journal

J. Am. Ceram. Soc., 74 [10] 2630–33 (1991)

The Preference of Silicon Carbide for Growth in the Metastable Cubic Form

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A paradox is discussed concerning the growth of SiC polytypes from the vapor or the melt, based on recent ab initio quantum calculations of the relative energies of several polytypes in bulk. Why does the cubic (3C) structure grow in preference to all others, although the calculations indicate it is not the stable phase at any temperature? This can be explained from the calculations, with some further approximations, as due to the constrained equilibrium when adding one atomic double layer at a time to the growing crystal in the hexagonal direction without allowing rearrangement of the lower layers. The differing roles of donor and acceptor impurities are also discussed, with donors being found to favor the cubic structure. [Key words: silicon carbide, crystal growth, crystal structure, calculations, stability.]

I. Introduction

THE purpose of this paper is to discuss the paradox of why SiC grows in its metastable cubic phase. Why does it appear not to crystallize directly into the stable structures, one or other of the ⟨2⟩/⟨3⟩ family of polytypes (in the Zhdanov[1] notation)? We will discuss this question in the light of some recent quantum-mechanical energy calculations.[2–9] Our treatment may be the first application of such calculations to a question in crystal growth.

As is well-known, SiC exists in many polytypes, namely the cubic zinc blende structure ⟨∞⟩ (or 3C), the wurtzite structure ⟨1⟩ (2H), and the polytypes ⟨2⟩ (4H) and ⟨3⟩ (6H) with many intermediate phases such as ⟨23⟩ between these last two. All the structures consist of nearly identical SiC atomic double layers, each of which can be stacked in two orientations,[1] designated as $\sigma = \pm 1$, on the layer below (Fig. 1). Recent very careful quantum-mechanical calculations[2–4] have computed the relative energies of the main polytypes with the results shown in Fig. 2. We shall not be concerned here with the very small (free) energy differences between ⟨2⟩, ⟨3⟩ and their intermediate polytypes which have been discussed elsewhere:[5–7] for present purposes we treat the whole ⟨2⟩/⟨3⟩ family of polytypes as having nearly enough the same (free) energy. The main point of Fig. 2 is that the cubic ⟨∞⟩ and wurtzite ⟨1⟩ structures have significantly higher energy than the ⟨2⟩/⟨3⟩ polytypes at temperature $T = 0$ K, and the phonon free energy[5] at higher T and the small relaxations of the interplanar spacings[6] do not alter that picture. Incidentally, Fig. 2 also shows that the overall energy scale in SiC is similar to that for Si: the collapse of all the energy differences is not the origin of polytypism in SiC (unlike ZnS[4]). The energy differences in Fig. 2 include the effects of relaxation of the interlayer spacing from the cubic value which occurs in the noncubic polytypes.[6] We should point out for readers not familiar with such calculations that their validity has been widely accepted when applied to energy differences between similar structures, e.g., the forces giving phonon frequencies which can be checked by experiment.[8] There seems no reasonable doubt that neither the cubic nor the wurtzite structure is ever the stable phase of perfect pure SiC. This is consistent with modern experiments which indicate that ⟨3⟩ is the stable form at high T (see, for example, Refs. 10 to 12 and other authors cited there) and probably ⟨2⟩ at low T with calculations suggesting some other intermediate polytypes being stable phases in between.[5,7] (However see Ref. 13 for some contrary indication.)

