# Stress-Driven Surface Reconstruction Studied by X-ray Diffraction: β-SiC(001)3x2 Sub-surface Alternating Long- and Short Dimers

M. D'angelo,[1] H. Enriquez,[1] V.Yu. Aristov,[1,*] P. Soukiassian,[1]
G. Renaud,[2] A. Barbier,[2] M. Noblet,[2] S. Chiang [3] and F. Semond [4]

[1] Commissariat à l'Energie Atomique, DSM-DRECAM-SPCSI-SIMA, Bâtiment 462, Saclay, 91191 Gif sur Yvette Cedex, France and
Département de Physique, Université de Paris-Sud, 91405 Orsay Cedex, France

[2] Commissariat à l'Energie Atomique, DSM-DRFMC-SP2M, 85 X, 38041 Grenoble Cedex, France

[3] Department of Physics, University of California-Davis, Davis, CA 95616-8677, U.S.A.

[4] Centre National de la Recherche Scientifique, CRHEA, Sophia-Antipolis, 06650 Valbonne, France

Abstract

The Si-rich β-SiC(001)3x2 surface structure is solved by grazing incidence x-ray diffraction yielding to atomic coordinates. The measurements allow accurate surface and sub-surface structure determination. The first plane Si-dimers are asymmetric with a 0.15 Å height difference between Si atoms while the second plane Si-dimers have alternating long (2.55 Å) and short (2.24 Å) lengths (ALSD) resulting in long range influence with no buckling of the top surface dimers, in strong contrast to other group IV semiconductors. The results suggest stress is the origin of this complex surface organization.

* On leave from: *Russian Academy of Sciences, Chernogolovka, Moscow District, Russia*

Silicon carbide (SiC) is a IV-IV wide band gap compound semiconductor which is of a strong interest for advanced applications in ceramics, in nanotechnologies, in micro- or opto-electronics devices and sensors, and also as an electronic material for harsh environments [1]. From a more academic view, unlike other group IV semiconductors, SiC is not fully covalent with a significant charge transfer between C and Si atoms [1]. Because of expected similarity to Si or Ge in surface structure, the cubic β-SiC phase is of special interest [2]. There are however some very significant differences such as the central role of stress in SiC surface ordering due to large mismatches in lattice parameters (20% smaller than for Si) [1]. It is only recently that atomic control of β-SiC(001) surfaces has been achieved with the material showing many reconstructions such as Si-rich 3x2, 8x2, 5x2, 7x2, … 2n+1, Si-terminated c(4x2), C-terminated c(2x2) and C-rich graphitic 1x1 [1].

In this context, the Si-rich surface is of special interest because its 3x2 reconstruction includes, depending on the model considered, one or two additional Si atomic planes on top of a Si-terminated β-SiC(001) stressed surface and thus, has no equivalent among corresponding Si or Ge surfaces [2]. Various structural models have been proposed for this particular reconstruction based on well established low and high energy electron diffraction techniques (LEED, RHEED) [3,4]. The β-SiC(001)3x2 surface has also been studied by other structural probes such as medium energy ion scattering (MEIS) and real-space atom-resolved scanning tunneling microscopy (STM), non-structural ones as Auger electron or photoemission spectroscopies [5-8], and a few theoretical calculations [9,10]. The proposed models include i) the double dimer row model - DDRM (Fig. 1a) with a surface terminated by a 2/3 monolayer (ML) Si [3,6,8], ii) the single dimer row model - SDRM (Fig. 1b) terminated by a 1/3 ML Si [5], iii) the alternate dimer row model - ADRM (Fig.

