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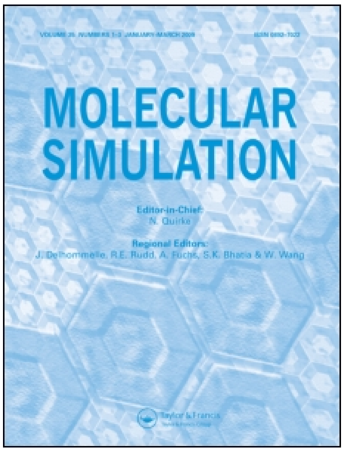

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Molecular Dynamics Simulation of Transition Metals as Silicon Substrates

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MOLECULAR DYNAMICS SIMULATION OF TRANSITION METALS ON SILICON SUBSTRATES

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In recent years the growth of epitaxial layers and strained layer superlattices have been simulated by using the method of molecular dynamics. We have used this method to study the formation of transition metal silicides as the metal is deposited on a silicon substrate. We propose effective empirical potentials to describe the interaction between the metal and silicon and use the Dodson and Stillinger–Weber potentials to model the silicon–silicon interaction. We report on the evolution of nickel layers on the substrate as a function of temperature.

KEY WORDS: Molecular dynamics, nickel–silicon interfaces, silicides

INTRODUCTION

The study of the metal – silicon interface is of great importance in VLSI technology. Transition metals have been widely used in the semiconductor industry to form metal contacts for devices. When a transition metal is deposited on a silicon substrate, they react with the substrate and silicides are formed. It is important to know the type of silicide formed as well as the kind of interface because this will affect the properties of the device constructed. For example, when nickel is deposited on a silicon substrate there can be any number of six silicides formed at the interface of which $NiSi_2$ and Ni_3 Si are the two extremes in composition.

$NiSi_2$ is of fluorite structure and is almost lattice matched to the Si $\{111\}$ surface. It has been shown that when Ni is deposited on the $\{111\}$ surface of Si, at a temperature between 300C and 450C, subsequent annealing results in the formation of NiSi at the interface. However, the silicide can form in two different orientations called type A and type B. Tung [1] found that the Schottky barrier heights (SBH) are different for the two different orientations. Although there has been some controversy over this finding, it now appears to have been confirmed by other workers [2]. Calculations of the SBH appear to give some contradictory results. Bisi and Ossicini [3] have found that the type A interface has a higher barrier height than the type B which is at variance with the experimental results. Yongnian et al. [4] and Rees and Matthai [5] have performed tight binding calculations and have found that the SBH are the same for both configurations. It has been proposed that defects at the interface might play a role in determining the SBH. However, it would appear that dislocations do not effect the SBH and so the experimental observation must be due to either point defects at the interface or a non-abrupt interface. It is for this reason that we have decided to undertake an investigation of the silicide–silicon interface by the use of simulation techniques. The fully relaxed atomic configuration of the interface could then be used as input in an electronic structure calculation to determine the SBH.

In recent years there has been some interest in the study of silicon surfaces and interfaces. For example, Schneider et al [6] have studied the epitaxial growth of Si on silicon and Dodson and Taylor [7] have looked at strained Si/Ge layers on a Si $\{111\}$ substrate.

Before embarking on a complex calculation on the silicide – silicon interface we have set ouselves the easier task of studying the nickel–silicon interface in an attempt to see if chemical reactions at the interface can be simulated by means of these simplistic empirical potentials. To do molecular dynamics (MD) on this system, one needs to have a knowledge of the various interactions. There are, in the literature, numerous interatomic potentials describing the silicon–silicon [8] and nickel–nickel [9] interactions. Following the work of Ding and Anderson [10], we propose interatomic potentials for the nickel–silicon interaction. With the use of these potentials we have performed simulations of layers of the metal on the Si $\{111\}$ surface as well as of the metal–silicon interface.

INTERATOMIC POTENTIALS

We have chosen to use empirical potentials to describe all the interactions present in our system. The silicon–silicon interaction has been the subject of interest in recent years. The Keating potential [8] has proved successful in describing the elastic properties and phonon spectra in silicon. However, this potential can only be used to describe small displacements from the ideal tetrahedral geometry. Stillinger and Weber (SW) [11] proposed a new form of potential to describe silicon in the solid and liquid phases. This makes it very suitable to use in molecular simulations and has infact been used by Schneider et al [6] to study the growth of silicon on the silicon $\{111\}$ substrate. Biswas and Hamann [12] and Tersoff [13] have also constructed interatomic potentials for silicon. The latter has been modified by Tersoff and by Dodson [14] and both appear to provide good descriptions of the solid phases and have also been used in MD simulations.

We have performed calculations using the SW and Dodson potentials. The results presented in this paper are those obtained using the SW potential which consists of a two-body and a three-body term. The pair potential is given by

$$v_2(r_{ij}) = \varepsilon f_2(r_{ij}/\sigma) \tag{1}$$

where

$$\begin{aligned} f_2 &= A(Br^{-p} - r^{-q}) \exp[1/(r-a)]; && r < a \\ &= O \qquad ; && r \geqslant a \end{aligned} \tag{2}$$

ε, σ are energy and length units respectively. The three-body interaction is

$$v_3(r_i, r_j, r_k) = \varepsilon f_3(r_i/\sigma, r_j/\sigma, r_k/\sigma) \tag{3}$$

where

$$f_3(r_i, r_j, r_k) = h(r_{ij}, r_{ik}, \theta_{jik}) + h(r_{ji}, r_{jk}, \theta_{ijk}) + h(r_{ki}, r_{kj}, \theta_{ikj}) \tag{4}$$

θ_{jik} is the angle between r_j and r_k at site i. The function h is

$$\begin{aligned} h(r_{ij}, r_{ik}, \theta_{jik}) &= \lambda\exp\,[\gamma/(r_{ij} - a)] + \gamma/(r_{ik} - a)]\,(\cos\theta_{jik} + 1/3)^2;\ r_{ij}, r_{ik} < a \\ &= O;\ \text{otherwise} \end{aligned} \tag{5}$$

Note that h is zero for the ideal tetrahedral geometry. This enables the diamond structure to be the most stable one.

