The transition from 3C SiC(111) to graphene captured by Ultra High Vacuum Scanning Tunneling Microscopy

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Abstract

In this paper we clarify the transformation mechanism of 3C-SiC into graphene upon thermal decomposition, by a combination of high resolution Scanning Tunneling Microscopy (STM) images and first principle calculations. We studied the transition from 3C-SiC to graphene by high temperature annealing of C-terminated 3C SiC(111)/Si(111) samples in Ultra High Vacuum. By using STM we were able to observe very clear atomic resolution images of the transition from SiC ($\sqrt{3}\times\sqrt{3}$)R30° to a new intermediate stage SiC ($\frac{3}{2}\times\sqrt{3}$)R30° (very close to the graphene (2×2) reconstruction) after annealing at 1250°C. We also obtained images of the transformation of the intermediate structure into a (1×1) monolayer graphene, caused by further sublimation of atoms in the subsurface layer. We have interpreted the results by using Density Functional Theory – Local Density Approximation calculations, which give full account of the SiC ($\sqrt{3}\times\sqrt{3}$)R30° reconstruction, but fail to describe the SiC ($\frac{3}{2}\times\sqrt{3}$)R30° structure due to its incommensurability with the 3C-SiC(111) lattice.

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1. Introduction

The growth of graphene by selective Si sublimation on Silicon Carbide (SiC) substrates is well documented [1-7]. This technique provides a reliable way to obtain a controlled and continuous epitaxial graphene layer [8, 9] leading to wafer size material for large scale device production. Even more important is the growth of graphene on SiC/Si substrates, to combine the low cost of Si with the epitaxial growth of graphene on SiC [10-13]. The considerable advantage of this method is the perspective of achieving perfect integration of graphene with the electronic circuitry developed on Si by using the traditional microelectronic platform. In order to achieve a full control of this technique it is of utmost importance to fully understand the steps leading to the formation of graphene from SiC. While the different reconstructions which appear on the SiC surface are well known, the details of the transformation from SiC to graphene are not completely clear, in spite of the large number of Scanning Tunneling Microscopy (STM) studies reporting atomic resolution images [1-7, 14-17].

The analysis of the graphitic structures obtained by high temperature annealing of SiC and its different stages of reconstruction have been studied by Low Energy Electron Diffraction (LEED) since 1975 [18]. It has been recognized that the reconstructions leading to graphene are different for silicon (Si)-terminated and carbon (C)-terminated faces of 6H and 4H SiC, but it can be applied also to 3C SiC which has the same stacking in the top layers.

For the Si-terminated face the reconstruction proceeds by increasing the annealing temperature through (3×3) , $(\sqrt{3}\times\sqrt{3})R30^\circ$, $(6\sqrt{3}\times 6\sqrt{3})R30^\circ$ and graphene (1×1) . (3×3) is a Si-rich phase and a very stable structure which consists of a complete Si

adlayer on top of an uppermost bulk like SiC substrate layer which is usually obtained by annealing at 850°C under Si flux. The adlayer contains no vacancies or corner holes, and it is covered by tetrahedral adatom clusters with three Si base atoms and one top Si atom per unit cell [19]; the base Si trimer lies on a twisted Si adlayer forming cloverlike rings on the Si-terminated face. This (3×3) translational symmetry is present under very Si-rich conditions [19], while the alternative $(\sqrt{3}\times\sqrt{3})R30^\circ$ reconstruction is favoured by less Si-rich preparation conditions[16]. The amount of Si supply and the heating time and temperature thus determine the reconstruction of SiC before the graphene formation [20-22]. The $(6\sqrt{3}\times 6\sqrt{3})R30^\circ$ phase has a complicated surface reconstruction and consists of (13×13) unit cells of graphene. This surface reconstruction is attributed to a C-rich phase but does not have any graphitic properties, as the adlayer has a strong interaction with the substrate, and so it is considered a buffer layer or an interface layer. The buffer layer passivates the SiC surface so that the subsequent C planes are only weakly bound to the substrate [23-25]. Finally, the (1×1) graphene surface structure appears when the formation of graphene layer is complete on the surface. The above surface reconstructions do not depend on the SiC polytype, and they have been found on all the hexagonally arranged surfaces of 3C, 4H and 6H SiC [23, 26-31].

