

Density functional study of the initial stage of the anneal of a thin Co film on Si

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Plane-wave pseudopotential calculations are performed to study the initial stages of an anneal of a thin Co film/Si couple. Preliminary calculations provide $\text{Co}_x\text{Si}_{1-x}$ structures and formation energies that are in reasonable agreement with experiment. The early stages of the anneal are then investigated from two viewpoints: starting from Co_2Si , and working backward in time; starting from bulk Si with low concentrations of Co, and working forward in time. The latter viewpoint indicates that the barrier to the growth of Co_2Si is the formation of isolated Co interstitials. Once formed, they diffuse quickly and find it energetically favorable to form clusters. These clusters then bring about a reconstruction of the lattice. The former viewpoint suggests that an intermediate structure consisting of equal numbers of Co and Si atoms exists that can transform either into Co_2Si by the addition of Co interstitials, or into CoSi by shearing. This provides an explanation of the simultaneous growth of CoSi and Co_2Si .

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I. INTRODUCTION

CoSi_2 is used to form low resistivity contacts in semiconductor devices.¹ Its popularity is based on the following properties: it has a very low resistivity ($14\text{--}17 \mu\Omega \text{ cm}$);² the anneal needed to bring about the phase transition from CoSi to CoSi_2 after growth occurs at a low temperature (around 620°C);¹ its lattice constant³ (5.365 \AA) is very close to that of crystalline Si (5.43 \AA), allowing for defect-free epitaxial growth; because it is a silicide, growth from previously deposited Si ensures that the gate contact is properly aligned.

The usual process for making CoSi_2 films is to deposit a Co film on a Si (001) surface, followed by an anneal. Co reacts with Si in a series of stages, leading ultimately to a CoSi_2 film on the Si substrate, with a very sharp interface between the two phases.

Extensive experimental work has been performed,^{2–29} from which we have learned much about the stages that the Co/Si system passes through, and the species that diffuse, during an anneal. The established series of events during the anneal for a thin Co film is as follows (thick layers yield a different sequence¹²). First, Co diffuses into the Si substrate forming Co_2Si and CoSi, with the CoSi layer lying between the Si substrate and the Co_2Si layer. The CoSi layer grows more slowly than the Co_2Si layer.^{4,6} The growth is characterized by an energy barrier of 1.5 eV .⁴ The Co_2Si layer grows at the $\text{Co}_2\text{Si}/\text{CoSi}$ interface, while the CoSi layer grows at the CoSi/Si interface.⁶ Once all the Co has been consumed, the Co_2Si layer transforms into CoSi. This is dominated by Si diffusion through the CoSi layer, possibly by means of a vacancy mechanism, and is characterized by an energy barrier of 1.9 eV .⁴ Finally, the CoSi layer transforms into CoSi_2 . It is probable that the dominant diffusing species is Co, though there is some uncertainty.¹⁶ This is initially a nucleation limited process, with $\text{CoSi}/\text{CoSi}/\text{Si}$ triple points acting as nucleation sites. Once nucleated, the

growth becomes diffusion limited.⁵

Most of the experiments cited above do not provide information at the atomic length scale. Important exceptions are experiments treating very low coverages of Co on Si (001),^{9,13,20,26} and experiments investigating the detailed structure of the final CoSi_2 film.^{8,11,17,19,21} However, in this paper we are interested in the complex processes that take place during the early stages of the anneal of a Co/Si couple. These do not fall into the above categories. Consequently we know very little about what is happening during these stages at the level of the atom. This is obviously unsatisfactory from a scientific point of view, but also problematic for technology. Microprocessors are already being manufactured for which the insulating oxide on a metal-oxide-semiconductor field-effect transistor gate is only 15 \AA thick. This is of order 10 atomic layers. At this length scale individual atoms are beginning to matter, so our understanding must reach down to the atomic level if future development is to be guided by knowledge rather than chance.