The seven parameters A, B, p, q, a, λ and γ were chosen so that the diamond structure was the most stable at low pressures and the melting point and the liquid structure factor was in good agreement with experiment.

There are quite a few interatomic potentials describing the nickel–nickel interaction [9]. With the exception of the Finnis–Sinclair type potentials [15], they are two-body potentials. Of the two-body potentials the one proposed by Miller and Bristowe [9] is of short range and is fitted to give the correct vacancy formation energy making it attractive for doing MD simulations.

To account for the nickel–silicon interaction we have followed the approach used by Ding and Anderson [10], who performed MD simulations on molybdenum–germanium alloys using interatomic potentials of the Stillinger–Weber type. Because of the tetrahedral bonds in silicon, it is necessary to invoke three-body as well as two-body potentials when considering the nickel–silicon interaction. When a silicon atom is bonded to another silicon atom the electrons tend localise into a tetrahedral configuration. We would therefore expect the three body interaction to be more important in the Ni–Si–Si interaction and negligible in the Ni–Ni–Si interaction. A two-body potential of the Morse type is used to describe the nickel– silicon pair interaction. The three body term representing the Ni–Si–Si interaction is given the same functional form as in equations (3)–(5).

The parameters for the nickel–silicon interaction should ideally be chosen so that

Table 1 Values of parameters used for Si–Si and Si–Ni two body potentials. in reduced units (ε = 2.1702 eV, σ = 2.0951 A)

	Si–Si	*Si–Ni*
p	4	4
q	0	0
a	1.8	1.8
A	7.050	5.30
B	0.602	0.495

Table 2 Values of parameters used for Si–Si–Si and Si–Si–Ni three body interactions in reduced units as for two body potentials.

	Si–Si–Si	*Si–Si–Ni*
λ	21.0	8.4
γ	1.2	1.2
a	1.8	1.8

the resulting potentials reproduce some bulk properties of the silicides. However, very little data in the form of elastic constants, etc., exist for these compounds. We therefore decided to try and fit only the cohesive energies and equilibrium lattice spacings of the more important silicides, namely Ni_3 Si and $NiSi_2$. Because of the similarity of the interactions, we have, to a first approximation, taken the potential cut-offs to be the same as for the silicon–silicon interaction and vaired the strength parameters. The parameters A, B, and λ were obtained by forcing the cohesive energy to be a minimum at the observed lattice spacings of 3.51 A and 5.40 A for Ni_3 Si and $NiSi_2$ respectively. The corresponding cohesive energis at these spacings were calculated to be 5.44 eV and 5.2 eV for these crystal structures. The values of all the parameters are given in Tables 1 and 2.