On the C-terminated face the $(6\sqrt{3}\times 6\sqrt{3}) R30^\circ$ reconstruction is not observed, while the $(\sqrt{3}\times\sqrt{3})R30^\circ$ has been rarely reported [5]. The most accepted sequence of graphene growth on the C-terminated face is $(2\times 2)_{Si}$, (3×3) , $(2\times 2)_C$ and (1×1) graphene [6, 23, 24, 32-34]. The two phases $(2\times 2)_{Si}$ and $(2\times 2)_C$ occur from different surface treatments leading to Si and C rich structures respectively [23, 34]. The $(2\times 2)_{Si}$ phase develops upon annealing in Si flux. This procedure also helps to remove surface oxides from the

SiC samples [13, 23]. Further annealing of the surface leads towards (3×3) and $(2\times2)_C$ surface reconstructions [6, 23] and finally to graphene growth.

In the case of the Si face of SiC(0001), the graphitization process is slow, and it is easy to control the number of graphene layers, while for a C-terminated (000-1) surface the graphitization process is very fast and large number of graphene layers are formed (up to 100). The resulting electron mobility, however turns out to be low for the Si face and high for the C face [35].

While excellent graphene quality has been achieved in the last few years by annealing bulk SiC [8, 9], the cost of the substrate compared to Si and the limited diameter of the wafers are a stumbling block towards large industrial-scale fabrication of graphene from bulk SiC. To overcome these problems, 3C SiC epitaxially grown on Si wafers has been proposed as a suitable substrate for the synthesis of epitaxial graphene (EG) [10, 12, 36-39]. The most suitable surface in this case is 3C SiC (111) as its top four layers are identical to those of 6H SiC(0001) (Fig-1).

Figure 1: Cross section of the 3C SiC(111) structure (left) and 6H SiC(0001) (right) showing the different layer stacking

3C SiC (111)/Si (111) has also two polar faces (as 6H and 4H). Little attention has been given to the C-face while the Si-face has been studied comparably well. Graphene on Si terminated 3C SiC/Si (111) follows the same sequence of reconstructions towards graphene as on 6H SiC (0001) or 4H SiC (0001) [6, 28, 39, 40]. As mentioned above, the well known reconstruction phases on these polytypes are (3×3) , $(\sqrt{3}\times\sqrt{3})R30^\circ$, $(6\sqrt{3}\times6\sqrt{3})R30^\circ$ and graphene (1×1) [22, 23, 40-43]. Recently Darakchieva et al [44] reported on the reconstruction of the C face of 3C SiC (111), confirming by LEED the absence of the $(6\sqrt{3}\times6\sqrt{3}) R30^\circ$ phase as in 6H and 4H SiC.

Thermal decomposition of heteroepitaxially grown 3C SiC/ Si (111) for EG is possible in Ultra High Vacuum (UHV) [8] at temperatures lower than 1400°C, below the melting point of Si. UHV growth results also in a contaminant free surface, providing a perfect starting material for nanoelectronic applications and devices.

In spite of the number of studies reported for EG on 3C SiC [10-13, 28, 38, 45, 46], so far the details of the atomic transformation leading to the formation of graphene have not been clarified.

In the present work we analyse by STM the transformation of 3C-SiC(111) in graphene caused by high temperature annealing in UHV. We have been able to capture high resolution images of the different kind of reconstructions leading to graphene formation. We explain the sequence for the first time with the help of Density Functional Theory – Local Density Approximation (DFT-LDA) calculations, thus achieving a full picture of the reconstructions and graphene growth on 3C SiC (111).

