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1997 J. Phys.: Condens. Matter 9 8213

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Energetics of stacking boundaries on the {0001} surfaces of silicon carbide

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Received 30 May 1997, in final form 4 August 1997

Abstract. Silicon carbide often grows in the cubic phase under conditions where this is not the most stable phase. *Ab initio* calculations are presented which determine the energy of a stacking reversal at the (0001) and (000 $\bar{1}$) surfaces of silicon carbide, and thus whether the cubic form is preferred in the vicinity of a free surface. In these calculations the surfaces are not reconstructed but hydrogen terminated, and care is taken to eliminate the spurious dipole–dipole interaction caused by the imposition of periodic boundary conditions, and also in estimating the amount of residual ionic relaxation. These calculations do show a clear distinction of 13 meV per surface pair between the silicon and carbon surfaces, although the results are not in complete agreement with experiment.

1. Introduction

Silicon carbide has long been known as a polytypic substance, but forming a phase diagram for it is difficult, for annealing is slow, different forms grow under almost identical conditions, and small quantities of impurities have significant effects. Previous studies have found that the cubic form grows under conditions where one of the hexagonal polytypes is more stable. An explanation for this in terms of the energy of a stacking reversal at a surface and based on bulk polytype energies was offered by Heine *et al* [1]. The present paper extends this idea to include a distinction between the two different {0001} surfaces, and tests the validity of applying bulk-derived parameters at a surface.

Different electronic structure calculations all place the cubic phase higher in energy than the 4H and 6H phases at zero degrees Kelvin [2–4], and as theoretical studies also give the cubic phase a higher phonon free energy [5], these results combine to suggest that the cubic phase is unstable at all temperatures. Solid-state transformations of 3C have been observed experimentally by many people including Jepps and Page [6] and Tagai *et al* [7] working in the range 1800 °C to 1900 °C. The transformations are slow, with Jepps and Page finding that just 63% of a sample transformed after one hour at the high temperature of 2300 °C [8].

The cubic phase does grow quite readily epitaxially at temperatures below 2000 °C [9, 10]. It is important to distinguish between slightly off-axis growth, in which growth occurs at the steps on the faces and produces more of the underlying polytype, and on-axis growth occurring on the flat terraces themselves. It is this latter mechanism which often produces cubic growth and which is considered in this paper.

When considering the {0001} surfaces of silicon carbide, there is also a distinction between the carbon-terminated and the silicon-terminated surfaces. These have different

physical properties, most notably surface diffusion lengths differing by an order of magnitude [11], and there are several reports of different surfaces producing different polytypes under otherwise identical conditions [12, 13].

As growth is a non-equilibrium process, there is no fundamental reason for which SiC should grow in its lowest-energy structure. Growth is a complicated process, and can be approached theoretically and computationally only via simplified models. For the layered polytypic structure of SiC, a good model is that of Heine *et al* [1], in which growth is considered to be a layer-by-layer process, with each layer, whilst on the surface having the freedom to orient itself into its most energetically favourable position, then being buried in that position by subsequent layers without subsequent change. Naturally the lowest-energy configuration for a surface layer under these conditions need not be the same as that which it would take up in the bulk if subsequently allowed to anneal. Although this model is necessarily a simplification of the growth process, it is evident that a partial layer at a surface, or even a complete surface layer, will have greater freedom to reorient than a layer in the bulk. Thus this model includes some of the aspects of growth, and permits non-equilibrium phases to grow.

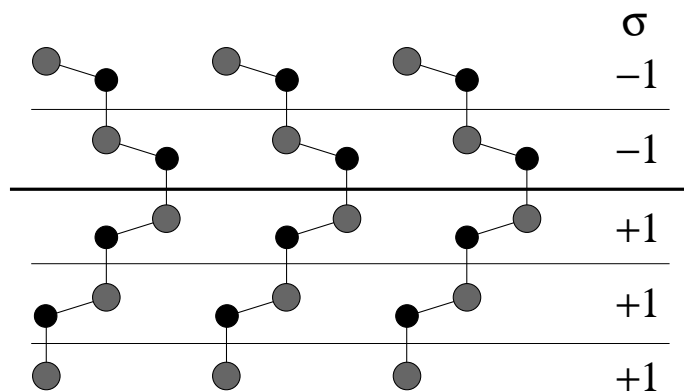


Figure 1. A diagram of the repeat unit of a simple polytype showing how SiC is formed from layers stacked on top of each other, and that each layer can be assigned a ‘spin’, σ , of ± 1 . The stacking reversal is highlighted.

