure for 2 ML Co. The atomic structures for the Co surface of 1 ML Co and the Si surface of 2 ML Co are displayed in figure 1. Other structures for 2 ML Co are presented in table 2. The representations of Si₂ and Co₂ in square brackets of figure 1 and table 2 mean the lattice structure which consists of twice as many atoms in each layer of alloy film. For instance, for 2 ML Co the layered Co–Co–Si–Si, Co–Si–Co–Si, Si–Co–Co–Si, Si–Co–Si–Co and Si–Si–Co–Co structures on the substrate are a diamond lattice, which consists of eight atoms in a conventional unit cell. The layered Si–Co₂–Si–Co₂ structure of the Co₂Si phase (i.e., SiCo₂SiCo₂/Si(001)) is an fcc lattice containing a simple cubic array of Co atoms which consists of a half lattice constant inside the unit cell (light solid line in figure 1). The layered

Table 1. The interdiffusion, cluster formation and segregation energies (in units of eV). The interdiffusion and the cluster energy are defined as $E_{\text{SiCo/Si}}^{\text{total}}(\Delta z) - E_{\text{CoSi/Si}}^{\text{total}}(\Delta z)$ and $E_{(\text{CoSi})/\text{Si}}^{\text{total}}(\Delta z) - \frac{1}{2}(E_{(\text{CoCo})/\text{Si}}^{\text{total}}(\Delta z) + E_{(\text{SiSi})/\text{Si}}^{\text{total}}(\Delta z))$, respectively. At present, the interlayer relaxation is neglected ($\Delta z = 0$). Here T_s denotes the interdiffusion from the Co site of $c(2 \times 2)$ surface structure to a tetrahedral (fourfold) site. D_e denotes the direct exchange between adatom Co and Si atoms without changing the Si lattice structure. The results are obtained from calculations neglecting any atom relaxation.

Interaction	Model	Energy difference (eV/atom)
Interdiffusion	T_s	-1.434
	D_e	-0.990
Clustering		-0.975
Segregation		+0.345

$\text{Si}_2\text{-Co-Si}_2\text{-Co}$ structure of the CoSi_2 phase, if we consider only the top three layers, consists of four subcells which have two simple cubic arrays of Si atoms and two bcc lattice arrays of Si atoms containing a Co atom at their centre. The layered Si-CoSi-Si-CoSi structure of figure 1(b) is an fcc lattice, which arranges the atoms of other kinds at the corners of a simple cubic array which consists of a half lattice constant inside the unit cell. The sites of Co atoms in figure 1(b) are the tetrahedral (fourfold) sites. The lattice structures having the Co_2Si and CoSi_2 phases consist of 12 atoms in a unit cell. For the Co_2Si_2 film of the CoSi phase, the layered $\text{Co}_2\text{-Si}_2\text{-Co}_2\text{-Si}_2$ or $\text{Si}_2\text{-Co}_2\text{-Si}_2\text{-Co}_2$ structure of the top three layers consists of four subcells of bcc lattice arrays of Co or Si atoms containing a Si or Co atom at their centre. The total number of atoms in the top five layers of a unit cell is 14 atoms.

The reason we consider these lattice structures for the deposited Co atoms on the Si substrate is as follows. First, as shown in table 1, the cluster formation energy between Co and Si atoms in the nearest neighbouring sites at the surface is compared with the interdiffusion energy of Co to the tetrahedral site below the surface layer and the interdiffusion energy between Co and Si atoms without a change of Si lattice (i.e., substitution). The value of -0.975 eV is comparable with the previous works [17, 23]. The interdiffusion of the Co atom is energetically more favourable than the formation of the cluster at the surface layer. This shows that the Co atom at the subsurface layer is energetically more favourable than the surface layer. Here, the energy of cluster formation is defined as the difference in total energies between the system of the ordered CoSi $c(2 \times 2)$ structure and the average of total energies determined by 1 ML Co and 1 ML Si structures on $\text{Si}(001)$. That is, it describes the interaction between the nearest neighbouring sites of Co and Si atoms at the surface layer. The clustering is modelled by the formation of 1 ML of adatoms. The formation of thicker layers is neglected in this paper. In these calculations, we find that the paramagnetic state is energetically more favourable than the magnetic state. Next, we consider the energetics of the Co silicides with the stoichiometries of CoSi , Co_2Si and CoSi_2 , which are the possible structures occurring during the deposition of Co atoms on $\text{Si}(001)$. This will be discussed in the next section. We also discuss the interdiffusion and surface segregation of Co in detail. Accordingly, these works provide an opportunity to study the geometries of the structures of the ultrathin film, which reveal some general ideas about the annealing mechanisms.