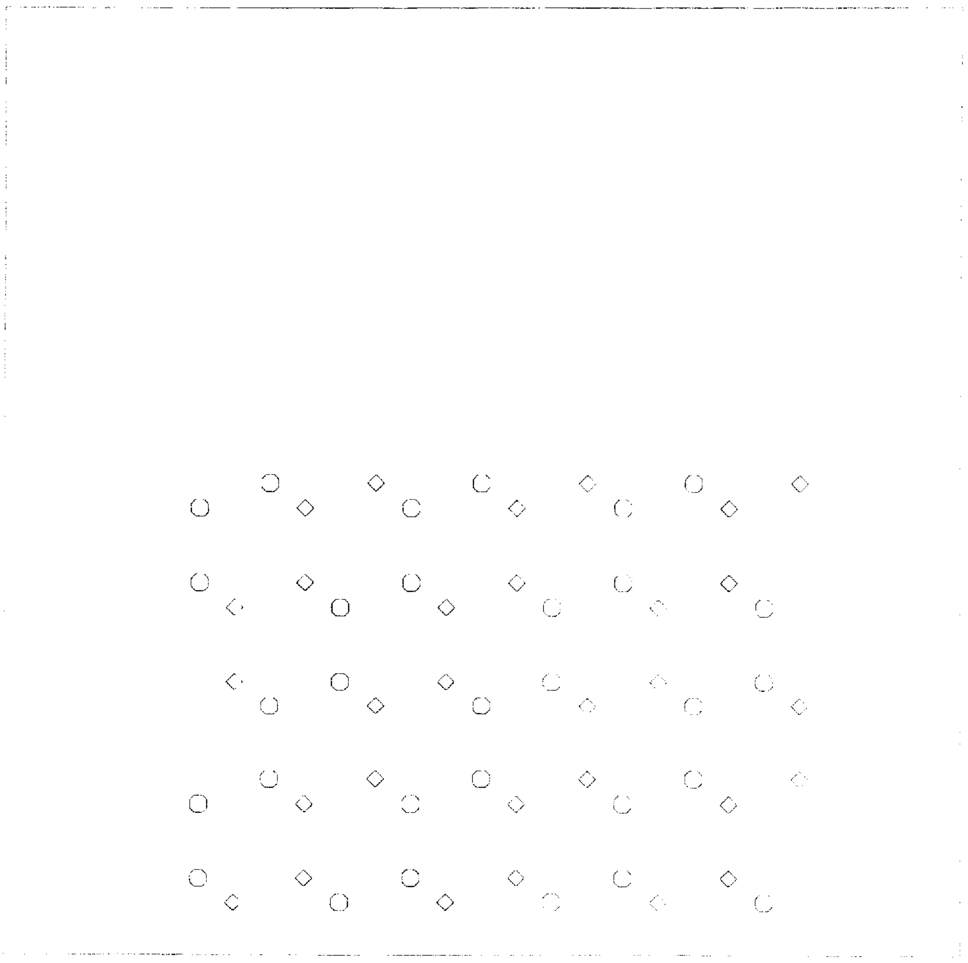

Figure 1 Projection in the $(1\bar{1}0)$ plane of atom positions in the silicon crystal block with a free (1 1 1) surface. Atoms denoted by the two symbols belong to the two sublattices.

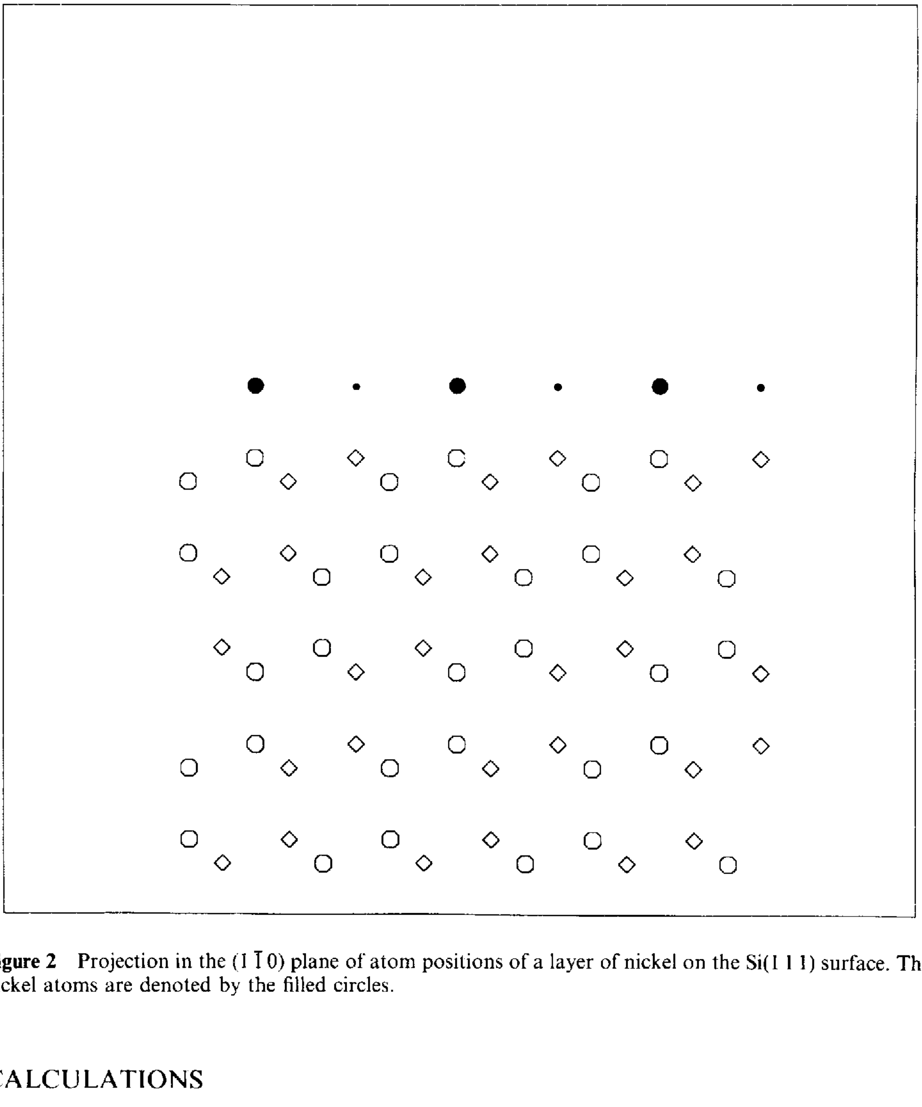

Figure 2 Projection in the (1 $\bar{1}$ 0) plane of atom positions of a layer of nickel on the Si(1 1 1) surface. The nickel atoms are denoted by the filled circles.

CALCULATIONS

All the computations were done on a crystal block of 720 moveable atoms. A crystal with diamond structure was constructed with block edge vectors x = [1 1 0]; y = [1 1 2] and z = [1 1 1]. Periodic boundary conditions were assumed in the x and y directions and fixed boundaries were applied in the z direction. Because of the number of interactions involved, near neighbour tables were constructed so as to reduce the number of computations. The neighbour list, which is the same for all lattice sites of a sublattice, contains only those lattices sites within the interaction range. However, the tables were associated with lattice sites and not atoms so that movements of an atom from one site to another site there is a change in its index.