As each layer in SiC can take one of two possible orientations, it is possible to assign a ‘spin’, σ , to a layer, taking values of ± 1 . This is shown in figure 1 where five layers forming the repeat unit of the 15R polytype are shown. The total energy of a bulk system can then be approximated as

$$E = J_0 N - \sum_{i,n} J_n \sigma_i \sigma_{i+n} \quad (1)$$

where the index runs over layers, J_0 is the self-energy of a layer, and J_n is the interaction strength for two layers of separation n . Terms with an odd number of σ s are forbidden by the invariance of E under the transformation $\sigma_i \mapsto -\sigma_i$. This form assumes no multi-layer interactions, and is used and discussed by Heine *et al* [14–16], who considered J_n to be zero for n greater than three.

This model can be used to consider the energy of a layer at a surface simply by considering the interactions between the surface layer and the layers below it in a semi-infinite slab. For the energy of a single layer on the surface of a cubic substrate, one would

obtain

$$E_s = J_0 - \sigma_s \sum_n J_n \quad (2)$$

where $\sigma_s = 1$ if the surface layer is in the same orientation as the substrate, and -1 if it is reversed.

This argument, used by Heine *et al* [1] and Chien *et al* [17], suggests that a cubic substrate will continue to grow cubic if

$$J^* = \sum_n J_n > 0 \quad (3)$$

for then the surface layer has a lower energy when lying in the same orientation as the substrate. The first few terms dominate in this sum, and Heine *et al* found that the inequality holds when using values of J_n calculated from the bulk material.

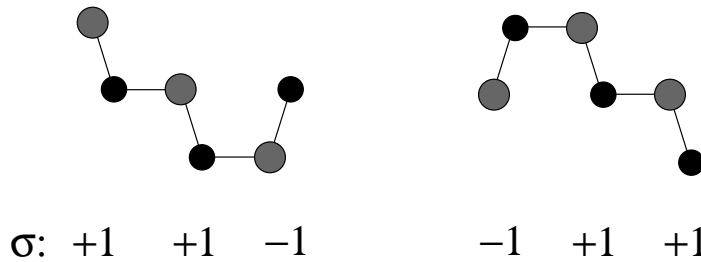


Figure 2. Two three-layer blocks. If each block represented the repeat unit of an infinite system, the systems would be related by a translation. If each block was finite, but all of the atoms identical, the blocks would be related by a rotation. Only in the case of distinct atoms and finite blocks are these configurations distinct.

Not only does this analysis ignore any surface energy or surface relaxation effects, but it has one other significant deficiency: it does not distinguish between the two types of surface, the carbon-terminated and the silicon-terminated surfaces. Indeed, although Shaw and Heine [16] showed that equation (1) contains all terms involving fewer than four layers for any bulk system, and certain finite systems such as silicon or diamond, they also showed that additional terms can arise in finite systems of low symmetry such as silicon carbide slabs. For a simple three-layer block, such as that shown in figure 2, they showed that the energy should be written as

$$E = 3J_0 - J_1\sigma_1\sigma_2 - J_1\sigma_2\sigma_3 - J_2\sigma_1\sigma_3 - \alpha(\sigma_1\sigma_2 - \sigma_2\sigma_3). \quad (4)$$

The last term can distinguish between systems whose spins are 1, 1, -1 and -1 , 1, 1. If all of the atoms were of the same species, this pair of systems would be related by a rotation, and α would therefore be zero. Even if α is non-zero, it makes no contribution to the energy of an infinite crystal as all of the terms containing it cancel. Thus α cannot be determined from bulk calculations alone.