1c) predicted theoretically and having 2x3 reconstruction with a 1/3 Si ML coverage and asymmetric dimers [9], iv) another ADRM (Fig. 1d) having a 3x2 surface array and asymmetric dimers as established by atom-resolved STM [7] and finally, v) a two adlayer asymmetric dimer model - TAADM (Fig. 1e) predicted by *ab-initio* pseudopotential total energy and grand canonical potential calculations [10]. The TAADM was apparently supported by other calculations of the reflectance anisotropy spectroscopy (RAS) [11]. The calculated spectrum was claimed to be in agreement with available data from experimental reflectance difference spectroscopy (RDS) [12]. However, the calculated RAS spectrum [11] for the DDRM [3,6,8] is also close to the experimental one [12]. In addition, the experimental $\Delta R/R = 2(R_{[1\ \bar{1}0]} - R_{[110]})/(R_{[110]} + R_{[1\ \bar{1}0]})$ [14] spectrum is incorrectly reported in Ref. 11 with the opposite sign as $2(R_{[110]} - R_{[1\ \bar{1}0]})/(R_{[110]} + R_{[1\ \bar{1}0]})$, making a comparison with theory impossible. Thus, no real insight could be drawn from these optical studies [11,12]. Therefore, there is an urgent need for an accurate surface structure knowledge which requires advanced probes. In the recent years, grazing incidence x-ray diffraction (GIXRD) using synchrotron radiation has been especially successful in solving complex surface structures accurately [13].

In this letter, we use GIXRD to determine the β-SiC(001)3x2 surface structure which is found to be in qualitative agreement with the theoretical TAAD model. Our results lead to an accurate surface and sub-surface structure determination evidencing an unexpected feature: the second plane has alternating long (2.55 ± 0.06 Å) and short (2.24 ± 0.05 Å) Si dimers (ALSD) that minimize the surface stress. Such an array has a long range influence that explains the lack of dimer anticorrelation in the top-most atomic layer, in strong contrast to Si or Ge.

The GIXRD experiments are performed using a 12 KeV X-ray beam on the French CRG-IF (BM32) beamline (ESRF-Grenoble) at a $3x10^{-11}$ Torr pressure, resulting in the ability to maintain a very high surface quality during all measurements. The incident angle is kept at the critical value (0.176°). The high quality of β-SiC(001)3x2 surfaces are checked by RHEED and GIXRD. The basis vectors ($a_S$,$b_S$,$c_S$) of the surface reconstruction unit cell are related to the bulk ones by $\mathbf{a}_S = [1\ \bar{1}0]_{bulk}$, $\mathbf{b}_S = [110]_{bulk}$, $\mathbf{c}_S = [001]_{bulk}$, with $a_S = b_S = 3.088$ Å and $c_S = 4.367$ Å. The reciprocal space is described by its reduced coordinates ($h,k,l$), $l$ being perpendicular to the surface. Two complete sets of data measured from two distinct 3x2 surfaces are in excellent agreement. For each set, we measure 78 inequivalent in-plane and 276 out-of plane reflections, including 8 inequivalent rods, and 14 crystal truncature rods (CTR) [13]. The diffraction pattern exhibits a nearly p2mm symmetry, allowing a 10% systematic uncertainty estimate from equivalent in-plane rod intensities. Details about high quality 3x2 surface preparation and GIXRD can be found elsewhere [1,7,13].

We first explore the validity of the 5 above models on the basis of the $\chi^2$ factor [13] to judge the agreement between experimental and calculated in-plane rod intensities. Table I provides the $\chi^2$ factors: all models yield $\chi^2$ values much larger than the ideal value of 1, the TAADM ($\chi^2 = 6$) being the closest. So, the in-plane data clearly exclude all possible models except the last.

We now focus on the TAADM and explore its suitability for the reconstructed Si layer by relaxing the atomic position i) in plane and ii) out of plane. After least squares residuals minimization on $\chi^2$, we find in-plane and out-of-plane values of 0.7 and 1.1 respectively, close to the satisfactory $\chi^2$ value of 1 [13]. Fig. 2a provides a view comparing the in-plane experimental (measured at $l = 0.05$) and calculated structure factors showing a very good agreement between them. The measured x 2 diffracted spots are not represented because they have intensities more than 10 times weaker than the x 1 ones, making any comparison with the calculated intensities difficult. This much weaker intensity is correlated to the dimer-pair B defects identified by STM [7], these are at the origin of long antiphase boundaries tending to weaken the x 2 intensity as also observed in LEED and RHEED diagrams, leaving the x 1 one dominant [1,3].