The paradox is that SiC appears to prefer to grow in the cubic form, more than in any other, in spite of the fact that this is never the stable structure. The cubic form is so commonly observed that in the past it was often supposed to be a stable phase at some T: see, for example, Fig. 4 of Ref. 10 and references there. More to the point, recent work indicates that the cubic form is the structure that first grows whether as crystals[10,11] or whiskers,[14] from the melt or from the saturated vapor.[15] The more complex ⟨2⟩/⟨3⟩ polytypes appear to form subsequently by a solid-state transformation. Of course, crystal growth is not an equilibrium structure. Nevertheless it is a bit surprising. (We ignore the wurtzite form ⟨1⟩ which only grows under unusual conditions,[16] consistent with its having a much higher energy as seen in Fig. 2.) We shall discuss this in Section II and show that the quantum-mechanical calculations[3] do shed some light on this. They were carried out for

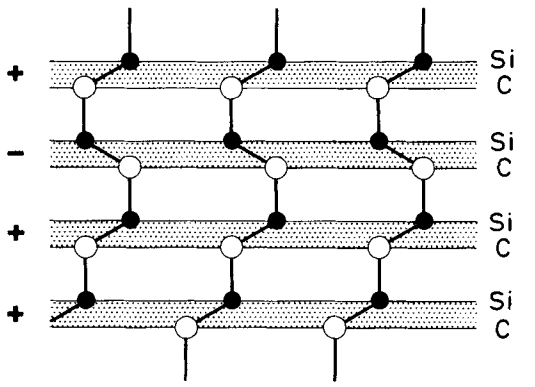

Fig. 1. Stacking of identical atomic double layers of SiC in two orientations, labeled + and − according to the direction of the bond in the layer.

D. Johnson—contributing editor

Manuscript No. 197365. Received August 13, 1990; approved June 24, 1991.

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Fig. 2. Computed relative energies ΔU for some polytype structures of Si and SiC. The structures ⟨2⟩ and ⟨3⟩ for SiC have equal energy within the accuracy of the calculations. Left scale: meV per SiC or Si_2 pair of atoms. Right scale: kcal/mol for SiC or double-mol for Si. (1 eV = 23 kcal/mol.) Results for SiC and Si from the J_n in Ref. 3.

bulk SiC structures and hence cannot be applied strictly to a surface,[17] but if one just proceeds with the simplest obvious assumptions one immediately obtains the result that the material should always grow in the cubic form.

As a separate issue we consider in Section III the differing roles of electron and hole carriers from donor and acceptor impurities, based on ideas of electronic structure.[9,18] Electrons are expected to favor the cubic structure, with holes having a more minor effect. This is consistent with the observation that nitrogen under high pressure can induce the transformation from ⟨3⟩ to ⟨∞⟩,[10] nitrogen being a known donor.[19] Thus stray donor impurities may be an additional reason for the growth of the cubic structure.

Neither of these stories constitutes a conclusive theory. They are put forward as plausible interpretations of the observed facts in the light of recent computations and as pointers to future avenues of research. They appear sufficiently probable that at least one may say there is no mystery about SiC growing in the metastable cubic structure rather than the equilibrium phase(s). Most theories and calculations are constructed with a particular end in view, and in choosing what to look for one puts in to some degree the answer one wants. However, the calculations cited here were all for the bulk structures, with no thought about surfaces or crystal growth. To that extent the present considerations are an unplanned and unbiased byproduct. We put them forward here because the computational capabilities to follow up most of them still lie some years in the future, e.g., the energy of a surface layer in contact with a melt.

II. Growth of the Cubic Phase

As already remarked, we can consider an arbitrary polytype as consisting of identical SiC atomic double layers (hereafter referred to as "layers"). Each layer can be stacked in two different orientations on the one below, which we designate for the nth layer by the symbol $\sigma_n = \pm 1$. For example, the two common structures ⟨∞⟩ and ⟨3⟩ are as follows:

$$\langle\infty\rangle = \ldots{+}{+}{+}{+}{+}{+}\ldots \quad \text{or} \quad \ldots{-}{-}{-}{-}{-}{-}\ldots$$
$$\langle 3\rangle = \ldots{+}{+}{+}{-}{-}{-}{+}{+}{+}{-}{-}{-}\ldots \tag{1}$$