Therefore the present work attempts to calculate J^* by considering a surface directly, rather than extrapolating from bulk behaviour. Thus it avoids the need to consider the many additional terms arising at surfaces of which the α term discussed above is an example.

Using recent advances in technique and computing power, it is possible to calculate the energy changes on reversing a surface layer on a silicon carbide slab directly within the LDA formalism. This change is simply twice J^* , if α is ignored. The calculation can be done separately on each surface in order to find any surface dependency.

In such calculations small energy differences of very much less than kT per atom at typical growth temperatures are significant, because a whole plane of atoms must be switched together as a single unit, and such planes may be hundreds or thousands of atoms across, for the energy cost of roughening such a plane is very high. The energy change on switching such a unit will therefore be greater than kT even for very small energy changes per atom.

2. Method

This work uses the Cambridge *ab initio* plane-wave LDA code called CASTEP [18], with the exchange–correlation energy as parametrized by Perdew and Zunger [19], and norm-conserving pseudopotentials in the Kleinman–Bylander form [20] produced following the method of Lee [21].

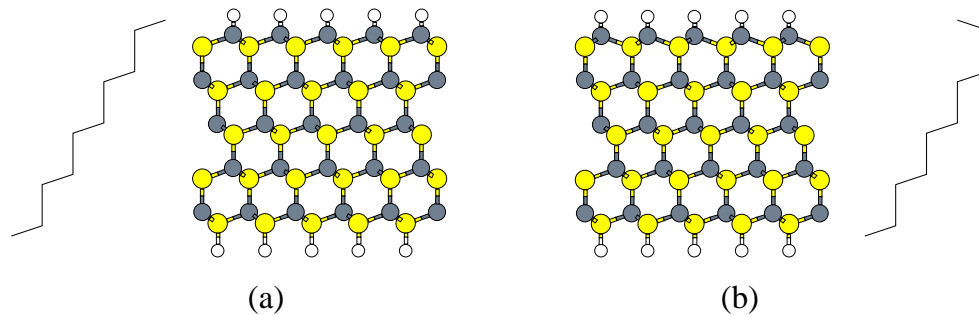


Figure 3. Diagrams of a stacking reversal at the (0001) surface in SiC. In (a) a wholly cubic slab is shown, whereas in (b) the top (carbon) layer has had its orientation reversed. Hydrogen atoms terminate both surfaces. The basic stacking structure is shown at the side of each diagram.

Calculations were performed on the SiC surfaces shown in figure 3 and on the corresponding silicon-terminated surfaces. Thus the energies of pairs of systems, one with and one without a stacking reversal on the surface, are being compared, and the energy of the stacking reversal can be determined from the difference. According to the simple layer-by-layer growth model above, the configuration with the lower energy will determine the growth structure.

Although the unit cells used are relatively small, the computation cost is still high due to the presence of carbon which requires a high cut-off in the plane-wave basis set. In these calculations 560 eV was used, a $7 \times 7 \times 1$ Monkhorst–Pack k -point set [22], and 9 Å of vacuum, as measured between the hydrogen nuclei. Atomic relaxation was permitted perpendicular to the surface in the four double layers closest to the surfaces considered.

The hydrogens were placed on the surface in order to reduce the computational cost. By saturating the surface ‘dangling bonds’ with hydrogen, the need to reconstruct the surface is avoided. A simple 2×1 reconstruction would not only double the cell size and thus increase the computation involved in calculating the wavefunction at a single k -point, but the resultant reduction in symmetry caused by the reconstruction would also increase the

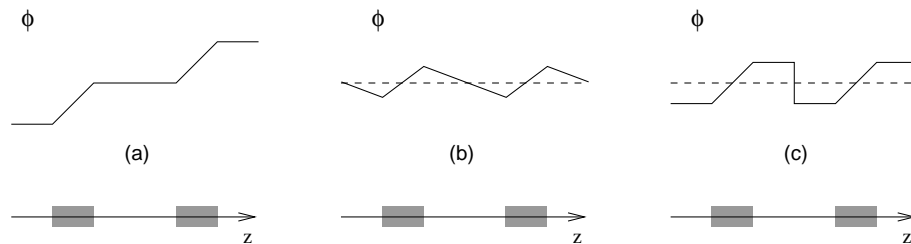


Figure 4. Diagrams showing schematically the effect of applying periodic boundary conditions to the potential of a cell with a dipole moment. In (a) the potential before periodic boundary conditions are imposed is shown, in (b) the potential after they are imposed is shown, and in (c) the use of a discontinuity in the potential to recover the form of (a) with periodic boundary conditions is shown. The shaded regions along the z -axis indicate the positions of the SiC slabs.