A complementary view could be found by looking at the experimental and theoretical Patterson functions (Fig. 2b & 2c) which provide a real space information with in-plane interatomic vectors. As can be seen by simple visual inspection, the agreement between the pair correlation

functions is excellent. We now move to the truncature rods that provide insights on the out-of-plane structure of the reconstructed planes. Fig. 3 gives a set of representative intensity profiles along the (5 0 l), (5 -2 l), ( 1 0 l) and (8 0 l) rods. The fitting curve exhibits a modulation period varying from 2.5 to 2.8 in reciprocal lattice units, i.e. a direct space thickness of ≈ 1.7 Å (instead of 1.09 Å for the bulk interlayer), indicating that the 3x2 reconstruction involves more than 2 Si atomic layers.

Next, we turn to the atomic bond lengths and positions that can be derived from previous fits. Table II gives the reduced *(X,Y,Z)* coordinates of the 12 Si atoms involved in the 3x2 reconstructed unit cell, while Fig. 4a displays a schematic of the surface, with top and side views of the β-SiC(001)3x2 reconstruction. It shows that the 3x2 reconstruction extends up to 3 atomic planes distant by ≈ $a_0/3$ ($a_0$ being the lattice parameter) instead of $a_0/4$ in the bulk, emphasizing the open character of this surface. For the top-most Si dimer $A_U$-$A_D$, we find a 2.42 ± 0.06 Å projected distance significantly larger than the theoretical value of 2.24 ± 0.05 Å [10]. The top Si-Si dimer is found to be asymmetric with the $A_U$ up atom being 0.15 Å higher than the $A_D$ down one, i.e. much smaller than the calculated value (0.5 Å) [10]. This value, however, is similar to the height difference (0.2 Å) between up- and down-dimers in the Si-terminated β-SiC(001) c(4x2) surface reconstruction [14]. Most interestingly, in the second plane, we find that the underlying dimers do not have the same bond lengths with alternating long $D_L$ (2.55 Å) and short $D_S$ (2.24 Å) dimers (ALSD). The long $D_L$ and short $D_S$ dimers are bonded on both sides to the $A_U$ and $A_D$ atoms belonging to the top asymmetric dimer [7]. Finally, the third deeper Si atomic plane located just above the first C plane is not really affected with only slight deviations from bulk atomic positions at $\Delta x = 0.02$ Å (0.2%), $\Delta y = 0.09$ Å (1.4%) and $\Delta z = 0.05$ Å (1%) as derived from the CTR fits.