3.2. The energetic stability and magnetic properties

We calculate the structural energies of 1–2 ML $\text{Co/Si}(001)$ systems in the nonmagnetic (P) and ferromagnetic (F) configurations. In order to investigate the energetically favourable

structure, we compare their structural energies for various CoSi surface alloy films having different stoichiometries. The stability of surface alloy films of CoSi, Co₂Si and CoSi₂ phases is investigated in terms of structural energy,

$$\Delta E_S(\{M\}, \{\Delta z_M\}) = \frac{1}{2}[E_{(\text{CoSi})/\text{Si}}(M, \Delta z_M) - \{2E_{\text{free Co ML}}(M) + E_{\text{substrate}}(\Delta z)\}], \quad (1)$$

which denotes the total energy difference between the systems containing surface alloy ($E_{\text{CoSi}/\text{Si}}(M, \Delta z_M)$) and the sum of total energies determined by isolated 1 ML Co ($E_{\text{free Co ML}}(M)$), and the clean Si(001) surface ($E_{\text{substrate}}(\Delta z)$). The structural energy depends on the magnetism ($M = \text{P, F}$) of surface alloys as well as the atomic positions of each of the three terms entering equation (1). One should at least include the minimum energy relaxation of surface layers in each of the first and third terms.

The formation of Co silicides on Si(001) may not be simple. The stability for the structure of CoSi or Co₂Si phase may be lower than that of CoSi₂ phase at least. As we see in table 2, the stability of various Co silicides according to their structural energies is as follows: CoSi < Co₂Si < CoSi₂. For the surface alloy films of 1–2 ML Co, the energetically favourable phase is CoSi₂. The energetically favourable structures are Si₂CoSi/Si(001) and Si₂CoSi₂Co/Si(001) for 1 and 2 ML Co, respectively. In this paper, these atomic structures are called the ‘sixfold Si surface’ structural model. The atomic structure of 2 ML Co consists of a Si–Co–Si–Co layered one [24].

In table 2 or figure 2, we compare the structural energies resulting from non-spin-polarized and spin-polarized calculations for the 2 ML Co film on Si(001). $\Delta E_S(\text{P}, 0)$ and $\Delta E_S(\text{F}, 0)$ are negative for all Co silicide phases. The phase separation energy ($-\Delta E_S$) is relatively large for all Co silicide phases. The phase separation for the surface alloy films by 2 ML Co is rather larger than the case of a 1 ML CoSi surface alloy film (not listed in the table). The magnetic state is not energetically more stable than the paramagnetic state. For Co/Si since the Co atom remains the nonmagnetic state, $\Delta E_S(\text{P}, 0)$ is the structural energy of the ground state. The 1 ML Co overlayer film on Si(001) is nonmagnetic, while the 2 ML Co overlayer film is antiferromagnetic with a magnetic moment of $-1.55 \mu_B/\text{atom}$. But, the magnetic exchange splitting is low (~ 0.68 eV, determined by the energies of spin-up and spin-down states). As shown in table 2, the magnetic state of a structure such as SiSiCo₂Co/Si(001) or SiSiCo₂Co₂/Si(001) is energetically more favourable than the nonmagnetic one. However, the Stoner criterion is not satisfied. That is, it does not form a magnetically stabilized CoSi surface alloy film. From the ratio of exchange splitting to magnetic moments we can estimate a Stoner parameter (in units of eV/ μ_B).

In order to further investigate the formation of a thin Co silicide film on Si(001), we discuss the interdiffusion and surface segregation of Co atoms. The interdiffusion energy (D_e in table 1) is determined by the difference in total energy of the SiCo/Si buried system as an interlayer in Si(001) and that of the CoSi/Si system as an overlayer on Si(001) (i.e., a substitutional surface alloy). The method of calculation is presented in the caption of table 1. The calculated result in energy is negative, which means that the Co atom gains energy by interdiffusion. The interdiffusion energies for the cases of T_s and D_e are -1.434 and -0.990 eV, respectively. The interdiffusion energy for the case of T_s in table 1 is defined as the difference in total energies between the tetrahedral Co system in the subsurface and the surface Co system (i.e., the $c(2 \times 2)$ surface structure). Here there is a difference between the systems of T_s and D_e . We proceed to the discussion of the surface segregation energy of the Co atom. The surface segregation energy is defined as the energy difference between the Co atom in the first surface layer and that in the bulk. The calculated surface segregation energy of Co is a positive value of $+0.345$ eV/atom. Positive energy means that the surface position of the Co atom is unfavourable. The positive segregation energy of Co can be modelled by Co–Si bonds being stronger than Si–Si bonds.