number of k -points in the irreducible Brillouin zone. The atomic relaxation would also be complicated, for with no reconstruction the symmetry constrains the atoms to move perpendicular to the slab only. Thus choosing to terminate the slab with hydrogen, which is present anyway in large quantities when SiC is grown by gas decomposition, reduces the computational cost by a factor of ten or more.

When modelling a slab with a plane-wave basis set, the requirement to impose periodicity in the third dimension can cause difficulties, as the periodic images of the slab interact with each other. These interactions tend to zero as the separation of the periodic images is increased, but they do so slowly. The most slowly decaying interaction is that caused by the dipole moment of the slab. It produces a change in the potential from one face to the other. As the potential must be periodic, a compensating uniform electric field is introduced automatically throughout the cell. This is shown in figure 4.

This electric field can be removed self-consistently by placing a discontinuity in the potential in the middle of the vacuum region, as has been shown by Neugebauer and Scheffler [23]. This gives much faster convergence of both energies and forces with respect to vacuum size than would otherwise be the case. This correction has been described in a more general manner by Makov and Payne [24], who considered the case of isolating a molecule from its images in all three directions.

The pseudopotentials used were tested by calculating the lattice constants and bulk moduli of silicon, carbon and silicon carbide. The lattice constants were reproduced to within $1\frac{1}{2}\%$ of experimental values [25] and the bulk moduli to within 6% of the best experimental values [25, 26].

In order to test the pseudopotentials further, calculations were also performed on the main bulk polytypes of silicon carbide. The structures in these tests were not permitted to relax, but the ideal tetrahedral bond angles and lengths were imposed. Their relative energies as calculated are shown in table 1. These calculations used a 600 eV cut-off and a $7 \times 7 \times 1$ Monkhorst-Pack [22] mesh referred to a 12-layer supercell, and these results are in broad agreement with previous work [3, 4].

From these results, and assuming that $J_n = 0$ for $n > 3$ in equation (1), values for J_1 , J_2 and J_3 , and hence also J^* , can be calculated [15]. The resulting values are given in table 2 where it can be seen that $|J_n|$ does decrease rapidly with increasing n , and J^* is indeed positive. It is hoped to recalculate in the future the relaxation of the bulk structures in view of the different conclusions reported by different authors [4, 15].

Table 1. Relative energies of selected unrelaxed bulk polytypes of SiC. Units are meV/SiC pair.

Polytype	Energy
2H	6.0
3C	0.0
6H	-2.2
4H	-2.4

Table 2. J_n s from unrelaxed polytype energies. Units are meV/SiC pair.

J_1	J_2	J_3	J^*
3.47	-2.71	-0.47	0.29

3. Results

The energies sought are simply the energy changes on reversing a surface layer. These are presented in table 3, both before and after atomic relaxation was permitted. It can be seen that a reversal on the silicon face is energetically favourable, whilst this is not so on the carbon face. These can be compared to the estimation of $2J^*$ from table 2 which yields 0.58 meV. The best comparison would be with the energy change of a reversal averaged over the Si and C surfaces and with no relaxation, that is -0.96 meV. The averaging will remove the affects of the α -terms discussed above, and the use of the unrelaxed geometries is then common to the bulk and surface calculations.

Table 3. Energy changes on the reversal of a surface layer from the cubic orientation of a (0001)-type face of SiC. Units are meV.

