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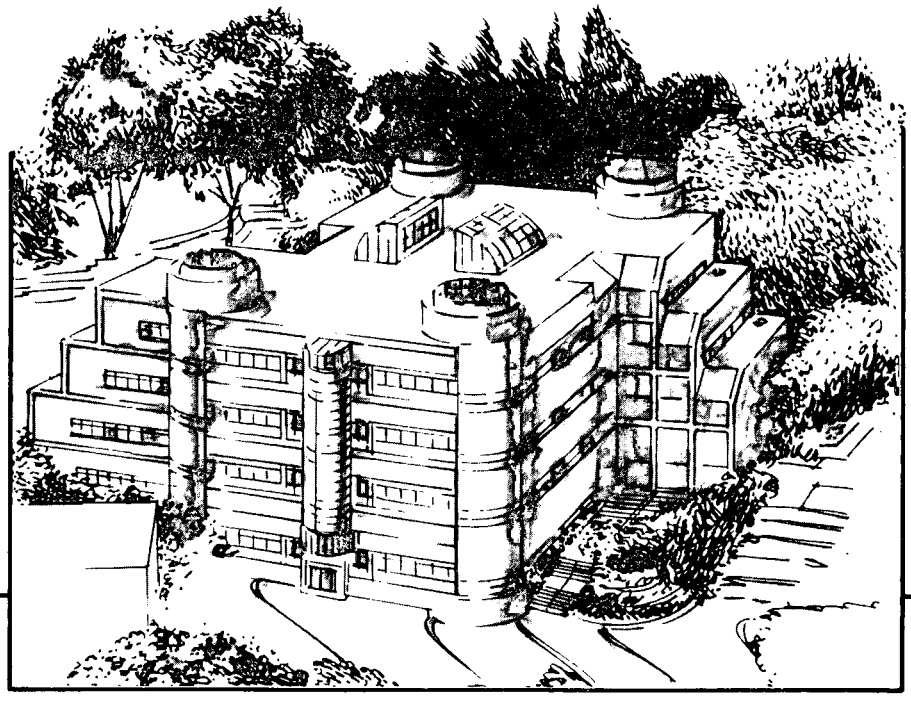

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LBL-28521

COMPOSITION OF THE RECONSTRUCTED α SiC(000$\bar{1}$) SURFACE

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Abstract.

Selfconsistent total energy quantum chemical (AM1) calculations were performed on clusters modelling unreconstructed as well as $(\sqrt{3} \times \sqrt{3})R30^o$ reconstructed α SiC$(000\bar{1})$ surfaces. In order to preserve the partially ionic nature of the bonds terminating the clusters in bulk-like positions, the investigated clusters were saturated by two different types of hydrogen-like pseudoatoms. The approach was first tested on the clusters modelling bulk and then it was applied to model the surface. Calculated surface energies clearly favour the Si adatom terminated $(\sqrt{3} \times \sqrt{3})R30^o$ reconstructed surface with the Si atoms directly under adatoms (second layer in the unreconstructed surface) substituted by carbon. The mechanism which favours this particular composition is also discussed.

1. Introduction.

The growing perspective of repeatable manufacturing of high quality epitaxial SiC films has attracted considerable interest in studying properties of SiC surfaces [1,2]. This paper addresses the reconstructed $(000\bar{1})$ (C-terminated) surface of the (hexagonal) α SiC phase. After annealing the surface is known to assume the $(\sqrt{3} \times \sqrt{3})R30^o$ reconstruction pattern hereafter referred to as R3 [3,4]. The process is accompanied by the depletion of silicon, which suggests possible excess of carbon in the reconstructed surface. Nevertheless the final composition of the reconstructed surface has not been resolved experimentally. This situation then leaves room for theoretical investigation.