In this work, density functional theory is used to provide insights into what happens during the early stage of the anneal at the level of the atom. Three questions are addressed: (1) What do the geometries of key phases tell us about the reactions that take place during an anneal? (2) What are the energetics of key reactions? (3) What processes take place at the level of the atom during the early stages of the anneal of a Co/Si couple?

The calculated geometries of the important $\text{Co}_x\text{Si}_{1-x}$ structures are found to be in good agreement with experiment. The calculated lattice constants are always slightly smaller than the experimental ones, but the errors are less than 1.4%. The formation energies of the relevant structures are in reasonable agreement with experiment (the silicides are overbound by about 0.13 eV per atom), and are found to ensure that all observed reactions are exothermic. Thus the calculations should yield qualitatively correct results.

The early stages of the anneal are then investigated from

two viewpoints. First, starting from Co_2Si and working backward in time; second, starting from bulk Si with low concentrations of Co, and working forward in time. The latter viewpoint indicates that the barrier to the growth of Co_2Si is the formation of isolated Co interstitials. Once formed, Co interstitials diffuse quickly and find it energetically favorable to form clusters. These clusters then bring about a reconstruction of the lattice. The former viewpoint suggests that an intermediate structure consisting of equal numbers of Co and Si atoms exists that can transform either into Co_2Si by the addition of Co interstitials, or into CoSi by shearing. This provides an explanation for the observed simultaneous growth of CoSi and Co_2Si .

II. PRELIMINARY CALCULATIONS

As a test of the methods used in this work, the energetics and structures of the main phases (Co, Si, CoSi, Co_2Si , and CoSi_2) that appear during the anneal of the Co/Si system are studied. This also provides an opportunity to review the geometries of these structures, which reveal some general ideas about the anneal mechanisms.

All the calculations are based on the Kohn-Sham formulation of the density functional theory of the electron gas.³⁰ Vanderbilt ultrasoft pseudopotentials³¹ are used, with nonlinear core corrections³² included for Co. The plane-wave basis set is well converged (a cutoff of 340 eV is used throughout). The gradient corrections of Perdew, Burke, and Ernzerhof³³ are used for the exchange and correlation functional. The primitive translation vectors and the atomic coordinates are relaxed simultaneously. All calculations are performed using CASTEP.³⁴ Pure Co is ferromagnetic, so a spin-polarized calculation is carried out in this case. All other calculations are non-spin-polarized. All calculations are performed on a Fujitsu VX vector-parallel machine which achieves very high performance with CASTEP.³⁵ The tolerances used to determine when a relaxation is complete are 0.000 02 eV/atom for the total energy, 0.001 Å for the root mean square atomic displacement, 0.05 eV/Å for the root mean square atomic force, and 0.1 GPa for the root mean square stress.

A. Structures

The structures of Co, Si, CoSi, Co_2Si , and CoSi_2 have all been determined by experiment. Their structures are *A3*, *A4*, *B20*, *C23*, and *C1*, respectively. Starting from the experimental structures, these phases are relaxed using CASTEP.³⁴ The primitive unit cells from calculation and experiment are presented in Table I. The calculated lattice constants are consistently smaller than the experimental ones, but are still in very good agreement, with errors being below 1.4%. The calculated atomic coordinates are given in Table II. The lattice vectors and atomic coordinates are given in a format convenient for computer calculations.

The structures are displayed in Fig. 1. They are significantly different from each other, which suggests that complex atomic rearrangements take place during the anneal of a Co/Si couple. However, there are some apparent similarities that can be exploited. In panels (a), (c), and (e), hexagonal

TABLE I. The unit cells of the phases appearing during the annealing of a Co film on a Si substrate. All lengths are in Å and angles in degrees.