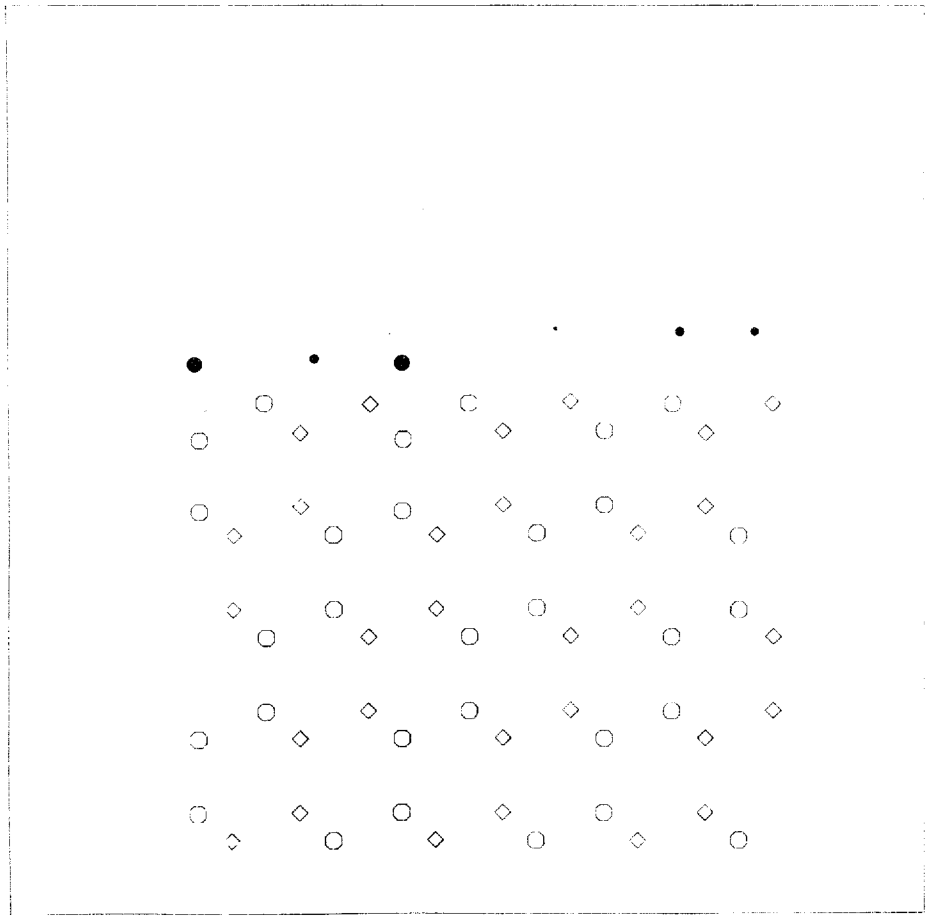

Figure 3(a) Projection in the ($1\bar{1}0$) plane of the relaxed atom position with a Ni layer on Si. The variation in symbol size denotes displacement perpendicular to the plane of projection. Very small atoms have moved a long way almost to the next plane.

Thus, the neighbour lists generated for the perfect crystal are always valid, irrespective of the extent of atom migration. This results in a considerable saving of computational time. Once a surface or an interface was constructed, the atoms were allowed to move according to the usual equations of motion with a time step of 2* 10^{15} seconds.

Temperature was introduced into the system either by giving all the atoms in the inner region initial random velocities scaled to the desired temperature or by giving velocities only to those atoms at the interface or surface. The latter is the more realistic for epitaxial growth studies as the incoming particles impart their kinetic energy to the surface atoms. The system is then allowed to evolve for between 500–1000 time steps so that the kinetic energy is dissipated throughout the block and the system is in thermal equilibrium. The system is then repeatedly quenched by equating all atom velocities and forces to zero whenever the kinetic energy reaches a maximum. The