To shed some light on the possible composition of the α SiC$(000\bar{1})$ R3 reconstructed surface I performed total energy selfconsistent quantum chemical (AM1) [5] cluster calculations modeling the unreconstructed relaxed (1×1) surface and the different compositions of the R3 reconstructed surface. The selection of the particular computational method was based on previous experience with MINDO/3 [6] and MNDO [7], two older methods of which AM1 is a further improvement. Already MINDO/3 and MNDO based cluster calculations have been shown to give very good results on silicon and diamond surfaces [8-11]. Therefore one can expect that the improved method AM1 will perform well also when applied to SiC.

Calculations presented here assume the adatom induced reconstruction. In absence of a convincing experimental evidence regarding the atomic arrangement in the R3 reconstructed surface, the idea of the adatom induced reconstruction is appealing because of the analogy with the (adsorbate induced) R3 reconstructions of the (111) surfaces of silicon and germanium [12,13,14]. Moreover, the results presented later in this paper further support the claim that the simple adatom induced structure makes a feasible model for the R3 reconstruction of the SiC$(000\bar{1})$ surface, at least as far as the energetics of the process is concerned.

2. Termination of the clusters.

To reduce boundary effects associated with the finite sizes of the investigated clusters, dangling bonds in a cluster which in reality would embed the cluster in the crystal bulk are, in cluster calculations, usually saturated by hydrogen. The method works very well for carbon and to a certain extent also for silicon [8-11]. However, further down the Periodic Table the electronegativities of atoms forming the cluster differ so much from the electronegativity of hydrogen that cluster terminating bonds to hydrogen are strongly ionic and are no longer good imitations of the back bonds which embed the cluster in the crystal bulk [15]. A possible universal solution to the problem is to introduce an ideal artificial monovalent capped bond (Cb) element [16] which due to a very large resonance energy

forms perfectly covalent bonds with practically every other element. Unfortunately this in principle good idea has serious disadvantages. Forcing a covalent nature on chemical bonds by an extremely large resonance energy rather than by matching energies of the relevant atomic orbitals is likely to disturb the character of neighboring bonds which in turn can influence the accuracy of the results and make their analysis rather difficult [15,17]. Moreover, as capped bonds cannot participate in partially ionic bonds, one should not expect them to be acceptable saturators in clusters modelling heteropolar crystals like SiC.

To reduce the above problem I introduced two types of saturators, one imitating carbon and saturating the Si back bonds and one imitating silicon and saturating C back bonds. Knowing that hydrogen is an acceptable saturator for diamond modelling clusters, I used hydrogen to saturate Si back bonds. To saturate C back bonds I introduced an additional H-like pseudoatom. In comparison to hydrogen, the pseudoatom parameter responsible for the ionisation energy (USS in MOPAC) was reduced from -11.396427eV to -10.31eV. As can be seen from table 1, the introduction of the additional saturator allowed to reduce the boundary effects present in the charge distribution of the fully saturated test SiC clusters.

Table 1. Optimized bulk bond lengths d in Å and examples of atomic charges in differently saturated SiC bulk modelling clusters.

Cluster	$C_6Si_6 + 18saturators$			$C_{13}Si_{13} + 30saturators$			$C_{16}Si_{14} + 34saturators$		
Saturator	H	Cb	New*	H	Cb	New*	H	Cb	New*
d(Si-C)	1.855	1.867	1.848	1.866	1.874	1.861	1.869	1.881	1.864
$q(Si_a)$†	—	—	—	1.07	1.09	1.10	1.06	1.06	1.09
$q(C_a)$	—	—	—	-1.09	-0.87	-1.09	-1.12	-0.98	-1.12
$q(Si_b)$‡	0.99	0.73	1.03	0.97	0.69	0.99	0.96	0.68	0.99
$q(C_b)$	-0.93	-0.66	-1.03	-0.91	-0.66	-1.01	-0.91	-0.69	-1.01

* Two different saturators described in the text.
†Si_a and C_a are atoms in the center of a cluster, bonded to four C (Si) atoms.
‡†Si_b and C_b are peripheral atoms bonded to three C (Si) atoms and to one saturator.

3. α SiC(000$\bar{1}$) surface.