2. Experiment

A 250 nm thick layer of 3C SiC (111) was grown on Si (111) by the alternating supply epitaxy method [47]. Our 3C-SiC/Si(111) samples are preferentially C-terminated by the CVD growth process[47], although due to stacking faults and defects this termination is not guaranteed. As received samples were cut to the size of (1.5×12) mm² for STM measurement, cleaned by 5 mins of ultrasonication with isopropanol, 2 mins by deionised water and then dried by N₂ gas. The samples were then introduced into our UHV Omicron system (base pressure in 10⁻¹¹ mbar range) equipped with a Variable Temperature XA STM . After degassing for a few hours at 600°C, the samples were annealed 10' by direct current heating at 1250° C for the graphene formation, leading to an average of 3 graphene layers as determined by XPS [13, 48]. However, due to the roughness of the SiC surface we expect to find regions where the number of layers is larger or smaller. The temperature was measured by a pyrometer (IRCON Ultimax Plus UX 20P) with an uncertainty of about 10° C. The sample was left in UHV for 30 mins to cool down, and then transferred to the STM stage. Tungsten tips used for STM characterization were fabricated by electrochemical etching.

3. Results

Based on our STM images we found that the transition occurs in two subsequent steps:

1. Transition of SiC surface from $(\sqrt{3}\times\sqrt{3})R30^\circ$ to $(\frac{3}{2}\times\sqrt{3})R30^\circ$.¹
2. Transition from $(\frac{3}{2}\times\sqrt{3})R30^\circ$ to monolayer graphene.

¹ We will show later that $(\frac{3}{2}\times\sqrt{3})R30^\circ$ reconstruction fit more with a quasi (2×2) symmetry of graphene, but we will maintain this notation for a straightforward comparison with the close $(\sqrt{3}\times\sqrt{3})R30^\circ$ symmetry commensurate with SiC(111) surface.

3.1 Transition from $(\sqrt{3} \times \sqrt{3})R30^\circ$ to $(\frac{3}{2} \times \sqrt{3})R30^\circ$

In Figure 2(a) we observe the coexistence of two different reconstructions, with a progressive transition from one to the other. We follow the transition going from the right to the left in the image, as we believe this is the direction of the transformation. To enhance the effect we have drawn circles around the brighter atoms in figure 2(b), with black circles in the left region and blue circles in the right region. At the right side of the image we notice the formation of hollow hexagons with 3 brighter and 3 darker atoms. The holes at the centre of the hexagons and the brighter atoms form a quite regular hexagonal centered network with a lattice constant of 5.3 Å (Fig 2c), very close to $(\sqrt{3} \times a) = 5.35$ Å, indicating a $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface reconstruction of the SiC.

Figure 2: STM images of 3C SiC(111)/Si(111) after annealing at 1250 °C. (a) $(3.6 \times 3.6) \text{ nm}^2$ STM image ($V=60 \text{ mV}$ $I=80 \text{ pA}$) showing the coexistence of two different reconstructed phases. (b) Same image with black and blue circles around the brighter atoms to indicate the two different reconstructions. (c) the $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ reconstruction (d) the $(\frac{3}{2} \times \sqrt{3})\text{R}30^\circ$ reconstruction. The panels are labeled following the direction of reconstruction.

On the left side of the image the central holes and the hexagons have shrunk and the atoms now appear arranged in parallel lines with alternated dark and bright atoms. The periodicity along these lines is $5.2 \text{ \AA}$. The two bright atoms across the lines are spaced by $4.6 \text{ \AA}$, matching a nominal $(\frac{3}{2} \times \sqrt{3})\text{R}30^\circ$ surface reconstruction (fig 2d). The smoothness of the transition from one reconstruction to the other is clearly shown in Fig.3, where the profile of two nearby lines of atoms indicates the shrinking of the interatomic distance going from right to left. In fact the periodicity along line 2 changes from 5.3 to $4.6 \text{ \AA}$ (coherently reading from right to left) while along line 1 the length of the oscillations is constant, equal to $4.6 \text{ \AA}$. In fact, looking at the orientation of the two-atoms element identifying the cell, one can notice their axis progressively twisting by 30° .

