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2002 J. Phys.: Condens. Matter 14 4527

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INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **14** (2002) 4527–4532 PII: S0953-8984(02)31921-0

A simple, effective tight-binding parametrization for Si–Ge interactions on Si(001)

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Received 14 December 2001
Published 18 April 2002
Online at stacks.iop.org/JPhysCM/14/4527

Abstract
We describe a simple yet extremely effective tight-binding parametrization for Ge–Ge and Si–Ge interactions in near-tetrahedral bonding situations, in particular on the (001) surface of Si and Ge, and present results of tests on various systems (including ad-dimers of Ge and the square structure found during gas-source growth).

1. Introduction

Strained growth of semiconductors can lead to self-assembly of nanostructures, for instance the spontaneous formation of Ge 'hut' clusters on Si(001) [1]. Si–Ge alloys and superlattices of Si/Ge are attractive for the semiconductor industry because of the compatibility with existing Si-based technologies, and the possibility of using the Ge hut clusters as quantum dots is intriguing. Ge on Si is also a model system for the study of strained growth, exhibiting classic Stranski–Krastanow behaviour: formation of a strained, pseudomorphic wetting layer followed by three-dimensional islands when the strain becomes too large. Understanding the growth of Ge on Si(001) is of great importance for the successful development of devices based on Ge/Si and for exploring the possibilities of self-assembled quantum dots in nanotechnology.

In order to study strained semiconductor surfaces, where large two- and three-dimensional reconstructions and features are important, a compromise between computational effort and accuracy is required: tight binding [2] is a method which retains quantum mechanics but makes a clearly defined set of approximations which allow large systems to be simulated in a reasonable amount of time. With the advent of many successful linear scaling techniques (where the computational effort increases only linearly with the number of atoms in the system rather than with the cube in traditional methods) [3], modelling of significant features on semiconductor surfaces becomes possible.

The key drawback of tight binding comes from its very basis: the Hamiltonian is approximated by a set of parameters, which must be fitted to experimental or *ab initio* data. The transferability of these parameters (i.e. the accuracy of calculations where the atomic

Table 1. On-site energies for Ge and Si.

Element	E_s	E_p
Si	−12.20	−5.75
Ge	−13.88	−6.39

environment is far from that in which the fitting was performed) is always of great concern; fitting a good set of parameters can often involve complicated scaling functions and a large investment of time. In this paper, a simple parametrization is described which was created rather quickly, and yet proves to be extremely effective for near-tetrahedral bonding situations; in this way, it is similar to a recent parametrization created for Bi/Si(001) interactions [4] where a simple parametrization has proved remarkably effective [5, 6]. However, it should be noted that, due to the simple scaling form and limited fitting, the parametrization will not be very transferable away from near-tetrahedral bonding situations. The Si–Si interactions are taken from an earlier work [7], which uses a slightly more complicated scaling form.

The rest of the paper is organized as follows: in the next section, the fitting procedure is described. Section 3 presents tests of the parametrization, compared with *ab initio* modelling. In section 4 the stability and appearance of four-membered rings of Ge on Si(001) (which are potentially the nucleus for gas-source growth) is investigated, followed by concluding discussions.

2. Methodology

Tight binding postulates (and in more recent, *ab initio* tight-binding methods, specifies) a basis set of local, atomic-like orbitals. The Hamiltonian is written in terms of matrix elements between these orbitals, which are then parametrized, generally being written as an equilibrium hopping integral multiplied by a scaling term. Cohesive energies are obtained by adding a pair-wise repulsive term to account for all interactions previously neglected; the whole procedure (in particular the use of pair-wise repulsive terms) has been rather elegantly justified by Sutton *et al* [8]. Details of the parametrization for Si–Si bonds (and Si–H which are used to terminate the base of the slab) are given elsewhere [7].

The hopping integrals (which define the Hamiltonian at equilibrium bond lengths) can be fitted analytically to certain high-symmetry points in the band structure, and this has already been done for many tetrahedral semiconductors [9]. We chose to use these parameters for the equilibrium hopping integrals, with one exception: after fitting the bands with the usual sp^3 basis set, Vogl *et al* added *post hoc* an s^* orbital to improve the shape and fit of the lowest conduction bands; we shall ignore this complication (as we are not concerned with these bands or their effects).

The value of the on-site energies (E_s and E_p) can be arbitrarily shifted provided the separation is maintained. For the Si–Si parameters, we use a separate parametrization [7], and have shifted the Vogl *et al* values of E_s and E_p for Ge so that the offset of E_s in Ge relative to E_s in Si is preserved between the parametrizations. The values of the on-site energies are given in table 1 and the hopping parameters are given in table 2. To find hopping parameters for the Si–Ge interactions, the geometric mean of the Si–Si and Ge–Ge parameters was taken (this is remarkably effective, and follows Chadi [10]).