The energy of the structure can be written[17]

$$U = \sum_n [E_0 - J_1\sigma_n\sigma_{n+1} - J_2\sigma_n\sigma_{n+2} - J_3\sigma_n\sigma_{n+3} - K\sigma_n\sigma_{n+1}\sigma_{n+2}\sigma_{n+3}] \tag{2}$$

where interactions beyond the third nearest layer are neglected. The values of the parameters were fitted to the total energies computed for five different polytypes.[3] The calculations were carried out with modern norm-conserving pseudopotentials, a basis set of about 2500 plane waves for each Bloch electron wave function, the usual local density approximation for exchange and correlation in the context of density functional theory, and the most careful sampling of **k**-points in the Brillouin zone (see Refs. 2 and 3 for details). The values of the parameters are[3,4] (in meV per SiC pair of atoms)

$$J_1 = 4.40, \quad J_2 = -2.56, \quad J_3 = -0.05, \quad K = -0.45 \tag{3}$$

These numbers have been refitted to the calculations of Ref. 3, taking into account that the ⟨1122⟩ structure[3] was calculated only to a lower level of convergence than the other polytypes. We have estimated the energy it would have at the higher level by adding in the average of the convergence corrections found for the ⟨1⟩ and ⟨2⟩ structures, and then refitted all the constants. They should be taken as superseding all previously published values.[2-4] The differences from the previous values[3,4] are part of the computational uncertainties. The small quantities J_3 and K are very uncertain except for order of magnitude and probably sign.

Let us apply this formalism (2) blindly to a semi-infinite crystal (i.e., a crystal with a surface), leaving a critique until later. We can write down from Eq. (2) the extra energy ΔU (σ_{new}) for adding one new layer specified by σ_{new} on top of the previous surface layer specified by σ_s, without allowing the underlying layers designated by σ_{s-1}, σ_{s-2}, etc., to change. We obtain

$$\Delta U(\sigma_{new}) = E_0 - J^*\sigma_{new}\sigma_s \tag{4}$$

where

$$J^* = J_1 + J_2\sigma_s\sigma_{s-1} + J_3\sigma_s\sigma_{s-2} + K\sigma_{s-1}\sigma_{s-2} \tag{5}$$

as can easily be verified by inserting Eq. (5) into Eq. (4) and noting $\sigma_s^2 = 1$. Clearly the value of J^* depends on the orientations of the underlying layers s − 1 and s − 2. The point about Eq. (5) is that (with positive J_1) the value of J^* ranges between the maximum and minimum values

$$J_1 \pm (|J_2| + |J_3| + |K|) \tag{6}$$

which with the values (3) become (in the same units)

$$J^*(\max) = 7.47, \quad J^*(\min) = 1.33 \tag{7}$$

The crux of our argument is now as follows. We see from Eqs. (7) that J^* is always positive. Applied to Eq. (4) this means that the new layer will always go down oriented parallel to the previous surface layer. Here we assume that the crystal grows by adding new SiC atomic double layers in the c (hexagonal) direction. We also assume a new layer orients itself such as to minimize its energy, with the constraint that the underlying layers are *not* allowed to anneal to some new global energy minimum. If the process is continued, clearly all layers will have the same orientation and we have built up the cubic polytype, irrespective of the original substrate or occasional accidental misorientations. This is what we set out to show. Our concept of the constrained equilibrium is completely analogous to the spinodal condition in Refs. 12, 20, and 21.

Is our argument a matter of the accident of numbers? Not entirely. Let us start from the experimental fact of the existence of what we have called the ⟨2⟩/⟨3⟩ family of polytypes, all of which we therefore suppose to have very nearly the same energy. This multiphase degeneracy[2-5] occurs from Eq. (2) when[22]

$$J_1 + 2J_2 - 3J_3 - 4K = 0 \tag{8a}$$

with

$$J_2 < -\frac{1}{2}(J_1 - K), \quad J_1 > 0 \tag{8b}$$

The fact that SiC, rather than some other compound, is near this degeneracy is of course a numerical accident (although it is also part of a wider trend[2,3]): it implies that conditions (8) are nearly satisfied. If we simplify the argument by dropping the