Our GIXRD measurements support a model of the β-SiC(001)3x2 reconstruction having three Si atomic planes (1/3 + 2/3 + 1 ML from top to bottom) above the first C plane, in qualitative agreement with the theoretical TAADM [10]. They definitely rules out all other models, especially the DDRM and SDRM which are based on electron diffraction techniques [1,3] and the ADRM-2x3 which is solely based on calculations [9]. They are in agreement with the presence of asymmetric dimers perpendicular to the dimer rows, all tilted in the same direction, as evidenced by real space atom-resolved empty states STM which, however, cannot provide insight into the sub-surface [7]. Hence, our results show significant differences from the theoretical TAAD model. First, we find a smaller height difference between the up- and down-atoms of the top dimer at 0.15 Å (instead of 0.5 Å [10]). Most interestingly, we find that the second Si atomic layer ($\theta_{Si}$=2/3) includes dimer rows having alternating long and short dimers (ALSD) with lengths of 2.55 Å and 2.24 Å. Indeed, one should remember that this second Si layer is lying onto a 1 ML Si atomic stressed plane [10,14]. Without being covered by an excess of Si atoms as in the 3x2 surface reconstruction, this 1 ML atomic plane would form a Si-terminated β-SiC(001) c(4x2) surface reconstruction with alternately up- and down-dimers (AUDD) reducing the surface stress [14]. One can therefore easily imagine that when this surface is covered by additional Si atomic layers, the AUDD arrangement cannot take place leading to stress transfer to the upper Si layer. Our GIXRD results precisely indicate that in the 1ML Si layer, the atoms deviate only slightly from bulk positions. A possible arrangement for the 2/3ML Si sub-surface layer would consist of dimers with alternating heights (like the AUDD for the c(4x2)). This cannot take place, however, because this sub-surface Si layer is itself also covered by an additional 1/3 ML Si. Therefore, another way to relax the stress and minimize the energy in this intermediate layer would be to have dimers with alternating long and short lengths (ALSD) precisely as found here (Fig. 4). In turn, this would affect the above $A_U$-$A_D$ dimer, the long $D_L$ dimer tending to push-up the $A_U$ atom while the short $D_S$ dimer would instead tend to pull-down the $A_D$ atom, leading to an asymmetric dimer, as evidenced by real space atom resolved STM [7] and later by calculations [10]. Most interestingly, this has a long range influence explaining why the asymmetric $A_U$-$A_D$ dimers forming the 3x2 surface reconstruction are all tilted along the same direction (not anticorrelated) [7] in strong contrast to Si(001) or Ge(001) c(4x2) reconstructions [2].

In conclusion, we have determined the atomic structure of the Si-rich β-SiC(001) 3x2 surface reconstruction using GIXRD. Our results rule out the DDRM, SDRM and ADRM-2x3

models, but are in qualitative agreement with the theoretically predicted TAADM giving a good surface morphology description. There are some significant differences, however, concerning atomic positions and bond lengths. The reconstruction involves three Si atomic planes having Si coverages of 1/3, 2/3 and 1 ML from top to bottom. Most significantly, we find a sub-surface layer having alternating long (2.55 Å) and short (2.24 Å) dimers (ALSD). Such an ALSD array tends to minimize strain and significantly influences the surface organization leading to the top atomic plane dimers all being tilted in the same direction, in strong contrast to the behavior of elemental group IV semiconductor surfaces. This study clarifies the β-SiC(001)3x2 surface atomic structure which has been under investigation for more than a decade. It also brings significant quantitative insight into stress-driven surface and sub-surface atomic organization that can lead to complex structures.

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**Figure captions**

Figure 1: Schematic top views of the β-SiC(001)3x2 surface reconstruction proposed models: a) DDRM [3,6,8], b) SDRM [5], c) ADRM 2x3 [9], d) ADRM 3x2 [7] and TAADM [10]. The corresponding primitive 3x2 (2x3) surface unit cell is indicated by a dashed line.

Figure 2: a) In-plane diffracted intensity map for the β-SiC(001)3x2 surface measured at l = 0.05 and compared to the proposed model. The full half and empty circles correspond to the experimental and calculated intensities respectively. The radii are proportional to the structure factor modulus. The measured x 2 diffracted spots are not represented. The *h* and *k* indexes are related to the 3x2 reconstructed unit cell.
b) Experimental and calculated Patterson contour plots for the β-SiC(001)3x2 surface for the TAADM, represented over the whole 3x2 unit cell.

Figure 3: (5 -2 l), (1 0 l), (5 0 l) and (8 0 l) rod profiles with the error bars and corresponding fits. The logarithm of the absolute value of the structure factor is represented as a function of the out-of plane reciprocal lattice coordinate l.

Figure 4: a) Top and b) side views of the β-SiC(001) 3x2 surface reconstruction showing the 3 Si atomic planes with the top $A_U$-$A_D$ asymmetric dimers (1st plane) and the ALSD dimers having alternating long $D_L$ and short $D_S$ lengths in the second plane.