Using hydrogen and the adjusted hydrogen-like pseudoatom described in sec.2 as saturators terminating the clusters I looked at the relative stabilities of four different SiC(000$\bar{1}$) surfaces: bulk-like terminated (1 x 1), R3 with Si adatoms (re1), R3 with C adatoms (re2) and R3 with Si adatoms and with the second layer Si atoms under adatoms replaced by C atoms (re3). The investigated clusters contained 16 to 17 C and 16 to 17 Si atoms plus

the necessary saturators and represented four layers of SiC (plus a possible adatom).

The comparison of surface energies of surfaces with different compositions is a delicate issue. Basically, the problem is in determining chemical potentials of the auxiliary atoms at their source [18]. In particular, to compare surface energies of the reconstructed surface with adatoms and of the unreconstructed surface one has to calculate:

$$\Delta E = F_{re} - F_{1\times1} = E_{slabr} - [E_{slab1} + \mu_{ad} \cdot n_{ad}]. \quad (1)$$

Here F_{re} and $F_{1\times1}$ are surface energies of the reconstructed (with adatoms) and the 1×1 (unreconstructed) surfaces respectively, E_{slabr} and E_{slab1} denote energies per surface unit cell (SUC) of the infinite slabs terminated by the reconstructed and 1×1 surfaces respectively, μ_{ad} denotes the chemical potential of the adatoms at their source, while n_{ad} is the number of adatoms per SUC in the reconstructed surface.

In case of homopolar surfaces the problem is usually not that severe, since one can expect the auxiliary atoms to come effectively from the crystal bulk [9]. In case of a surface of a heteropolar material like SiC the situation is more complicated. In principle, a single crystal SiC can be somewhat non-stoichiometric. To explore a range of similar compositions of the SiC bulk is beyond the scope of this paper. Calculations reported here assume the thermodynamically stable stoichiometric crystal bulk. However the experimentally observed depletion of silicon which accompanies the surface reconstruction [2,4] indicates that the reconstructing surface has, at least locally, an excess of carbon atoms. Therefore one can expect that the additional carbon atoms necessary to produce re2 and re3 reconstructed surfaces come from carbon rich islands, rather then from an ideal stoichiometric bulk. On the other hand, evaporation of Si from the surface suggests absence of analogous Si rich islands in the R3 reconstructing surface. Therefore, while comparing surface energies of different surfaces, I assumed that the necessary additional C atoms came from the carbon rich islands while the Si atoms come from the stoichiometric bulk. To keep the numerical calculations within manageable limits, only small islands indicated in fig. 1 were investigated in the reported calculations.

The relevant calculated surface energies, together with some geometrical parameters optimised in the total energy calculations, are listed in table 2. The results show that re3 is clearly the most stable of the investigated compositions. One can regard the re3 composition as an ideal surface with an additional 1/3 monolayer of carbon adsorbed in the so called B_5 location, directly below adatoms. In this respect the structure is analogous to the Si(111)R3:B, where there is a strong evidence for boron to occupy the B_5 location [13]. The mechanism which favours the particular atomic arrangement in the SiC(000$\overline{1}$)R3 surface is also likely to be similar to the one which is responsible for the particular B adsorption site on Si(111) surface.

I believe that the re3 composition is stabilized by the particular relation between the bulk bond length and the geometry of bonds in the vicinity of adatoms. To increase the bonding strength between the adatom and the surrounding layer 1 atoms (later referred to as L1), the L1 atoms have to rotate their (basically sp^3) hybrids, so that the hybrid which participates in the bond with the adatom points to the adatom rather than perpendicularly away from the surface. Three geometrical effects can contribute to this rotation:

compression of 2A-3A bonds, stretching of 2B-3B bonds and compression of L1-2A bonds (notation as in fig.2). In re1 and to even larger extent in re2 the combination of these effects produces a considerable stress in the structure, clearly indicated by the different elevations of atoms 3A and 3B (cf. Table 2). On the other hand the fact that the C-C bond is some 0.4Å shorter than the Si-C bond makes the combination of the first two geometrical effects natural in re3. Moreover, the fact that $2s$ and $2p$ orbitals of carbon have lower energies than the $3s$ and $3p$ orbitals of silicon supports some charge transfer from the 2B-3B bond to the C-C bonds which in turn weakens the 2B-3B bond and allows stretching it by about 0.03Å without significant cost in energy.