small long-range corrections J_3 and K, the conditions (8) reduce to

$$J_1 + 2J_2 = 0, \quad J_2 < 0 \tag{9}$$

We then have from expressions (6) and (9)

$$J^*(\min) = J_1 - |J_2| = (J_1 + 2J_2) + |J_2| \approx |J_2| \tag{10}$$

Since the term in parentheses in Eq. (10) is nearly zero from the degeneracy condition (9), we deduce from Eq. (10) that J^*(min) is necessarily positive, leading to the growth of the cubic form as argued before. The argument hinges on the coefficient of J_2 being 2 in Eqs. (8) and only unity in Eq. (5). This comes about because there are two second-neighbor interactions across a boundary between + and − layers whereas only one interaction is involved in adding a new layer at a surface (Fig. 3). Incidentally we can relate the energy of the cubic structure $\langle\infty\rangle$ in the same way to that of the polytypes, say the phase $\langle 3\rangle$. We have[2,3]

$$U\langle\infty\rangle - U\langle 3\rangle = -\frac{2}{3}(J_1 + 2J_2 - 3J_3 - 4K) - 4J_3 - 4K \tag{11}$$

Again the term in parentheses is nearly zero if the condition (8*a*) is nearly satisfied and the other two terms are relatively small longer-ranged corrections. Thus the free energy difference which would drive the reconstruction of the cubic phase is significant, but on a smaller scale relating to more distant neighbors (J_3, K) than the J^* (5), (10) of order J_2 which controls the orientation of the new layer. This is all just a generalization of the well-known multiphase degeneracy (9) in the ANNNI model.[22]

We see therefore that our conclusion about the growth of the cubic phase is "robust" in the sense that it does not depend critically on the numerical values of the J_n. Indeed as the argument of Eqs. (8) to (11) shows, it does not depend on calculations at all, although people might find it less convincing without the numerical backup. This is shown further by writing from Eq. (10)

$$J^*(\min) = \frac{1}{4}[E(1) - E(3)] - [E(\infty) - E(3)] + [\text{terms in } J_3, K] \tag{12}$$

Thus J^*(min) is inevitably positive if we believe that $E(1)$ lies much higher than $E(\infty)$ and $E(3)$ and that the longer-range couplings J_3, J_2 are small compared with J_1, J_2.

Our argument can also be seen from a different perspective. The MAS-NMR data,[23] the relaxation of the interatomic spacings,[24,6] the interplanar interactions,[3] and the interatomic force constants for atomic displacements[5] all bear witness to the fact that the orientation of one atomic double layer exerts a noticeable influence to a distance of about three double layers. This is discussed in Ref. 17 and elsewhere.[3,5,6,9,25] Our present argument in Eqs. (8), (9), (10) rests on the fact that $2|J_2|$ is approximately equal to J_1, i.e., that the orientational interaction between fourth-neighbor bonds is substantial and comparable to that between second-neighbor bonds. Thus we see that the long-range nature of the effects manifests itself also in connection with crystal growth. However, it is not possible to draw a more direct or quantitative connection between, for example, the observed relaxation of the interatomic spacings[6,24] and the present energetic considerations, except to say that both follow from our calculation of the electronic structure.

We must now return to the two caveats. A careful analysis[17] of Eq. (2) shows that it is valid only for an ideal infinite solid. For a slab of finite thickness or a semi-infinite solid with a free surface there are additional terms, first from the existence of the termination and second from any relaxation effects which there may be there. Shaw[17,26] has derived the terms due to the surface by considering a finite slab of four layers and expressed them as energy differences between different stacking structures. Similar arguments can be applied to our case of a semi-infinite solid. The termination corrections are in principle nonzero (they are small higher-order differences[17,26]) even for an ideal unreconstructed surface. However, in the case of growth from the melt, the original argument of Eqs. (4) to (10) based on Eq. (2) again becomes correct if we assume there is no surface reconstruction and if we can approximate the effect of the liquid as the mean of all possible solid structures of $\sigma = 1$ and $\sigma = -1$ layers: such an averaged solid with its lack of orientation but local tetrahedral bonding may not be a bad equivalent to the liquid. In growth from the vapor, the main surface reconstruction energy does not affect the discussion because it is a constant, moving forward as each layer is added. But the reconstruction can also modify the value of J_1, etc., for the surface layer.