Phase	<i>a</i>	<i>b</i>	<i>c</i>	α	β	γ
Co	2.51	2.51	4.08	90.0	90.0	120.0
(expt. Ref. 36)	2.51	2.51	4.07	90.0	90.0	120.0
Co_2Si	4.89	7.06	3.69	90.0	90.0	90.0
(expt. Ref. 37)	4.92	7.11	3.74	90.0	90.0	90.0
CoSi	4.40	4.40	4.40	90.0	90.0	90.0
(expt. Ref. 38)	4.45	4.45	4.45	90.0	90.0	90.0
CoSi_2	3.76	3.76	3.76	60.0	60.0	60.0
(expt. Ref. 39)	3.80	3.80	3.80	60.0	60.0	60.0
Si	3.80	3.80	3.80	60.0	60.0	60.0
(expt. Ref. 36)	3.84	3.84	3.84	60.0	60.0	60.0

rings of Si can be observed. This similarity has to be treated cautiously since we are looking at two-dimensional projections of three-dimensional structures, and indeed the positions of the Si atoms perpendicular to the plane are quite different for each structure. Despite this, the structures suggest that CoSi and Co_2Si form through the diffusion of Co down Si $\langle 110 \rangle$ channels. This idea is followed up below.

TABLE II. The calculated atomic coordinates for the phases appearing during the annealing of a Co film on a Si substrate. The coordinates are in fractions of the primitive translation vectors.

Phase	Atom	Coordinates		
Co	Co	0.333	0.667	0.250
	Co	0.667	0.333	0.750
Co_2Si	Co	0.037	0.786	0.250
	Co	0.173	0.436	0.250
	Co	0.537	0.714	0.250
	Co	0.673	0.064	0.250
	Co	0.463	0.286	0.750
	Co	0.327	0.936	0.750
	Co	0.963	0.214	0.750
	Co	0.827	0.564	0.750
	Si	0.706	0.391	0.250
	Si	0.206	0.109	0.250
CoSi	Si	0.794	0.891	0.750
	Si	0.294	0.609	0.750
	Co	0.146	0.146	0.146
	Co	0.854	0.646	0.354
	Co	0.354	0.854	0.646
	Co	0.646	0.354	0.854
	Si	0.344	0.656	0.156
	Si	0.656	0.156	0.344
	Si	0.156	0.344	0.656
	Si	0.844	0.844	0.844
CoSi_2	Co	0.000	0.000	0.000
	Si	0.250	0.250	0.250
	Si	0.750	0.750	0.750
Si	Si	0.000	0.000	0.000
	Si	0.250	0.250	0.250

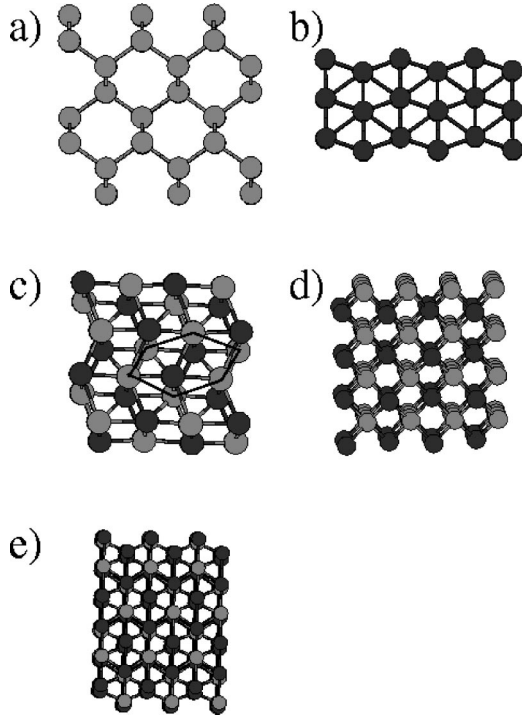
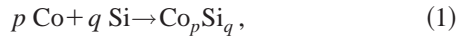


FIG. 1. The structures that appear during the anneal of a Co film on a Si substrate. The light disks represent Si, and the dark disks represent Co. Panel (a) is Si; panel (b) is Co; panel (c) is CoSi; panel (d) is CoSi₂; panel (e) is Co₂Si. In panel (c) a hexagonal ring has been drawn over the figure to highlight a sixfold ring of Si.