Figure 3: Profiles of the STM image in Fig 2, showing the change in the atomic positions: going from right to left the distance of profile-2 (green) is gradually decreasing until matching that of profile-1 (purple), which remains nearly same.

We have simulated the $(\sqrt{3}\times\sqrt{3})$ reconstruction of SiC by using density functional theory in the local density approximation (DFT-LDA) and a plane wave/pseudo potential scheme [49]. Surfaces were modelled using slabs containing 6 SiC (111) bilayers, back terminated with hydrogen, allowing the front most 4 atomic layers to relax. Hydrogen is used for the saturation of the back terminated part in order to get rid of dangling bonds which could give rise to spurious interactions or charge transfer between the two slab surfaces. STM images were computed at constant current using the Tersoff - Hamann approximation [50].

Figure 4: Simulated STM images of the $(\sqrt{3}\times\sqrt{3})$ phase using two different configurations: a) one missing Si atom per unit cell; b) with a C atom substituting a Si atom. Si atoms: larger in green; C atoms: smaller, in yellow

Figure 4 shows computed STM images of the bulk truncated 3C SiC(111) surface alongside models of the relaxed geometries (only the top layer is shown) featuring one missing Si atom per $(\sqrt{3}\times\sqrt{3})$ unit cell (a) and additionally with a C atom substituting a Si atom (b). The bottom image resembles very closely the observed image for the $(\sqrt{3}\times\sqrt{3})$ reconstruction (see Fig 2) and thus reflects the onset of the transformation of SiC into graphene.

We were not able to obtain a stable structural model of the $(\frac{3}{2}\times\sqrt{3})$ R30° reconstruction, due to the fact that this is incommensurate to the 3C SiC (111) surface cell, and it is thereby difficult to simulate within periodic boundary conditions. We interpret the incommensuration with the SiC surface as an indication of the transition to graphene, speculating on a possible detachment of the topmost layer from the bulk. Such a layer might not be stable when connected to the bulk due to the awkward coordination with the 3C SiC (111) cell underneath, while the detachment may help to lower the elastic energy. For the sake of completeness we show a tentative model for the $(\sqrt{3}\times\sqrt{3})$ R30° phase, the $(\frac{3}{2}\times\sqrt{3})$ R 30° phase and the transition between them (Fig 5). It is evident how the $(\sqrt{3}\times\sqrt{3})$ R30° closely matches the SiC structure, while the $(\frac{3}{2}\times\sqrt{3})$ R 30° is out of registry².

² One could speculate that the atomic composition gradually changes through further sublimation, which eventually leads to instability and detachment of the layer, e.g. Fig4a is the root(3), and Fig4b is a sort of strained 3/2 reconstruction before detachment of the upper layer.

Figure 5: Transformation model for $(\sqrt{3} \times \sqrt{3}) R30^\circ$ towards $(\frac{3}{2} \times \sqrt{3}) R30^\circ$ unit cell starting from right and going to towards left. The unit cells are represented in blue. Small red dots represent the (1×1) cell vertices of 3C SiC/Si (111), with a unit vector equal to a . Dots of light and dark blue represent the reconstructed atoms of higher and lower intensities on the 3C SiC. The rotation angle between the surface atoms and the bulk is 30° .

3.2 Transition from $(\frac{3}{2} \times \sqrt{3})$ to graphene

In figure 6 (a) we notice a residual of the $(\frac{3}{2} \times \sqrt{3})$ reconstruction evidenced by the left yellow rhombus in fig 6 (c). By measuring carefully the bright atoms distances we find that the cell parameter is now $4.9 \text{ \AA}$ instead of $5.2 \text{ \AA}$, This last distance corresponds to the graphene 2×2 reconstruction, and strengthens our hypothesis that the $(\frac{3}{2} \times \sqrt{3})$ is a precursor of the graphene formation. Figure 7a shows a tentative overlap of a $(4.6 \times 5.2) \text{ \AA}^2$ cell with the graphene (2×2) lattice cell. If we consider a (2×2) supercell of graphene, we obtain a $(4.9 \times 4.9) \text{ \AA}^2$ rhombus. From the picture it appears clearly that the $(\frac{3}{2} \times \sqrt{3}) R30^\circ$ cell can be fitted to the graphene (2×2) with a little compressive distortion. The surface ratio between $(\frac{3}{2} \times \sqrt{3}) R30^\circ$ and a (2×2) graphene is around 0.99, i.e. an area compression of only 1%. The ratio of $(\sqrt{3} \times \sqrt{3}) R30^\circ$ to the graphene lattice is instead 1.18 and it would require a high distortion energy, which makes the transition from $(\sqrt{3} \times \sqrt{3}) R30^\circ$ to graphene very expensive from an energetic point of view.