Once the equilibrium hopping parameters have been found, the question of scaling arises: how do they vary with changing atomic separation? There are many different scaling forms, ranging from simple [10] to extremely complex. In this work, as in an earlier

Table 2. Hopping parameters for Ge–Ge and Si–Ge interactions.

Interaction	$h_{ss\sigma}$	$h_{sp\sigma}$	$h_{pp\sigma}$	$h_{pp\pi}$
Ge–Ge	−1.695	2.366	2.853	−0.823
Si–Ge	−1.812	2.032	2.950	−0.941

Table 3. Scaling for Ge–Ge and Si–Ge interactions.

Interaction	r_0	n	m	ϕ_0
Ge–Ge	2.447	2.353	4.993	4.014
Si–Ge	2.398	2.289	5.306	3.714

parametrization [4], we choose to use a simple form for scaling which allows physical insight and analytical expressions for the fitting:

$$h(r) = h_{llm}\left(\frac{r_0}{r}\right)^n, \tag{1}$$

where r_0 is the equilibrium distance for the bond. The same form is used for the repulsive term, sharing the same value of r_0 but with a different exponent, m:

$$\phi(r) = \phi_0\left(\frac{r_0}{r}\right)^m. \tag{2}$$

To fit the scaling, total energies must be considered, which also requires fitting the scaling and magnitude of the pair-wise repulsive potential. These were fitted to density functional calculations of the binding energy curves for bulk Ge and a zincblende structure 50% Si–Ge alloy. The density functional calculations were fully converged with respect to $\boldsymbol{k}$-points (using a $4\times4\times4$ Monkhurst–Pack mesh, tested against $6\times6\times6$ and $8\times8\times8$ meshes for convergence) and plane wave cutoff (225 eV, tested against a 300 eV cutoff). The fitting procedure, which can be done analytically, involves three stages.

(i) Fit the magnitude of the repulsive potential, ϕ_0, to the total energy at equilibrium.
(ii) Obtain a minimum at the equilibrium lattice constant by varying either m or n.
(iii) Fit the shape of the binding energy curve (equivalent to fitting the bulk modulus) by preserving the ratio of m and n (this maintains the minimum at the equilibrium lattice constant) but varying their magnitude.

The initial values of n and m can be taken to be 2 and 4 respectively (there are good physical reasons for choosing these values [11]). The final values of ϕ_0, n and m are given in table 3. The Hamiltonian was cut off between first- and second-nearest neighbours (i.e. at about 3.0 Å, though there is some leeway on this distance).

3. Tests of the parametrization

As the parametrization is intended for modelling Ge on Si(001), a good series of tests will be the relative stabilities of Ge dimers on Si(001). The ad-dimer can sit in one of two sites (on top of the dimer row, or on top of the trench between dimer rows) and in one of two orientations (parallel to the underlying dimers, or perpendicular (referred to below as 'rotated') to them). This will involve relatively long bonds between both Si and Ge, as well as a large range of bonding angles, testing the parametrization rather well.

The calculations were performed with two different electronic structure techniques: tight binding (using the density matrix method (DMM) [12] in an implementation by Goringe [13]

Table 4. Relative stabilities and bond lengths of Ge ad-dimers on Si(001) from *ab initio* and tight-binding calculations. Energies are given relative to the rotated dimer over the Si dimer row, which is the lowest-energy structure in *ab initio* DFT calculations. Units are eV for energies and Ångstroms for distances.

Position	δE_{DMM}	δE_{Diag}	δE_{DFT}	Ge–Ge_{DMM}	Ge–Ge_{Diag}	Ge–Ge_{DFT}
Row para.	−0.04	0.10	0.20	2.57	2.56	2.56
Row rot.	0.00	0.00	0.0	2.57	2.59	2.59
Trench para.	0.28	0.37	0.65	2.79	2.78	2.72
Trench rot.	0.11	0.16	0.06	2.52	2.52	2.47

and an exact diagonalization technique); and for *ab initio* results to check the tight binding, the local density approximation (LDA) to density functional theory (DFT), using the VASP code [14]. Since the DMM technique is an $\mathcal{O}(N)$ technique, it makes an approximation by truncating the range of the density matrix. While it has been shown that the DMM technique works well with modest cutoffs (such as that used in this work) for situations such as semiconductor surfaces [15], in particular converging forces and energy differences extremely rapidly, we have also performed exact diagonalization simulations to check that the DMM is performing well in this situation. We performed simulations with the same parametrization, using a $4 \times 4 \times 1$ Monkhorst–Pack $\boldsymbol{k}$-point mesh (though the change from a $2 \times 2 \times 1$ mesh was less than 0.01 eV). The same unit cells were used for all the calculations (two dimer rows wide with four dimers in each row, and five layers deep with the bottom layer fixed in bulk positions and terminated in hydrogen). The DMM tight-binding calculations used a spatial cutoff on the density matrix of three Hamiltonian hops, while the LDA calculations used ultrasoft pseudopotentials, a plane wave cutoff of 150 eV and a $4 \times 4 \times 1$ Monkhorst–Pack $\boldsymbol{k}$-point mesh. The results are given in table 4.