B. Energetics

The energies of the calculated relaxed structures are used to determine formation energies of the silicides. The formation energy is defined as the energy change for the reaction



where Co and Si are taken to be in their lowest energy solid state form. A negative value indicates an exothermic reaction. Note that throughout formation energies are quoted per formula unit. From Table III we see that it is energetically favorable for Co and Si to react to form any one of the three

TABLE III. The formation energies of the cobalt silicide phases that appear during the anneal of a Co film on a Si substrate. The experimental values are Gibbs free energies evaluated at 298.15 K. The experimental value for Co₂Si is in square brackets because it is obtained from the calculated value with a correction for overbinding applied based on the other experimental values. Note that energies are per formula unit.

Phase	Calculated (eV)	Experimental (eV) (Ref. 40)
Co	0.00	0.00
Co ₂ Si	-1.45	[-1.06]
CoSi	-1.29	-1.04
CoSi ₂	-1.47	-1.07
Si	0.00	0.00

silicides. The agreement with experiment is as good as could be expected given the methods used (the silicides are overbound by about 0.13 eV per atom). Contributing factors to the errors include the evaluation of the experimental values at room temperature, whereas the calculated values are at the absolute zero of temperature (see below); the approximation used for the exchange and correlation functional (error of order 0.1 eV); the pseudopotentials. There could also be experimental errors that we cannot quantify. If we apply a correction of 0.13 eV/atom to the formation energy of Co₂Si, we get a revised formation energy of -1.06 eV. From Table III we see that the experimental results, together with this corrected result for Co₂Si, show that the three silicides have very similar formation energies.

The experimental numbers are *free energies* evaluated at finite temperatures, whereas the calculated numbers are *internal energies* evaluated at the absolute zero of temperature. If the temperature effect is large, this might change some conclusions. To correct the calculated numbers for finite temperature effects we first note that, since we are generally interested in the case where there is zero applied stress, we can use the Helmholtz free energy as this then equals the Gibbs free energy. Further, when evaluating the free energy we need only look at configurations in the neighborhood of the relaxed structures as long ranged diffusion is the origin of the reactions (which change the structures) we are interested in. If we make a harmonic approximation, we can write the free energy as $F \approx U_0 + F_{\text{harm}}$ where $F_{\text{harm}} = -kT \text{Tr}\{\exp(-H_{\text{harm}}/kT)\}$, U_0 is the energy of the relaxed structure, T is the temperature, k is Boltzmann's constant, and H_{harm} is the Hamiltonian for the harmonic modes. To determine an order of magnitude for the harmonic contribution, we use an Einstein approximation for the harmonic corrections, with a vibrational frequency of 10^{13} s^{-1} and a temperature of 300 K. This gives $F_{\text{harm}} \approx -0.1 \text{ eV}$ per atom. The formation energy is determined from Eq. (1). From experiment,³⁶ the temperature dependent contribution to the formation energy of CoSi is 0.01 eV per silicide unit. Thus we see that there is considerable cancellation of the temperature dependent terms between the reactants and the product. Since the net contribution is an order of magnitude smaller than the error bars on our calculated results, temperature dependent contributions to calculated formation energies will be ignored from here on.

To demonstrate that errors in the calculated formation energies should not lead to qualitatively wrong conclusions, we can look at the energy changes associated with possible important reactions taking place during an anneal. These are presented in Table IV. We see that all the reactions are exothermic, and thus are not prohibited on energy grounds. This suggests that the *ordering* of the formation energies is correct, and hence results based on energies should be at least *qualitatively* correct.

From the experimental results in Table IV (which includes two corrected calculated results) we see that reactions fall into two categories: reactions in which there are as many silicide units after the reaction as before (such as $\text{Co} + \text{CoSi} \rightarrow \text{Co}_2\text{Si}$); reactions in which an extra silicide unit is created (such as $\text{CoSi}_2 + \text{Co} \rightarrow 2\text{CoSi}$). The first type of reaction has

TABLE IV. Energies for reactions that are important during the annealing of Co on Si. The experimental values are Gibbs free energies evaluated at 298.15 K. The experimental values in square brackets are obtained using the estimated formation energy of Co_2Si , and are thus not true experimental values. Note that energies are per formula unit.