Table 2. The structural energies (in units of eV) for CoSi surface alloy films for each case of 2 ML Co deposited on Si(001). P and F denote the nonmagnetic and ferromagnetic states, respectively. In order to be more precise, this table is redisplayed in figure 2.

Phase	Atomic structure									
	CoCoSiSi/Si		CoSiCoSi/Si		SiCoCoSi/Si		SiCoSiCo/Si		SiSiCoCo/Si	
	P	F	P	F	P	F	P	F	P	F
2(CoSi)	-3.45	-2.74	-4.21	-2.88	-4.54	-3.17	-5.24	-3.73	—	
3(CoSi)	CoCo ₂ Si ₂ Si/Si		Co ₂ Si ₂ CoSi/Si		Si ₂ Co ₂ CoSi/Si		Si ₂ Co ₂ SiCo/Si		SiSi ₂ Co ₂ Co/Si	
	-5.61	-3.76	-8.25	-6.39	-7.18	-5.55	-8.07	-6.26	-5.92	-5.93
	—		CoSiCo ₂ Si ₂ /Si		SiCoCo ₂ Si ₂ /Si		SiCoSi ₂ Co ₂ /Si		—	
	—		-6.24	-4.69	-6.46	-4.75	-9.87	-8.02	—	
4(CoSi)	—		CoSi ₂ Co ₂ Si/Si		Si ₂ CoCo ₂ Si/Si		Si ₂ CoSiCo ₂ /Si		—	
	—		-9.46	-7.60	-6.93	-5.11	-7.76	-5.95	—	
	Co ₂ Co ₂ Si ₂ Si ₂ /Si		Co ₂ Si ₂ Co ₂ Si ₂ /Si		Si ₂ Co ₂ Co ₂ Si ₂ /Si		Si ₂ Co ₂ Si ₂ Co ₂ /Si		Si ₂ Si ₂ Co ₂ Co ₂ /Si	
	-3.22	-1.31	-9.29	-7.44	-8.35	-6.55	-10.64	-9.42	-6.94	-5.54
2(CoSi ₂)	CoCoSi ₂ Si ₂ /Si		CoSi ₂ CoSi ₂ /Si		Si ₂ CoCoSi ₂ /Si		Si ₂ CoSi ₂ Co/Si		—	
	-4.70	-3.20	-5.23	-3.98	-8.99	-7.49	-11.43	-9.93	—	
2(Co ₂ Si)	Co ₂ Co ₂ SiSi/Si		Co ₂ SiCo ₂ Si/Si		SiCo ₂ Co ₂ Si/Si		SiCo ₂ SiCo ₂ /Si		SiSiCo ₂ Co ₂ /Si	
	-2.88	-2.09	-3.09	-1.19	-5.04	-3.14	-4.61	-4.61	-2.42	-2.53

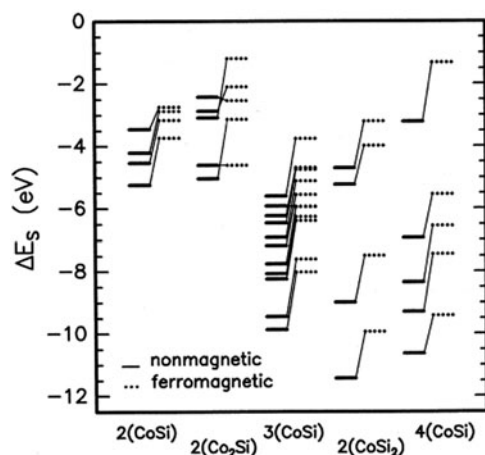


Figure 2. The structural energies (ΔE_s) for each Co silicide phase. This figure is plotted with table 2 to be more precise.

We also find that the structural energies of the Co atoms in the second and third layers are lower by -0.644 and -0.211 eV/atom, respectively, as compared with that of the bulk. The structural energy in the bulk site is settled to be zero. The Co atom in the subsurface site is energetically more favourable than at the surface as well as in the bulk sites. The Co atoms in the subsurface show very weak energetic driving force to the surface. Therefore, for 1–2 ML Co we can safely assume that the barrier for interdiffusion is small. Thus the interdiffusion of deposited Co atoms below the surface layer occurs easily. This configuration is consistent with the results of experimental works [10, 25]. Accordingly, the Co overlayer will disappear; a thin film of CoSi₂ phase is produced by the interdiffusion. The 1 or 2 ML Co deposited as overlayers on Si(001) is unstable against surface alloy formation. This is reasonable if we recall our results for the structural stability.