Table 2. Surface energies in eV per 1×1 surface unit cell relative to the relaxed 1×1 C-terminated surface and some geometrical parameters in Å for different compositions of the R3 reconstructed α SiC(000$\bar{1}$) surface. Notation as in fig.2.

Surface composition	re1	re2	re3
surface energy	0.82	1.24	-.23
h(2B)-h(2A)	0.47	0.68	0.37
Δx	0.14	0.32	0.33
h(3B)-h(3A)	0.29	0.43	0.01

For comparison I also calculated the surface energies of the different compositions of the R3 reconstructed surface following the assumption that the additional Si atoms come from the Si rich islands (fig. 2b) while the additional C atoms come from the stoichiometric bulk. This changed the energies of re1, re2 and re3 to 0.06eV, 1.65eV and 0.18eV per 1 × 1 SUC respectively. The result for re1 shows that even if one assumes unrealistically favourable conditions for the formation of re1, this composition of the R3 reconstructed surface is still of slightly higher energy than the unreconstructed relaxed surface. On the other hand, the numbers for re2 and re3 indicate that without the favourable conditions produced by the evaporation of Si from the reconstructing surface (like the formation of carbon rich islands), all compositions of the R3 reconstructed surface are probably of higher energy than the unreconstructed surface.

4. Concluding remarks.

To summarize, relative stabilities of different compositions of the $(\sqrt{3} \times \sqrt{3})R30^0$ reconstruction of SiC(000$\bar{1}$) surface were examined with the help of clusters terminated by two types of H-like saturators, one for carbon, another one for silicon. The pattern

of energies shows that the experimentally observed depletion of Si accompanying the R3 reconstruction is energetically important for the formation of the reconstructed surface. Without it the adatom terminated R3 reconstructed SiC(000$\bar{1}$) appears to be of higher energy than the relaxed unreconstructed surface.

Among the adatom terminated R3 reconstructed surfaces the surface with Si adatoms and C atoms substituting for Si in the H_5 locations is the most stable one. The result can be associated with the carbon covalent radius being considerably smaller than the silicon covalent radius. This particular relation between the two radii favours the re3 surface composition by relieving much of the stress present in chemical bonds in the vicinity of adatoms. Large differences between energies of different compositions of the α SiC(000$\bar{1}$) R3 reconstructed surface indicate that the qualitative picture of surface energetics which applies to this surface should also apply to the similar R3 reconstructed β SiC(111) C-rich surface.