Reaction	Calculated (eV)	Experimental (eV) (Ref. 40)
$\text{Co} + \text{Si} \rightarrow \text{CoSi}$	-1.29	-1.04
$\text{Co} + \text{CoSi} \rightarrow \text{Co}_2\text{Si}$	-0.16	[-0.02]
$\text{Co}_2\text{Si} + \text{Si} \rightarrow 2\text{CoSi}$	-1.13	[-1.02]
$\text{CoSi} + \text{Si} \rightarrow \text{CoSi}_2$	-0.18	-0.03
$\text{CoSi}_2 + \text{Co} \rightarrow 2\text{CoSi}$	-1.11	-1.01

a tiny energy associated with it (of order 0.01 eV), while the latter is highly exothermic (energy of order 1.0 eV). Thus energetics favors the formation of many silicide units, but not the type of silicide. The order in which the silicides appear must thus be a result of kinetics. This makes the formation of CoSi_2 from CoSi and Si hard to understand. One possible explanation is the reduction of the interface energy between Si and the silicide, as CoSi_2 is nearly lattice matched with Si. This is possible given that the growth of CoSi_2 occurs at the CoSi/Si interface, and occurs in a layer-by-layer manner.⁷

III. REACTION CALCULATIONS

As suggested above, we can think of the formation of CoSi and Co_2Si as resulting from the diffusion of Co through the $\langle 110 \rangle$ channels of Si. This is a natural place to begin for this must be how the reactions start. Given the complexity of the atomic rearrangements that take place, we look at this from two directions: starting from Co_2Si and removing Co; starting from pure Si and adding Co.

A. Starting from Co_2Si

From Fig. 1(e), we see that in Co_2Si there are two types of Co atom: those lying along lines perpendicular to the page which are also occupied by Si atoms, and those lying along interstitial lines, also running perpendicular to the page, containing only Co. If the interstitial Co lines are removed, the structure shown in Fig. 2(a) is obtained. It has the same ratio of Co to Si as CoSi . After relaxation the structure is stable, its unit cell has dimensions $4.40 \text{ \AA} \times 3.63 \text{ \AA} \times 6.73 \text{ \AA}$, and it has a formation energy of -0.58 eV per CoSi unit. Its structure is clearly different from that of CoSi , and its energy is higher by 0.71 eV per CoSi unit. The Co atoms are each fivefold coordinated, forming bonds only with Si atoms. Each Si atom is sevenfold coordinated, with five bonds being to Co atoms and two to Si atoms. The Co-Si bonds and Si-Si bonds are about 2.2 \AA and 2.4 \AA long, respectively. (For reference, in bulk Si, the Si-Si bond length is 2.35 \AA , and in CoSi the Co-Si bond length is 2.41 \AA .) The unusual coordination is presumably the origin of the high energy.

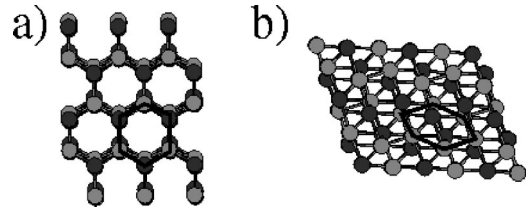


FIG. 2. Panel (a) is a proposed intermediate structure that can be transformed into Co_2Si by the addition of Co interstitial chains, or can be distorted by shearing into the CoSi ground state. Panel (b) shows the structure of panel (a) after a shear. It is not yet the CoSi structure, but lies between the structure of panel (a) and that of CoSi . A hexagonal ring has been drawn on both figures to highlight the nature of the shear.

If the structure is perturbed by moving some of the Si atoms in Fig. 2(a) horizontally and in the plane of the paper, the structure shown in Fig. 2(b) is obtained after relaxation. As can be seen from the superposed hexagons, the new Si sublattice is obtained from the old by a shear. The Co atoms move away from the Si atoms into positions that look more like interstitial sites. The structure is becoming more like CoSi [see Fig. 1(c)], and has an energy that is only 0.05 eV per CoSi unit higher than CoSi .