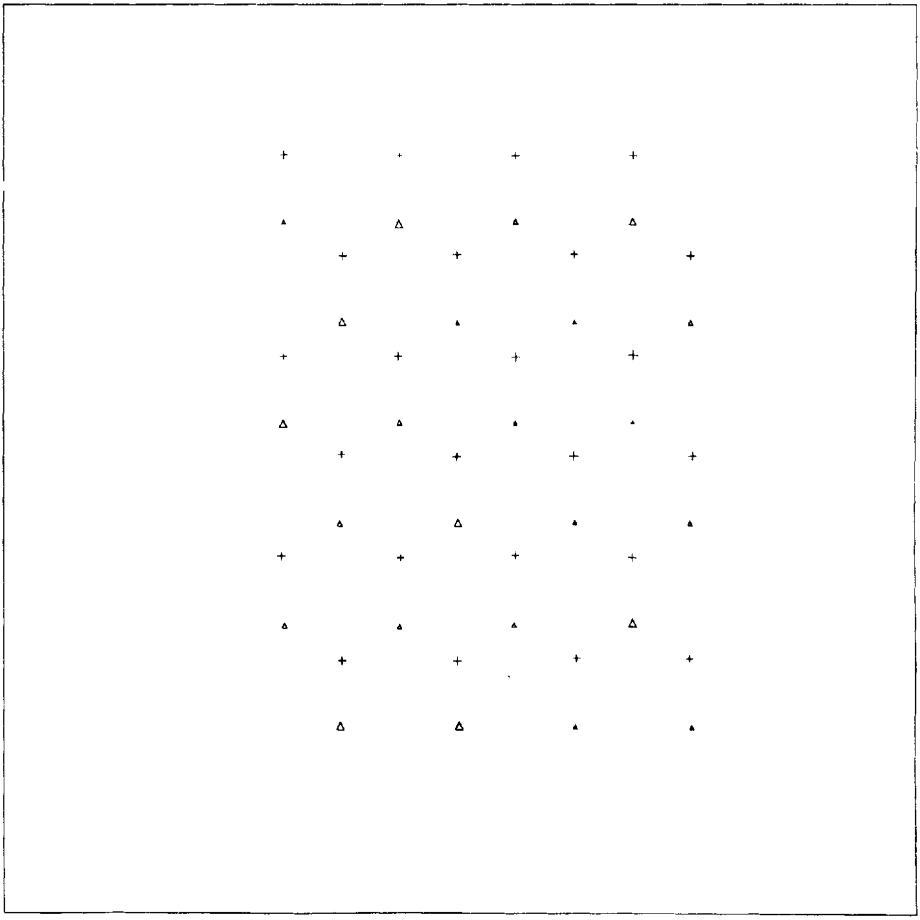

Figure 3(b) Projection in the (1 $\bar{1}$ 0) plane of the relaxed atom positions with a Ni layer on Si. The △ denote the Ni atoms and the + denote the Si atoms. The variation in symbol size denotes displacement perpendicular to the plane of projection. Very small atoms have moved a long way almost to the next plane.

evolution period depends on the time taken for the system to reach thermal equilibrium. Once this has been reached, quenching leads to the same relaxed energies and structures. The quenching process takes between 500 to 1000 time steps depending on the temperature of the system.

RESULTS

A silicon surface was constructed by putting Si atoms on all lattice sites with z $\leqslant$ O and vacancies on sites with $>$ O. In Figure 1 we show the y–z cross-section of the resulting crystal block. The free surface was then allowed to relax. One does not expect to see the 7 × 7 reconstruction because of the limited nature of the potential.

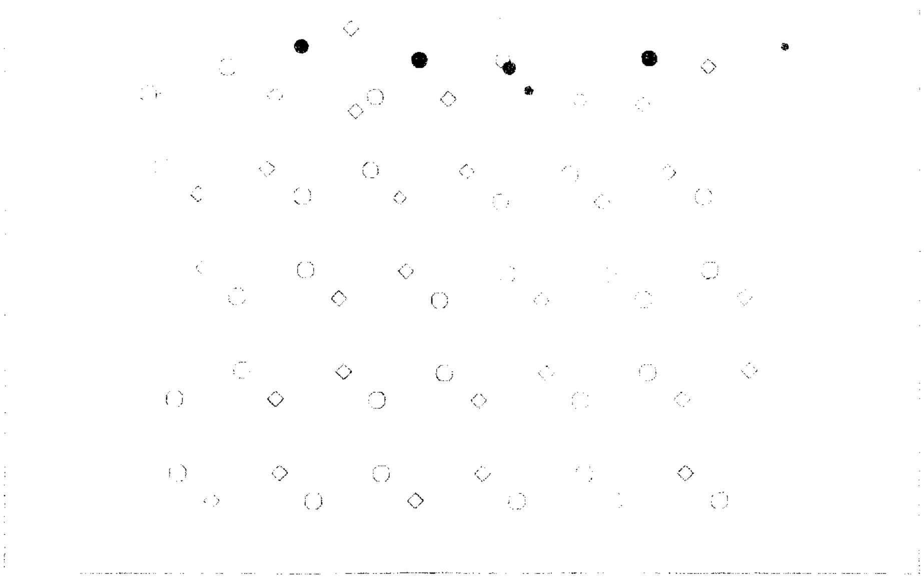

Figure 4 Projection in the (1 $\bar{1}$ 0) plane of relaxed atom positions of a hot layer of Ni on the Si substrate.

However one does observe an outward relaxation of the top two layers of atoms.

A layer of Ni was then placed on the Si (111) surface by putting Ni atoms on all the lattice sites in the plane above the silicon surface. In this configuration, the nickel atoms are placed at the end of each dangling bond as shown in Figure 2. With the temperatures initialised to zero, the atoms were then allowed to relax. The nickel atoms move downwards to the silicon layer and move transversely so that instead of sitting on top of the dangling bonds, they occupy sites above the second layer Si atoms. This can be seen clearly in Figures 3(a) and 3(b). This configuration is about 12 eV lower in energy than the unrelaxed one.

The nickel atoms were then given velocities scaled to a temperature of 1000K and the system was allowed to evolve after which it was quenched. As can be seen in Figure 4, the nickel atoms move into the silicon substrate forming a 'compound' phase. However there is no particular structure to the atomic positions and a x–y plot proves