Table 3 illustrates the cohesive energies for each structural model. For Si₂CoSi/Si(001) and Si₂CoSi₂Co/Si(001), the calculated cohesive energies per surface alloy film in the nonmagnetic state are 9.63 and 16.06 eV, respectively. The cohesive energies per film for the ‘fourfold Si surface’ structural model of 1–2 ML CoSi surface alloy films having the CoSi₂ phase are 10.16 and 17.34 eV, respectively. The cohesive energy is defined as the difference in total energies between free Co atoms and the CoSi alloy film. Here, the ‘film’ for 1 ML Co corresponds to the top three layers in the 13-layer slab. For 2 ML Co the film corresponds to the top four layers of the 15-layer slab. The structures of the fourfold Si surface in each case of surface alloy films of 1–2 ML Co are energetically more favourable than the ‘fourfold CoSi surface’ as well as the sixfold Si surface structures.

From the results of tables 2 and 3, we can see that the formation of Co silicides at the interlayer rather than at the first surface layer is energetically favourable. This shows that a cluster can be formed by interdiffusion into deeper layers. The difference in the formation energies between the hexagonal and tetrahedral interstitial sites is very small [17]. As the concentration of Co increases, the tetrahedral sites fill up and an expansion of the crystal takes place. As shown in table 3, we find that the formation of surface dimers for the 2 ML Co/Si(001) structures is unstable. Thus for the structure of Si(CoSi)Si(CoSi)/Si(001) with 2 ML Co, the calculated result in the relaxation perpendicular to the surface is as follows. The outward relaxation of the surface layer is 0.17 Å. A slab expands by 3.15% as compared

Table 3. The comparison with sixfold and fourfold structural models. Here, the ‘film’ in the unit for 1 and 2 ML Co corresponds to the top three and four atomic layers, respectively. P and F denote the nonmagnetic and ferromagnetic states, respectively.

Phase	Model	Structure (film/Si(001))	Reconstruction dimer	Cohesive energy (eV/film)	
1 ML Co on Si(001)				P	F
CoSi		CoSiSi/Si	—	6.78	5.57
		SiCoSi/Si	—	7.76	6.56
CoSi ₂	Sixfold Si surface	Si ₂ CoSi/Si	—	9.63	8.42
		SiCoSi ₂ /Si	—	9.39	8.18
CoSi ₂	Fourfold CoSi surface	(CoSi)SiSi/Si	—	9.93	8.72
	Fourfold Si surface	Si(CoSi)Si/Si	—	10.16	8.96
2 ML Co on Si(001)				P	F
CoSi ₂	Sixfold Si surface	Si ₂ CoSi ₂ Co/Si	Unstable	16.06	13.64
CoSi ₂	Fourfold CoSi surface	(CoSi)Si(CoSi)Si/Si	Unstable	14.43	12.01
	Fourfold Si surface	Si(CoSi)Si(CoSi)/Si	Unstable	17.34	14.92

Table 4. Surface and interface structure for the fourfold Si surface model of Si(CoSi)Si(CoSi)/Si(001) in Å. Δd_{ij} represents the change in the interlayer distance. The supercell is a slab with 15 atomic layers.

Layers (L)	Positions			Δd_{ij} (%)
	(X)	Y	Z)	
1st L Si	0.000	2.701	9.620	− 4.02(+10.20)
2nd L Co(Si)	1.350(1.350)	4.051(1.350)	8.324(8.132)	+ 16.35(+2.13)
3rd L Si	0.000	0.000	6.753	− 5.79(+1.98)
4th L Co(Si)	1.350(1.350)	1.350(4.051)	5.481(5.376)	+ 10.42(+2.65)
5th L Si	0.000	2.701	3.990	− 2.53
6th L Si	1.350	1.350	2.674	− 1.92
7th L Si	0.000	0.000	1.351	+ 0.02
Centre L Si	1.350	4.051	0.000	—

with the bulk lattice. The relaxations of Co and Si atoms in the second layer are +0.22 and +0.03 Å, respectively. For the second and fourth layers of 2 ML Co, a buckling of about 0.19 and 0.10 Å between Co and Si atoms takes place. These results are listed in table 4. After relaxation it shows that the structure becomes more stable, and the change of structural energy is very small. The equilibrium surface structure is determined through atomic force calculations with Pulay corrections for the change of atomic position [19].