Thus Fig. 2(a) appears to be a stable structure that is related to both CoSi and Co_2Si . It might thus be a short-lived structure during the reaction of Co with Si, which can transform into CoSi or Co_2Si depending on how much Co is present. Further, its open structure would facilitate diffusion. It will be referred to as the *intermediate* structure from here on. Below we see how this structure might be formed.

B. Starting from Si

We first look at the hexagonal and tetrahedral Co interstitials in Si. For these calculations a 32-atom cell of Si is used with sides corresponding to the directions $[110]$, $[\bar{1}10]$, and $[001]$. This is almost certainly not converged with respect to cell size if what is needed is the energy and structure of an *isolated* Co interstitial. However, in the situation we are interested in, the density of Co atoms will be rather high. Thus there is no reason to believe that the results would relate significantly better to experiment if we used a larger cell. The unit cell dimensions are kept fixed at the experimental values for Si.

The hexagonal and tetrahedral interstitials have formation energies of $+1.65$ and $+1.69 \text{ eV}$, respectively; thus energy is required to form the interstitials. They both relax by a small outward breathing of the Si atoms neighboring the Co atom. For the hexagonal interstitial, before relaxation there are six Co-Si bonds of length 2.25 \AA , and after relaxation four of the bonds have length 2.31 \AA and two have length 2.27 \AA . For the tetrahedral interstitial, the four Co-Si bonds expand from 2.35 \AA before relaxation to 2.40 \AA after relaxation.

The positive formation energies for the Co interstitials correspond to the amount of work needed to remove an atom from bulk Co and place it in the Si matrix. The close correspondence between the calculated formation energies of

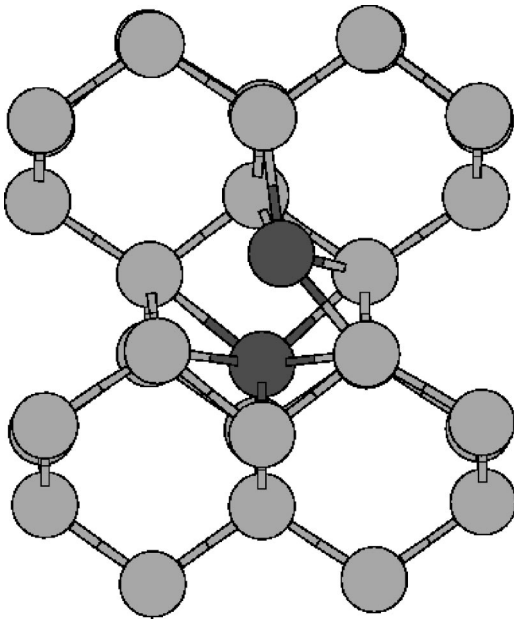


FIG. 3. The relaxed geometry for two Co interstitials in a 32-atom unit cell of Si.

about 1.65 eV and the experimental activation energy⁴ of 1.5 eV for the formation of Co_2Si suggest that it is this work that provides the reaction barrier.

The tiny difference in formation energies (0.04 eV) between the hexagonal and tetrahedral interstitials sites suggests that the energy surface for Co diffusion down $\langle 110 \rangle$ channels is very flat (on the reasonable assumption that the diffusion path passes alternately between hexagonal and tetrahedral sites). Thus bulk diffusion of Co should be very rapid even at room temperature. This is consistent with the experimental observations of Lee and Bennett¹⁵ who find that bulk diffusion of Co is much faster than surface diffusion.

We next look at two Co interstitials in the same 32-atom Si cell. The relaxed geometry is shown in Fig. 3. This structure has a formation energy of +2.24 eV. The binding energy for the two interstitials is defined as the difference between the formation energy for the system with two interstitials and twice the formation energy of the system with one interstitial. Using the hexagonal interstitial for the single interstitial, we get a formation energy of -1.06 eV. Thus there is a large binding energy between Co interstitials. The Co dimer will, presumably, be much less mobile than a single Co interstitial. Further, it will have a long lifetime for decaying into two Co interstitials on account of its large binding energy. Thus once two Co interstitials combine they will form a stable immobile object.