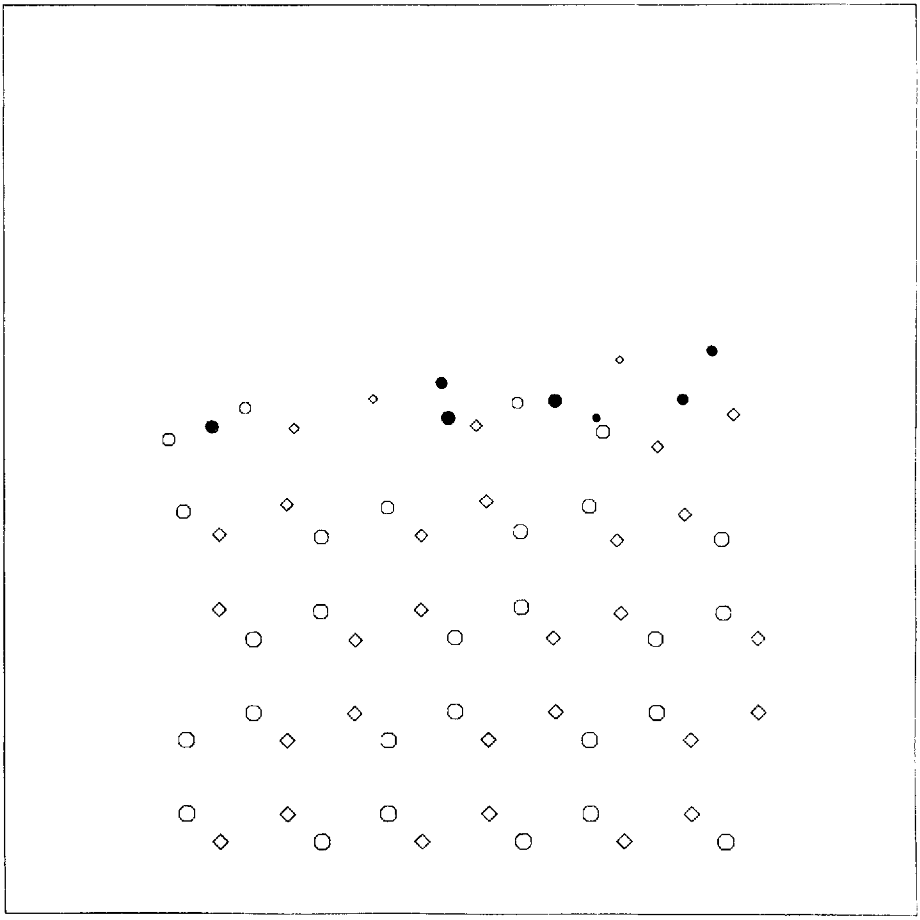

Figure 5 Projection in the $(1\bar{1}0)$ plane of the relaxed atom positions with two layers of Ni on Si.

quite complex and does not reveal any more information. The energy of this configuration is much lower than it was in the case above with the relaxation energy now almost 46 eV.

We decided to increase the number of Ni atoms so two layers of Ni were placed on the silicon surface and the same procedure repeated. The only difference being that both layers of Ni and the top layer of Si were heated. There is considerable movement of the atoms and the relaxation energy is over 80 eV. Again because of the complexity of the x–y cross-sectional plot, only the y–z plane is displayed (Figure 5)

Finally a nickel–silicon interface was constructed by treating the diamond structure for $z > 0$ as a zincblende crystal with nickel atoms and vacancies as the constituents. The nickel part of the crystal was then scaled to give the equilibrium nickel lattice spacing. Care was taken that the neighbour lists in this case were large enough to ensure that all nickel–nickel interactions were taken into account. In this case the atoms were not given any initial velocities but quenching was still applied so that the

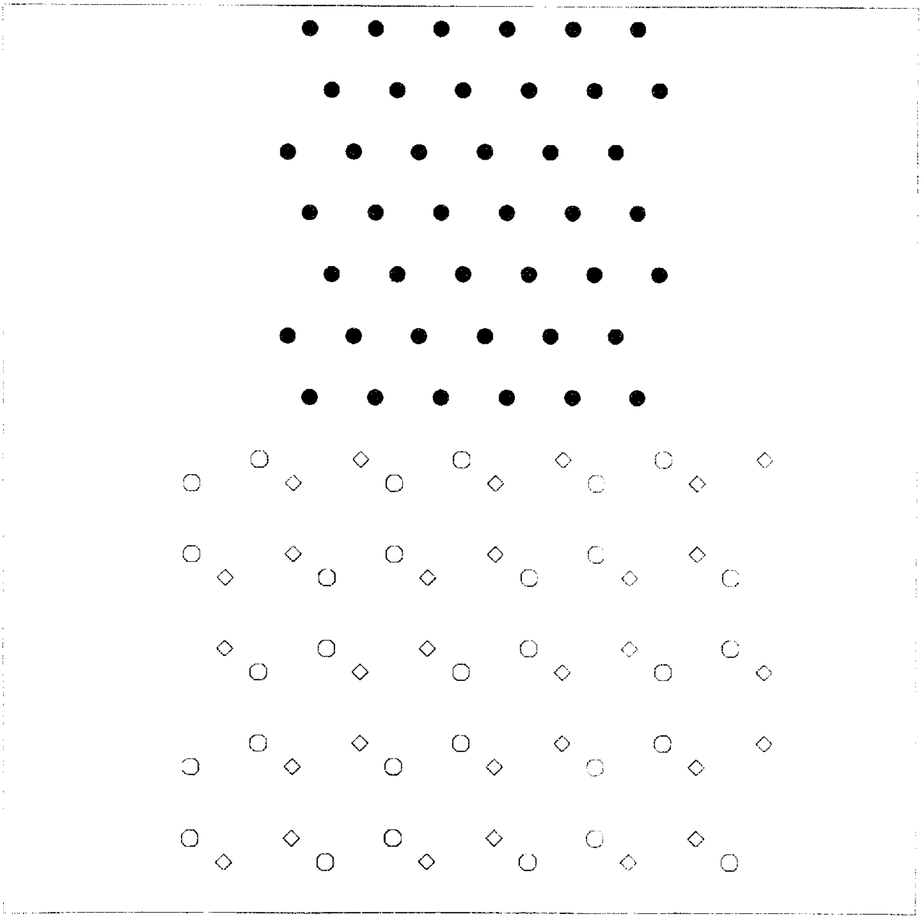

Figure 6(a) Projection in the (1 $\bar{1}$ 0) plane of the unrelaxed atomic positions for the Ni–Si interface.

system could settle down to its lowest energy local minimum. The atomic positions before and after relaxations are shown in figures 6 and 7. One observes that Si atoms move up into the metal layer as well as nickel atoms moving down. There is considerable lateral movement. The relaxation energy is about 44 eV.