**Table I:** $\chi 2$ structural factor for various existing models of the β-SiC(001) 3x2 surface reconstruction

| | DDRM [3,6,8] (3x2) | SDRM[5] (3x2) | ADRM [9] (2x3) | ADRM [7] (3x2) | TAADM [10] (3x2) |
|---|---|---|---|---|---|
| $\chi 2$ = | 14 | 21 | 21 | 21 | 6 |

**Table II:** Reduced *(X,Y,Z)* coordinates of the 12 Si atoms involved in the 3x2 reconstructed unit cell.

| Si atom number | X (in-plane along the x 3 direction) | Y (in-plane along the x 2 direction) | Z (out-of-plane) |
|---|---|---|---|
| **1 ($A_U$)** | 0.230 +/- 0.003 | 0.25 | 0.7120 +/- 0.0075 |
| **2 ($A_D$)** | 0.521 +/- 0.003 | 0.25 | 0.6771 +/- 0.0069 |
| **3 ($D_L$)** | 0.1780 +/- 0.0007 | 0.5430 +/- 0.0054 | 0.3506 +/- 0.0031 |
| **4 ($D_L$)** | 0.1780 +/- 0.0007 | 0.9570 +/- 0.0054 | 0.3506 +/- 0.0031 |
| **5 ($D_S$)** | 0.5600 +/- 0.0007 | 0.5693 +/- 0.0038 | 0.3360 +/- 0.0029 |
| **6 ($D_S$)** | 0.5600 +/- 0.0007 | 0.9306 +/- 0.0038 | 0.3360 +/- 0.0029 |
| **7** | 0 +/- 0.0006 | 0 +/- 0.0055 | -0.0156 +/- 0.0046 |
| **8** | 0.36900 | 0 | -0.0156 +/- 0.0046 |
| **9** | 0.7380 +/- 0.0006 | 0.0000 +/- 0.0055 | -0.0156 +/- 0.0046 |
| **10** | 0.0000 +/- 0.0006 | 0.5 +/- 0.0055 | -0.0156 +/- 0.0046 |
| **11** | 0.36900 | 0.5 | -0.0156 +/- 0.0046 |
| **12** | 0.7380 +/- 0.0006 | 0.5 +/- 0.0055 | -0.0156 +/- 0.0046 |

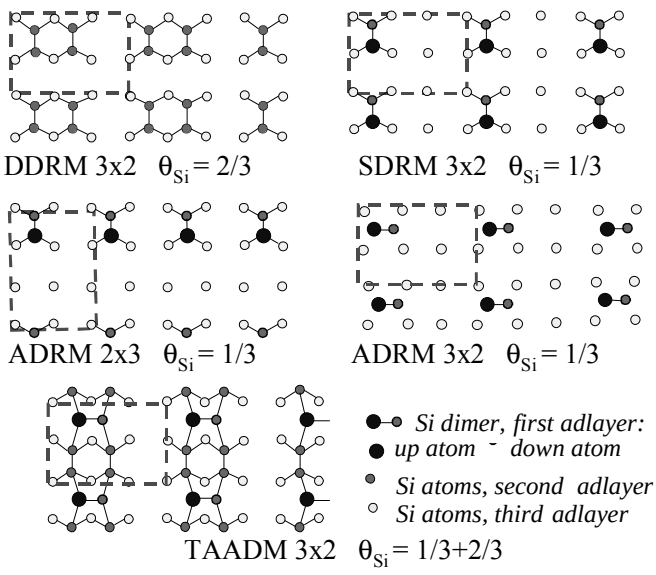
DDRM 3x2 θSi = 2/3
SDRM 3x2 θSi = 1/3
ADRM 2x3 θSi = 1/3
ADRM 3x2 θSi = 1/3
Si dimer, first adlayer:
up atom - down atom
Si atoms, second adlayer
Si atoms, third adlayer
TAADM 3x2 θSi = 1/3+2/3