We now look at the case where the $\langle 110 \rangle$ channels of Si are fully populated with Co (one Co for each Si, each initially on a tetrahedral interstitial site). A cell containing four Si and four Co atoms is used. For these calculations we assume that the cell size is constrained by the surrounding Si substrate. Thus cell relaxation is allowed only in the direction perpendicular to the plane of the silicides. After relaxation, the dimensions of the computational cell are $3.84 \text{ \AA} \times 3.84 \text{ \AA} \times 5.94 \text{ \AA}$ (for bulk Si they are $3.84 \text{ \AA} \times 3.84 \text{ \AA}$

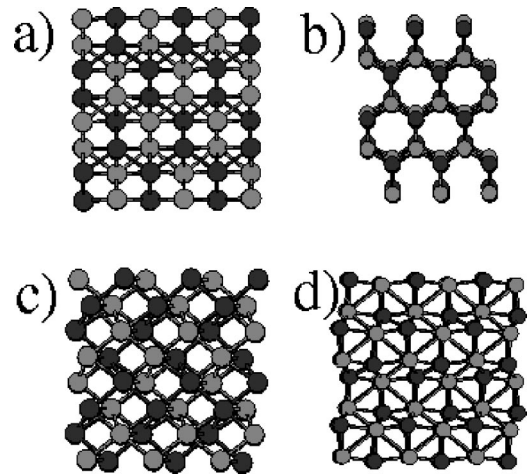


FIG. 4. A comparison of the structures obtained by relaxing Si with the number density of Co interstitials equal to the number density of Si atoms, and the Co_2Si lattice with the lines of Co interstitials removed. Panels (a) and (c) correspond to two $\langle 110 \rangle$ views of Si with Co interstitials, and panels (b) and (d) are corresponding views for the Co_2Si lattice with the lines of Co interstitials removed.

$\times 5.43 \text{ \AA}$). The formation energy per CoSi unit is -0.33 eV. Thus it is energetically favorable for very high concentrations of Co interstitials to occur. However, this structure is less stable than the intermediate structure by 0.25 eV. From Fig. 4, in which the two structures are compared, we see that there are great similarities between the Si sublattices, and that the Co sublattices are related by a rotation about the $\langle 110 \rangle$ axis. The simplicity of the transformation, together with the energy gain from making the transformation, suggest that the proposed intermediate structure is accessible from Si with a high concentration of Co interstitials.

IV. CONCLUSIONS

The results found from the above plane-wave pseudopotential calculations suggest that the following sequence of events take place during the reaction of Co with Si. First, Co atoms break free from the Co film, and become interstitials in the Si lattice. This is a process that requires the input of energy (about 1.6 eV), and so acts as a barrier to any reaction taking place. Once inside the Si lattice, Co interstitials migrate quickly through the $\langle 110 \rangle$ channels because of the flat energy landscape. Because there is a high density of Co interstitials, there is a high probability of collisions between Co atoms. When two Co interstitials collide, they bind together with an energy of about 1.06 eV. At this point they become immobile, and other Co atoms quickly combine to form a larger cluster. As the cluster grows, the $\langle 110 \rangle$ channels fill up and there is an expansion of the crystal perpendicular to the plane of the Si substrate. The formation energy of the high density of Co interstitials is about -0.33 eV per CoSi unit. This structure can lower its energy by 0.25 eV per CoSi unit by reconstructing to form what we have called the intermediate structure. This is an open structure that can either shear to form CoSi, or accept more Co atoms to form

Co₂Si. Experiment suggests that this structure initially accepts Co atoms, allowing further growth of this structure into the Si substrate and the formation of Co₂Si further away from the interface. Once there is no more Co metal at the surface, the intermediate structure at the silicide/Si interface collapses into CoSi.

Because of the complexity of the processes taking place, it cannot be said that the transformation from a high density of Co interstitials to the intermediate structure is the *only*

route taken by the system. However, it is an energetically possible route that does explain much of the experimental data.

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