We see two good sets of agreement: the DMM agrees well with the exact diagonalization, and the tight-binding results agree reasonably well with the LDA results, though there are slight problems. The exact diagonalization achieves correct ordering of the various dimers, though the magnitudes are not always correct. The DMM finds that the parallel Ge dimer over the row is too stable by 0.25 eV, and the parallel Ge dimer over the trench is also too stable, by 0.37 eV (compared with LDA results). The Ge–Ge bond lengths are well reproduced, capturing the trends in the bonding. From these results we can conclude that the parametrization performs respectably, though results for individual dimers are better for the rotated (epitaxial) dimers than the parallel ones. As we are primarily interested in modelling epitaxial growth of Ge on Si(001), our calculations should be well served. It is also reassuring to note that the DMM is remarkably accurate with a three-hop cluster, so that large scale calculations on strain-induced reconstructions can use this size of cluster with confidence.

We should make one final comment about tight binding in general, and this system in particular. This simple form of tight binding does not include any form of self-consistency (though it can be introduced through schemes such as local charge neutrality [8]) nor does it have any cost for moving charge. As a result, for some structures there will occasionally be large, unphysical charge transfer and an anomalously low energy. However, these situations are normally clear, and can often be avoided by a more careful choice of starting positions.

4. Square features on Si(001)

During gas-source growth of Si(001) (using disilane, Si_2H_6, as the source) square features were observed with STM on the growth surface; these features were always the first to form on

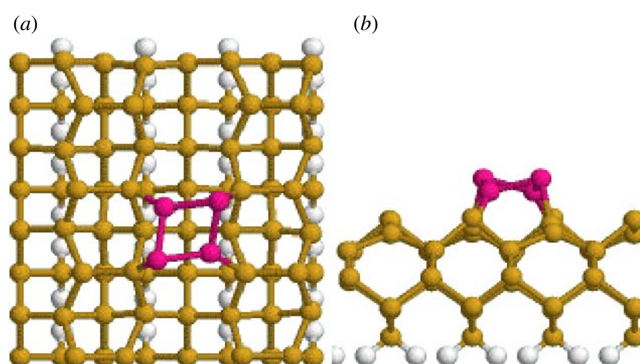

Figure 1. The structure of the relaxed germanium 'square' on Si(001). (*a*) Top view; (*b*) side view. Dark atoms are germanium, light silicon and white hydrogen.
(This figure is in colour only in the electronic version)

the newly grown islands [16]. They were identified as rhomboids of four silicon atoms which flipped rapidly between two equivalent configurations, giving rise to a square appearance, and were postulated as the nucleus of gas-source growth [16]. As such, they are of great potential importance. During subsequent experiments on gas-source growth of Ge on Si(001) (using germane, GeH_4, as the source) similar features were observed, and tentatively identified as being four germanium atoms sharing the same structure as the silicon squares with some preliminary modelling [17]. Here we investigate thoroughly their structure and the barrier to flipping from one configuration to another using the parametrization presented above.

Taking a square of germanium atoms, and allowing it to relax yields the structure shown in figure 1. This structure is 0.97 eV lower in energy than two isolated Ge dimers (in the row parallel configuration), which is similar to the stability of the Si square modelled previously with tight binding [16]. As can be seen, the structure is not symmetric, with figure 1 showing only one configuration. In order to confirm that this feature is indeed what is seen in STM (i.e. that it can flip easily at 300 K or above), we need to calculate the barrier to flipping between the two configurations. The key parameter in this change between configurations is the height difference between pairs of atoms—each 'up' atom has to change with a 'down' atom for the configuration to flip. We have fixed this height difference (in figure 1(*a*), the height difference between the two 'up' Ge atoms and the two 'down' Ge atoms has been maintained) to various values and calculated an energy barrier to flipping, which we find to be 0.59 eV.

A barrier of 0.59 eV, if we assume an attempt frequency of 10^{13} s^{-1} in an Arrhenius formula gives about 560 flips s^{-1} at 300 K. As the STM which took the images could only scan at a maximum speed of 10 lines s^{-1}, the square would have flipped 50–60 times during each scan line. As before, with the silicon square, this will result in a uniform, square appearance (just as dimers appear uniform though they are buckled). This confirms that the features seen in STM are what we predicted.

5. Conclusions

We have shown how a simple approach to fitting tight-binding parametrizations can be extremely successful. Using physical understanding, and fitting to a limited, simple fitting form, a useful tight-binding parametrization can be created with relatively low effort. We have used the Ge/Si parametrization to investigate square features on Si(001) formed during gas

source growth, and identified their structure. We plan to model a variety of the strain effects seen during epitaxial growth of Ge on Si(001) using the parametrization, which will be presented in future work.

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