III. Donor and Acceptor Impurities

The band gap of SiC is 2.39 eV for the cubic form and 3.1 ± 0.1 for the $\langle 2\rangle/\langle 3\rangle$ polytypes.[10] To see the effect of this substantial difference of 0.7 eV we need to consider the band offset between, say, cubic and $\langle 3\rangle$ SiC in the ususal sense of semiconductor heterojunctions.

The band offset has been calculated between the two extreme forms $\langle 1\rangle$ and $\langle\infty\rangle$ of SiC, with the result indicated schematically in Fig. 4. There is almost zero offset between the tops of the valence bands and almost the whole of the difference in the band gaps appears as a large offset between the conduction bands. This is also consistent with the fact that the state at Γ at the top of the valence band is exactly the same for all tetrahedrally bonded structures in a chemical tight binding picture.[18] On the other hand, the conduction bands are more sensitive to the detailed structure[18] and presumably account for the difference in band gap. Thus we expect Fig. 4 to represent qualitatively also the band offsets between cubic SiC and the $\langle 2\rangle/\langle 3\rangle$ polytypes.

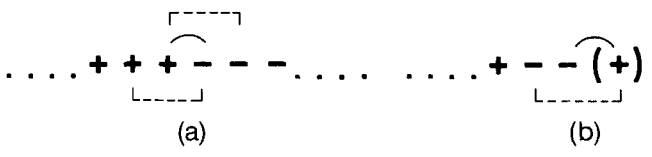

Fig. 3. Competition between nearest layer J_1 interactions (curved full line) and second nearest J_2 interactions (straight dashed box): (a) at a boundary between + and − stacking in bulk material, and (b) when an extra layer (bracketed) is added at a surface on the right. In case (a) there are *two* second-neighbor interactions involved, but only *one* in (b), thus accounting for the terms $2J_2$ and J_2 in Eqs. (8a) and (6), respectively.

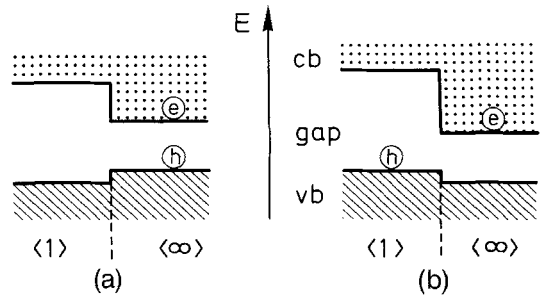

Fig. 4. Form of band offset between $\langle 1\rangle$ and $\langle\infty\rangle$ forms of SiC (afer Ref. 9). The valence bands line up with a very small offset of (b). The case of $\langle 2\rangle/\langle 3\rangle$ polytypes and the $\langle\infty\rangle$ structure is assumed to be similar with the difference of 0.7 eV in the band gap appearing mostly in the conduction band offset. In that case electrons (donors will strongly favor the $\langle\infty\rangle$ structure while holes (acceptors) will have a small effect.

We can infer from Fig. 4 that electrons in cubic SiC have about 0.7 eV lower energy than in the ⟨2⟩/⟨3⟩ SiC polytypes, whereas for holes there is little difference. Let us assume that the chemical bonding energy of an ionized donor is the same in either structure because of the local similarity. Then the whole impurity atom, electron plus ionized donor, also has 0.7 eV lower energy dissolved in the cubic form, while for acceptors the difference is small. In the crystallization process, this difference will act as a driving force favoring the growth of the cubic form, equal to an energy difference of 0.7 eV per donor incorporated into the crystal.