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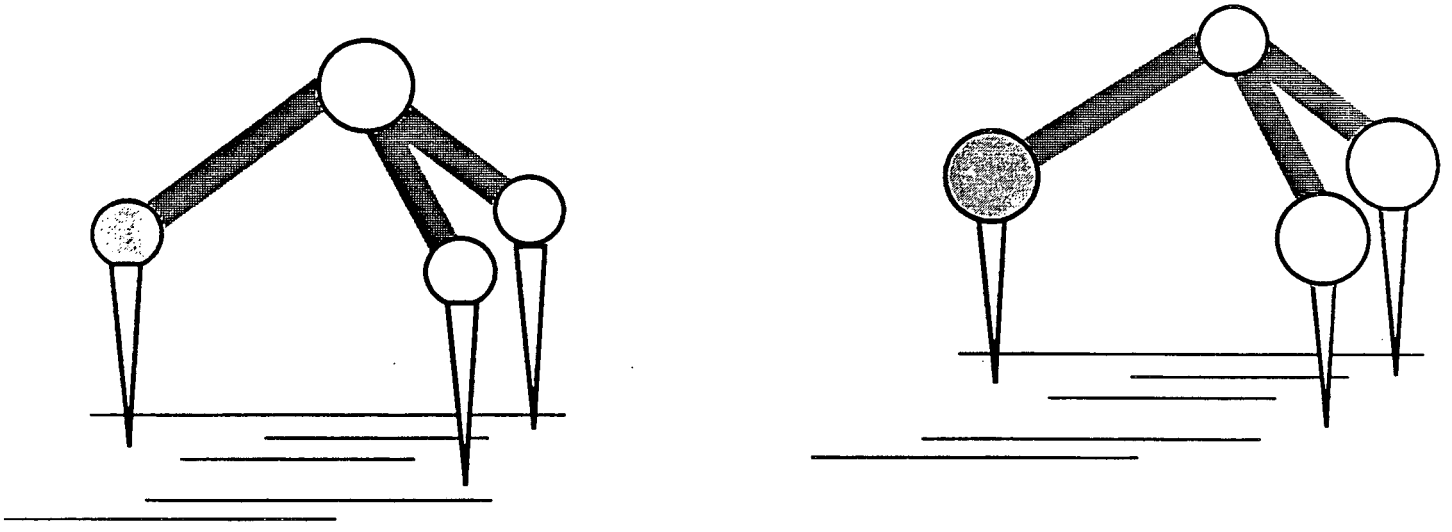
FIGURE CAPTIONS

Figure 1. Carbon rich (a) and silicon rich (b) islands. Atoms indicated by full circles are in the text examined as possible sources of additional carbon/silicon atoms necessary to form the investigated reconstructed surfaces. The dangling bonds on all island atoms but on those indicated by full circles were in the calculations saturated by hydrogen. Larger circles denote Si atoms, smaller C atoms. Triangles denote bonds between the islands and the surface. The individual surface layer atoms are not shown.

Figure 2. Geometry in the vicinity of an adatom, projection on the plane spanned by 3A–2A–marked L1.



(A) (B)

Figure 1

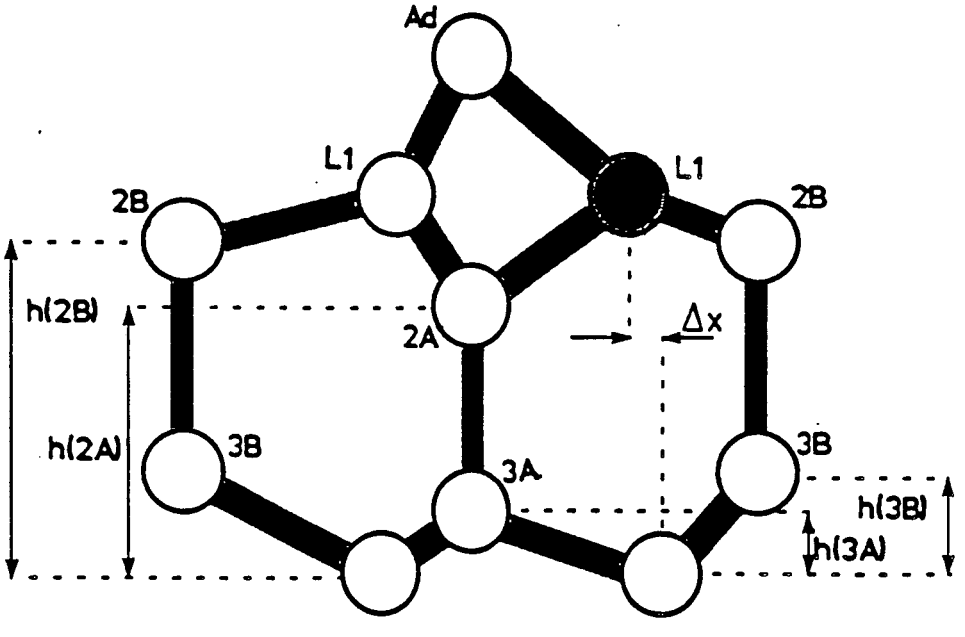


Figure 2

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