Fig. 1

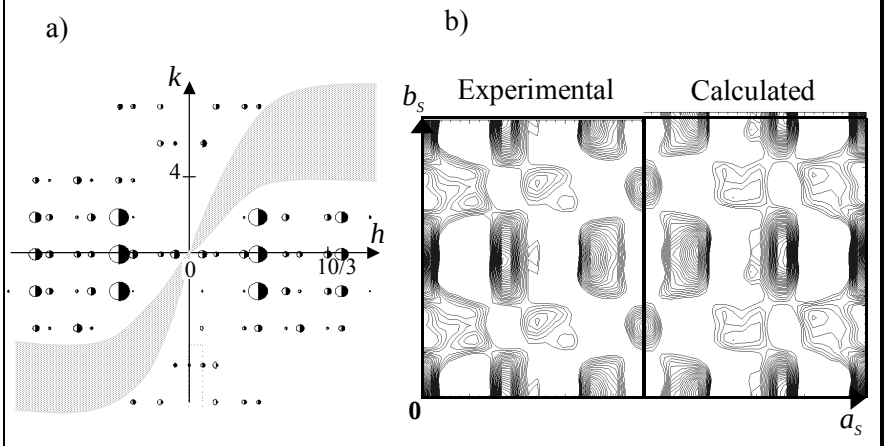
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Fig. 2

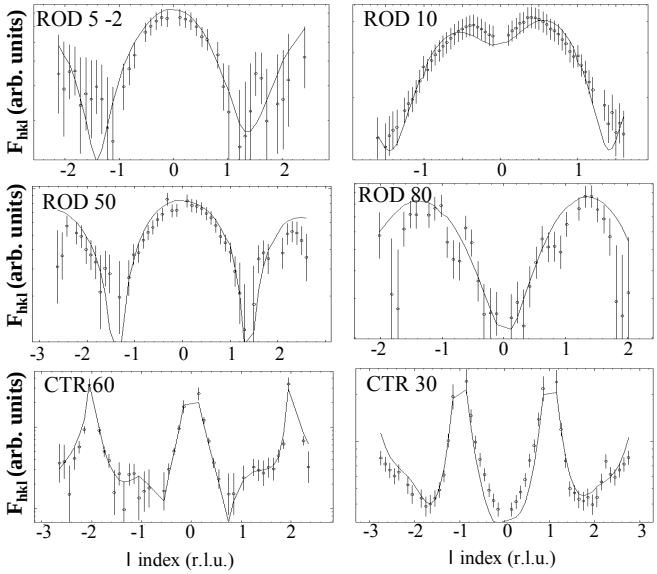
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Fig. 3

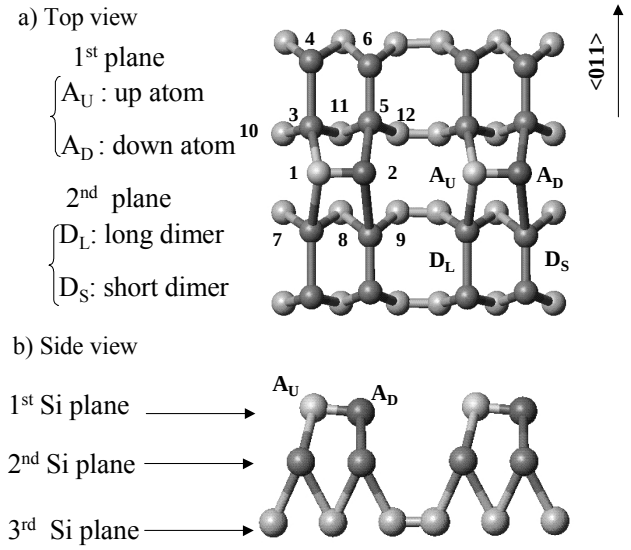
a) Top view
1st plane
A_U : up atom
A_D : down atom
2nd plane
D_L: long dimer
D_S: short dimer
b) Side view
1st Si plane
2nd Si plane
3rd Si plane
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Fig. 4