From our results, it would appear that some compound formation is taking place with considerable movement of both nickel and silicon atoms. It remains to be seen if this is due to the potential used or if it is a structural result.

DISCUSSION

In this paper we have shown that it is possible to do molecular dynamics simulations ot study the growth of silicides as a metal is deposited on a silicon surface. Of course, it is recognised that simple empirical potentials could not give the correct chemical

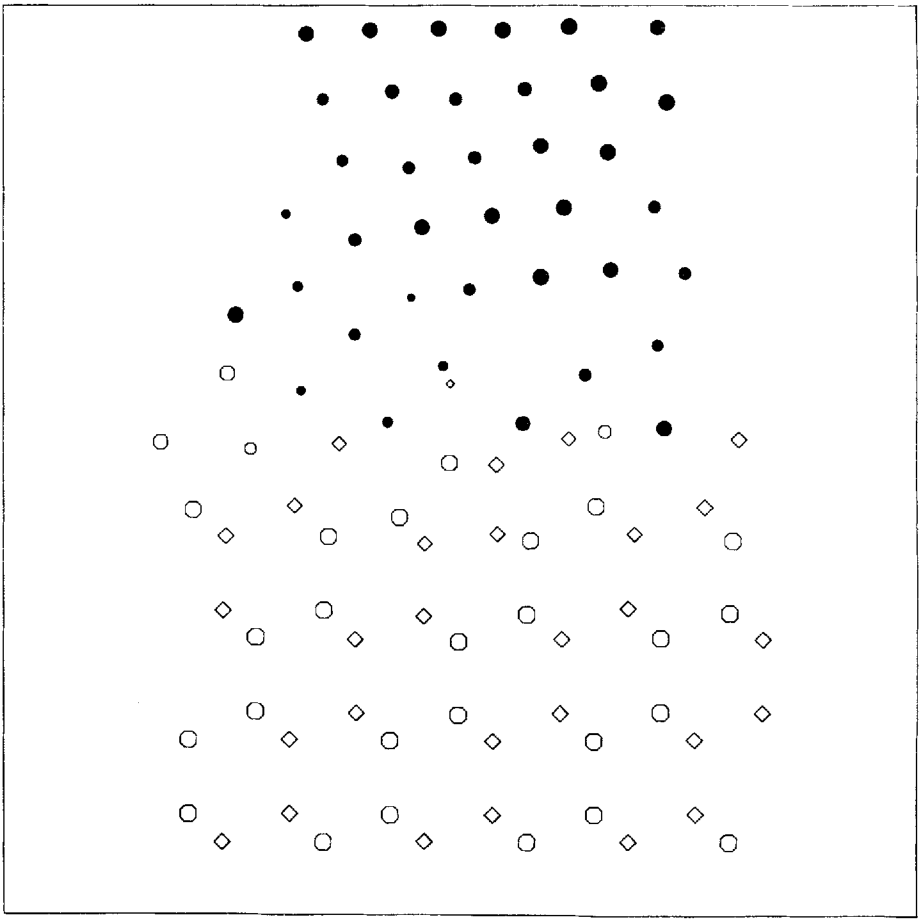

Figure 6(b) Projection in the (1 $\bar{1}$ 0) plane of the relaxed atomic positions for the Ni–Si interface.

composition. However, it would seem that even these simple potentials produce a region at the interface that could loosely be described as a silicide. The value of these potentials is in their ability to form silicon–nickel 'bonds'. It would therefore seem feasible to use them in a study of the silicide–silicon interface.

The main problem lies in the construction of interatomic potentials. One needs to ensure that the metal potential makes the observed crystal structure the most stable. We have not done this for the Bristowe–Miller potential. It is also important to be able to construct metal-silicon potentials by fitting to a number of bulk silicide properties. We are now in the process of performing first principles electronic calculations on these compounds so that the potentials can be fitted to the bulk properties. One also needs to reassess the silicon potential used. We have begun doing calculations using the Dodson and improved Tersoff potentials.

These calculations have been extended to study the silicide/silicon type A and type B interface and the resulting interface geometry has been used as input in electronic