Relaxation	C reversed	Si reversed
No	3.68	-5.59
Yes	1.4	-11.7

In order to test convergence with respect to the plane-wave cut-off, k -point sampling and number of layers of bulk, the calculation of the unrelaxed energy difference on the carbon surface was repeated with different values of these parameters. Increasing the cut-off to 650 eV changed the energy difference by 0.05 meV, using a $9 \times 9 \times 2$ k -point mesh produced a 0.1 meV change, and using six layers of bulk and an extra ångström of vacuum produced a 0.01 meV change. Thus we are confident of reasonable convergence with respect to these parameters.

Estimating the error due to the lack of complete ionic relaxation is more difficult. The scheme used was to consider the expression

$$\Delta E = \sum T_n^2 / 2k. \quad (5)$$

where the sum is over the region being relaxed, k is the spring constant of a typical bond, and T is not the residual force on each atom, but rather the residual tension in an idealized interlayer bond. Such tensions can be calculated in this simple geometry where only relaxation perpendicular to the slab is considered, and there is a free surface. This is

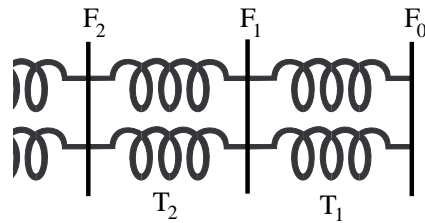


Figure 5. The relationship between the resultant forces on the layers and the tensions in interlayer springs.

shown in figure 5, where it can be seen that starting from the free end, it is trivial to derive the spring tensions T given the forces on the layers F , for T_n is simply the sum of the F_i s over i from zero to $n - 1$.

This method can be tested by applying it to the initial unrelaxed surfaces, where the relaxation energy is approximately known from the firm lower bound given by the almost-complete atomic relaxation performed. This comparison is given by table 4, where k is taken to be $18 \text{ eV } \text{\AA}^{-2}$ [27].

Table 4. Energy changes on the relaxation, predicted and calculated. Units are meV.

Surface	Reversal	$\sum T_n^2/2k$	Calculated
C	No	43	39
C	Yes	50	42
Si	No	49	35
Si	Yes	51	41

Thus this bond-based estimate of the relaxation energy can be seen to give a good estimate of the remaining relaxation, with a slight tendency to overestimation. By applying this estimate to the relaxed geometries, it is found that all of the relaxed structures are relaxed to within 0.2 meV of their equilibrium geometries.

4. Conclusions

These calculations show a clear distinction between the carbon and silicon surfaces, the one having a slight preference for remaining in the cubic orientation, the other a strong preference for reversing the stacking direction. The 1.4 meV/pair preference of the carbon surface for remaining cubic is hardly overwhelming, although significant at the level of the expected errors in these calculations. The 11.7 meV/pair preference for reversal of the topmost double layer at the silicon surface is much more significant. This distinction between the two surfaces, favouring cubic growth on the carbon surface, agrees with that found by Lilov *et al* [13], but disagrees with the more recent work by Stein and Lanig [12]. The experimental literature thus does not clearly show which surface favours which polytype, although slightly more evidence backs the results of Stein and Lanig. The major source of error in these theoretical calculations is expected to be the omission of any consideration of surface reconstructions.

The earlier analysis using J^* s calculated from bulk properties is not a particularly good predictor of the energies of boundaries at the surface. Even accepting that it can

only predict the average energy of a stacking boundary at a surface, without being able to distinguish between the two surfaces, the use of the bulk-derived data gives a reversal energy of 0.58 meV rather than -0.96 meV. As the sign of this energy is of great physical importance, as it could cause a change from cubic to hexagonal growth, these two methods have produced significantly different results. However, in a system where J^* did not lie so close to zero through partial cancellation of the J_n s, the analysis from the bulk results might have been adequate.

With the approach given in this paper, a clear difference between the energy of a stacking boundary on the (0001) and (000 $\bar{1}$) surfaces on silicon carbide has been found, a difference which would affect the subsequent polytypic growth of the surfaces, producing cubic growth on one surface and hexagonal growth on the other. There is much scope for further study in this area, considering the effect of surface reconstructions or stacking boundaries in the bulk close to the surface, and this work has shown the possible benefit of such study.

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