3.3. The electronic properties

The electronic states of Si on the surface and interface sites are similar to those in the bulk Si in term of sp^3 hybridization. Formation of the compounds CoSi₂, CoSi and Co₂Si leads to a narrowing of the main peak of the Co d band, to a shift of its centre of gravity to lower binding energies and to the appearance of bonding and antibonding states between Si p and Co d electrons (not shown in the figure).

Let us take a closer look at the calculated density of states (DOS) for the systems of 1–2 ML Co deposited on Si(001). Figure 3 shows the local DOS of Co for the most energetically favourable structure in the 1 and 2 ML Co/Si(001) systems (see table 3). The electronic structures of the Co silicide compounds differ from those of pure Co metal. The Co DOS peak for the Si(CoSi)Si/Si(001) system of 1 ML Co is located at −1.70 eV below E_F . The

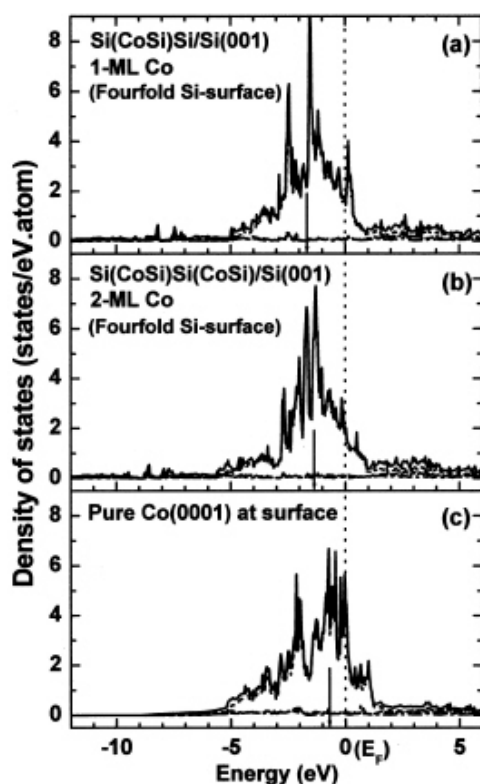


Figure 3. The calculated DOS for the most energetically favourable structure of (a) 1 ML, (b) 2 ML Co deposited on Si(001) and (c) pure hcp Co(0001) metal with ferromagnetism. (b) and (c) represent the average DOS of the surface and subsurface Co sites. (c) represents the average of the sum of up-and down-spin DOSs. Dash-dot, dash, dot and solid lines represent s, p, d and total electrons, respectively. Arrows indicate the positions of the main peak.

position of the Co DOS main peak is consistent with the result of photoemission spectroscopy data [26]. The main peak of the DOS for the Si(CoSi)Si(CoSi)/Si(001) system of 2 ML Co shifts toward E_F by 0.24 eV as compared with the Si(CoSi)Si/Si(001) system of 1 ML Co. For the pure Co(0001) system, it is located at -0.69 eV below E_F . The value of main peak position is comparable with spin-resolved inverse photoemission (IPE) data of a 10 ML thick Co(0001) film [27]. As the thickness of the Co layer increases, even if the result for a thicker Co layer is needed, the main peak of the DOS shifts toward E_F . This configuration clearly shows that the metallic Co grows gradually with the increase in the amount of deposited Co. The curves of (b) and (c) in figure 3 are the average DOS of the surface and subsurface sites of Co.

4. Conclusion

Detailed calculations for the structures of 1–2 ML CoSi surface alloy films on a Si(001) substrate have been performed. We have found that the interaction between Co and Si atoms at the surface is attractive. Even though there exists the complexity of the processes taking place for the formation of Co silicides, the obtained results from *ab initio* calculations suggest that the following sequence of events takes place during the deposition of Co on Si(001). The formation of CoSi surface alloy film is energetically more favourable than that of a Co film

as an overlayer on Si(001). The Co atom in the subsurface is energetically more favourable than at the surface as well as in the bulk. If there are no more Co atoms at the surface by interdiffusion, a thin film of CoSi₂ phase is produced at the silicide/Si interface. For a surface alloy film of 1 or 2 ML Co on Si(001), it turns out that the energetically stable structure is the fourfold Si surface structural model with the CoSi₂ species. In conclusion, these results suggest that the interdiffusion into the substrate (tetrahedral site) and the segregation of Co allows further growth of the layered Si–CoSi–Si–CoSi structure in the silicide/Si(001). The electronic structure of CoSi ultrathin film on Si(001) agrees with the experimental and other theoretical data.