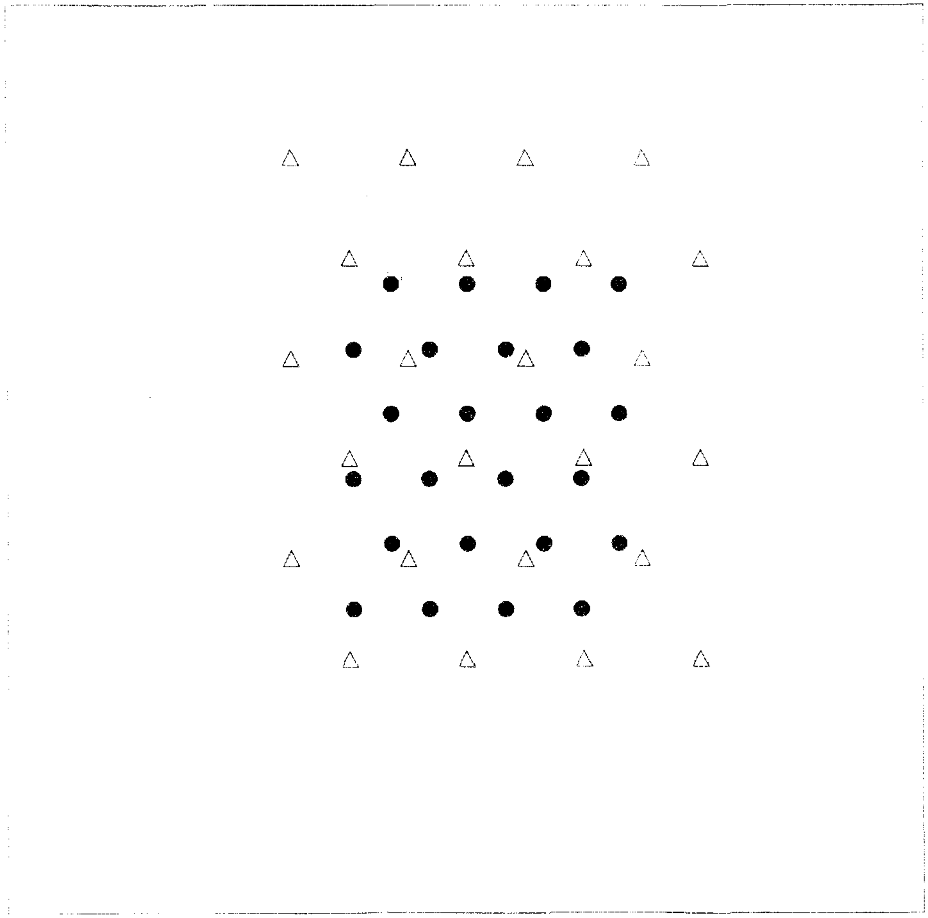

Figure 7(a) Projection in the (1 1 1) plane of the unrelaxed atomic positions for the Ni–Si interface. The △ denote the Si atoms in the plane below the interface. The filled circle denote the Ni atoms in the plane above the interface.

structure calculations. We have found the interface structure is critical in determining the SBH at an interface. This work is to be published shortly.

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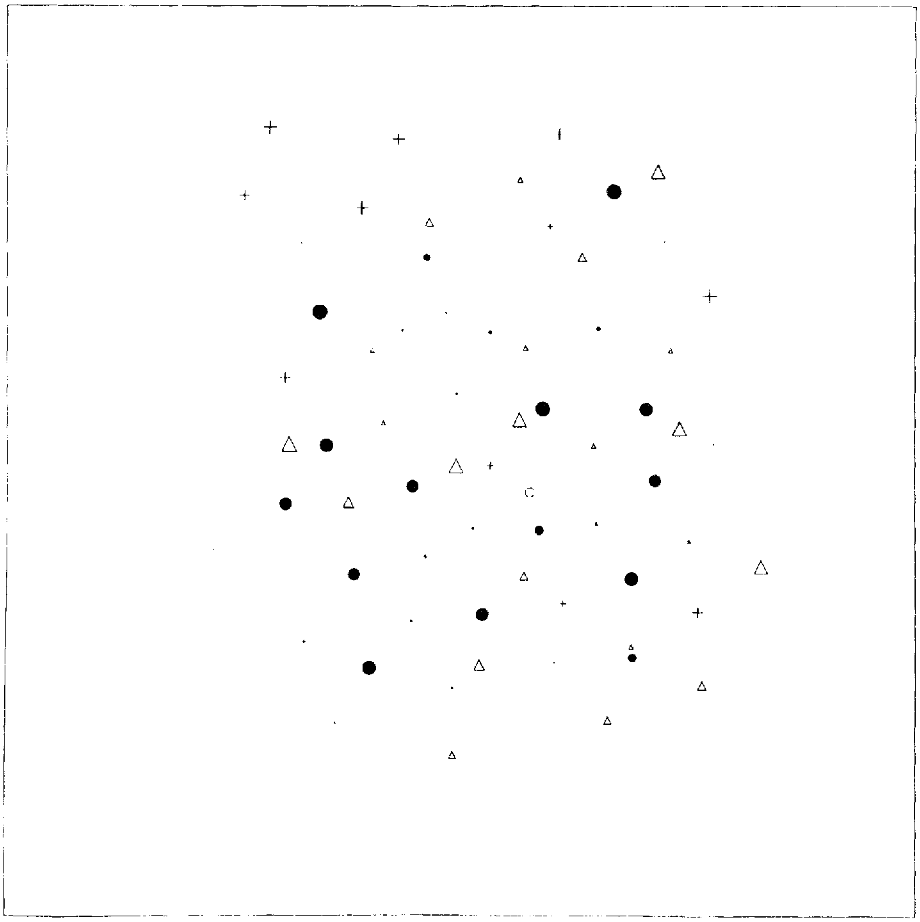

Figure 7(b) Projection in the (1 1 1) plane of the relaxed atomic positions for the Ni–Si interface. The open circle and the △ denote the Ni and Si atoms in the plane below the interface. The filled circle and the + denote the Ni and Si atoms in the plane above the interface.

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