Because of this relaxation we label the reconstruction as (2×2) in fig 6. It must be noticed as well that, going from the bottom to the top of the image in fig 6a, some atoms gradually disappear from the reconstruction, both from the topmost layer and from the layer below. At the top right end it is possible to see clearly the (1×1) cell of the monolayer graphene (hexagonal structure), with a periodicity of $2.45\text{\AA}$ (Fig 6b). The relaxation of the $\left(\frac{3}{2}\times\sqrt{3}\right)$ phase to a graphene (2×2) reconstruction is likely to be related to a further Si sublimation that disconnects locally the topmost layer from the bulk and allows the reconstruction to match the graphene symmetry.

Figure 6: Transformation of the $\left(\frac{3}{2} \times \sqrt{3}\right)$ R30° unit cell into a (2×2) cell and to graphene. (a) STM image (bias-0.02V; current-80pA) of the (2×2) region (former $\left(\frac{3}{2} \times \sqrt{3}\right)$ R30°) where it is possible to see the transformation going from bottom left to top right. (b) STM close up image of the graphene region (bias-0.02V; current-80pA) (c) Image (a) with the (2×2) structures superimposed. (d) Image (b) where the blue hexagons with a 2.45 Å periodicity indicate the graphene area. The yellow rhombus in the same area compares the (2×2) structure with the graphene hexagonal network.

Figure 7: Model of the SiC to graphene transformation. a) A comparison between $\left(\frac{3}{2} \times \sqrt{3}\right)$ R30° unit cell (black) and a graphene (2×2) cell (blue). b) a schematics of the transformation from $(\sqrt{3} \times \sqrt{3})$ R30° to $\left(\frac{3}{2} \times \sqrt{3}\right)$ R30° into graphene (1×1)

In summary, the $(\sqrt{3} \times \sqrt{3})$ R30° phase still matches the 3C SiC surface while the $\left(\frac{3}{2} \times \sqrt{3}\right)$ R30° is actually a distorted (2×2) graphene, which is likely to be induced by the Si atoms, i.e. by their residual sp^3 hybridization. Because of the Si atoms desorption the distances converge firstly to a (2×2) phase and finally to a (1×1) graphene layer, once the Si desorption has completed. A sketch of the full transition is depicted in fig 7b.

4. Conclusion

We performed a thorough STM study of the transformation of 3C-SiC(111) to graphene by high temperature annealing in UHV. By using a combination of STM and first principle calculations two main reconstructions have been recognized on SiC: a

$(\sqrt{3} \times \sqrt{3}) R30^\circ$ and a $(\frac{3}{2} \times \sqrt{3}) R30^\circ$. We suggest that these reconstructions are caused by the decrease of the density of Si atoms on the surface. The $(\frac{3}{2} \times \sqrt{3}) R30^\circ$ phase, which does not match well with the SiC cell, is actually a slightly distorted graphene (2×2), indicating the pathway for the transformation. The sublimation of more Si atoms leads in fact to the appearance of graphene (1×1) as confirmed by the STM images.

In conclusion we believe that our atomic resolution images of the sequence of reconstructions on 3C-SiC(111) provide for the first time a clear picture of the 3C-SiC(111) to graphene transformation. However, as the stacking sequence of the first four atomic planes in 3C SiC(111) is similar to that of 6H and 4H SiC (0001), the validity of our findings can be extended also to the 6H and 4H phases.

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