Acknowledgment

This work was supported by the Korea Research Foundation, grant No KRF-2001-005-D20009.

References

- [1] Ikegami H, Ikeda H, Zaima S and Yasuda Y 1996 *Advanced Metallization and Interconnect Systems for ULSI Applications in 1995 (MRS Bulletin)* ed R C Ellwanger and Shi-Qing Wang (Pittsburgh, PA: Materials Research Society) p 511
- [2] Schowalter L J, Jimenez J R, Hsiung L M, Rajan K, Hashimoto S, Thompson R D and Iyer S S 1991 *J. Cryst. Growth* **111** 948
- [3] Stalder R, Schwarz C, Sirringhaus H and von Kanel H 1992 *Surf. Sci.* **271** 355
- [4] Hayashi Y, Matsuoka Y, Katoh T, Ikegami H, Ikeda H, Zaima S and Yasuda Y 1998 *Advanced Metallization and Interconnect Systems for ULSI Applications in 1997* ed R Cheung, J Klein, K Tsubouchi, M Murakami and N Kobayashi (Warrendale, PA: Materials Research Society) pp 663–8
- [5] Murarka S P 1983 *Silicides for VLSI Applications* (New York: Academic) pp 72–7
- [6] Nemanich R J, Fiordalice R and Jeon H 1989 *IEEE J. Quantum Electron.* **25** 997
- [7] Hensel J C, Tung R T, Poate J M and Unterwald F C 1984 *Appl. Phys. Lett.* **44** 913
- [8] Ikegami H, Ikeda H, Zaima S and Yasuda Y 1997 *Appl. Surf. Sci.* **117/118** 275
- [9] Prokop J, Zybill C E and Veprek S 2000 *Thin Solid Films* **359** 39
- [10] Plusnin N I, Milenin A P and Prihod'ko D P 2000 *Appl. Surf. Sci.* **166** 125
- [11] Lau S S, Mayer J W and Tu K N 1978 *J. Appl. Phys.* **49** 4005
- [12] Lien C-D, Nicolet M-A, Pai C S and Lau S S 1985 *Appl. Phys. A: Solids Surf.* **36** 153
- [13] Heo Jinhwa and Jeon Hyeongtag 2000 *Thin Solid Films* **379** 265
- [14] Bennett P A, Cahill D G and Copel M 1994 *Phys. Rev. Lett.* **73** 452
- [15] Scheuch V, Voigtländer B and Bonzel H P 1997 *Surf. Sci.* **372** 71
- [16] Voigtländer B, Scheuch V and Bonzel H P 1997 *Phys. Rev. B* **55** R13444
- [17] Horsfield A P and Fujitani H 2001 *Phys. Rev. B* **63** 235303
- [18] Agrawal B K, Agrawal S and Srivastava P 1998 *Surf. Sci.* **408** 275
- [19] Savrasov S Yu and Savrasov D Yu 1992 *Phys. Rev. B* **46** 12181
Savrasov S Yu 1996 *Phys. Rev. B* **54** 16470
Savrasov S Yu 1994 *Phys. Rev. Lett.* **72** 372
- [20] Kang B S, Oh S K, Chung J S and Sohn K S 2001 *Physica B* **304** 67
- [21] Moruzzi V L, Janak J F and Williams A R 1978 *Calculated Electronic Properties of Metals* (New York: Pergamon)
- [22] Blöchl P E, Jepsen O and Andersen O K 1994 *Phys. Rev. B* **49** 16233
- [23] Pretorius R, Harris J and Nicolet M-A 1978 *Solid State Electron.* **21** 667
- [24] Rossi G, Santaniello A, De Padova P, Jin X and Chandresris D 1990 *Europhys. Lett.* **11** 235
- [25] Lee M Y and Bennett P A 1995 *Phys. Rev. Lett.* **75** 4460
- [26] Weaver J H, Franciosi A and Moruzzi V L 1984 *Phys. Rev. B* **29** 3293
Rangelov G, Augustin P, Stober J and Fauster Th 1994 *Phys. Rev. B* **49** 7535
- [27] Math C, Braun J and Donath M 2001 *Surf. Sci.* **482–485** 556