We conclude that donors favor cubic SiC whereas acceptors have little influence. The magnitude of the effect is estimated as follows. The energy difference between cubic SiC and the ⟨2⟩/⟨3⟩ polytypes is 1 meV per SiC pair of atoms[3] whereas one donor contributes a difference of 700 meV. A donor concentration greater than 1 in 1400 atoms would therefore result in the cubic form having the lower energy. This is consistent with the transformation of ⟨3⟩ to ⟨∞⟩ under a high pressure of nitrogen[10] which is a donor.[19] The numbers must only be taken as an order-of-magnitude estimate. We believe this band offset effect must be larger than any inherent difference in the heat of solution ΔG of the impurity in the polytype. For the latter effect to be comparable we would have to have $\Delta G_A - \Delta G_B$ of order 0.7 eV where A and B refer to cubic and ⟨3⟩ material: this seems to us unlikely in view of the close similarities between the polytypes.

Incidentally, similar considerations apply to the equilibria between ⟨2⟩, ⟨3⟩ and more complex polytypes. The difference in band gap between ⟨2⟩ and ⟨3⟩ is 240 meV whereas the free energy differences[3,5] in the pure form are of order 0.1 meV per atom.

We conclude that donor concentrations (atom fractions) of order 10^{-3} or more shift the equilibrium significantly in favor of the ⟨3⟩ form, which may account for some of the impurity effects observed.[10]

We can apply similar considerations to comment on the growth of the wurtzite ⟨1⟩ structure. It is not understood why this form of SiC grows at all, since it has a substantially higher energy (Fig. 2). It appears to be stabilized by acceptor impurities. Our present argument of Fig. 4 means that donor impurities would *de*stabilise the wurtzite structure by 0.9 eV per donor compared with acceptors. It is therefore hardly surprising that the impurities mentioned (aluminum and boron) are indeed acceptors.[16,27,28]

Finally, we might wonder about deviations of the Si/C ratio from stoichiometry. No calculations have been carried out but the dominant effect would presumably be a linear interpolation of the J_n, K between those for Si and SiC, respectively. Then one can easily infer from Fig. 2 that an excess Si concentration at least of order 20% would be needed to make the cubic form stable. We therefore do not believe this effect to be significant in reasonably pure material.

IV. Conclusions

The main conclusion is that a simple model can make it plausible why SiC most commonly grows in the cubic structure even though this is not the structure of lowest energy. Based on calculations and the bulk energies of different polytypes, one can formulate the energy difference $-2J^*$ of a new atomic SiC bilayer going down with bonds pointing in the same ("staggered") or opposite ("eclipsed") orientation. The crucial point of the argument is that J^* is necessarily positive, resulting in the cubic structure, if we assume a constrained equilibrium for the added layer. By this we mean it goes down in the orientation of lower energy, without allowing the lower layers to rearrange to some global minimum energy. The model envisages the crystal growing by adding successive layers in the c (hexagonal) direction, and assumes that surface effects do not destroy the positive sign of J^* deduced from bulk energies. It is not necessary to suppose a whole layer to be completed before the start of the next one: the argument applies to the initial island layer formed on the surface from which the rest of the layer grows.

A separate conclusion concerns the different roles of donor and acceptor impurities. Electronic structure calculations show that the valence band offset between different polytypes is small, so that there are large offsets between the conduction bands corresponding to the differences in band gap. In consequence acceptors will not favor any particular polytype (from this effect), whereas donors will favor the polytype with the smallest band gap. This is the cubic form, or among the ⟨2⟩/⟨3⟩ family of polytypes the ⟨3⟩ structure.

Acknowledgment: One of us (V. H.) is indebted to Prof. T. Page and Prof. R. Helbig for helpful conversations and to the Max Planck Institute, Stuttgart, for hospitality while this work was carried out.

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