Density functional study of carbon mono- and bilayers on SiC

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Content

1. Introduction

Today there is a huge interest in the „new" material graphene. Graphene, that is a single hexagonally ordered layer of carbon atoms, has a unique electronic band structure and therefore unique electronic properties. It is a 2D electron gas and it has a linear dispersion around the K point of it's two dimensional Brillouinzone. This leads also to an anormal quantum Hall effect and other effects, e.g. chiral tunneling [1]. So the prospect of graphene-based nanometer-scale electronics is very favorable. Up to now we know about two methods to recieve samples of graphene. The first method was developed in Manchester in 2004 and is a purely mechanical method. The graphene layers are simply ripped off graphite crystals and then positioned on a suitable substrate (SiO_2/ Si), that does (almost) not affect the electronic structure of the graphene layers. As a result we get almost „free-standing" graphene. The other method is more favorable when it comes to reproducability and technological applications. It is just annealing silicon carbide (SiC) at elevated temperatures. There an ultrathin graphite layer is formed due to the depletion of Si from SiC [2]. But the question remains, whether we really get a „free standing" graphene like electronic structure, because we would expect a covalent bonding between the SiC substrate and the graphite and hence significant changes in the electronic spectrum. Nevertheless experiments have shown that the transport properties as well as the electronic structure of a single graphene layer appear on the SiC/graphite interface. But still if we want to built a device containing this interface we will need more information about the exact surface states. Therefore the bonding and the electronic structure of the interface between one carbon layer and SiC and two carbon layers and SiC on both sides (on the Si-terminated as well as on the C-terminated side) were calculated [3]. In the following the method (density functional theory), with which the calculation was done, is explained. Also some facts about the bulk material SiC and the production of SiC/ Graphene are mentioned. Last the model interface and the actual results are discussed and we end with a conclusion.

2. Density functional theory (DFT)

The DFT is a method used in physics and chemisty to calculate the electronic stucture of many-body systems. The fundamentals of the theory are made up by the Hohenberg-Kohn theorem, which will be explained in the following.

The theorem is connecting the many-body wavefunction $\Psi(\mathbf{r}_i)$ to the electron density $n(\mathbf{r})$ of the system. This can be expressed through the statement, that every density $n(\mathbf{r})$ leads to a specific and unique potential $V(\mathbf{r})$ and the other way round.

According to the equivalence of wavefunction $\Psi(\mathbf{r}_i)$ and density $n(\mathbf{r})$ the energy E, normally a function $E(\Psi(\mathbf{r}_i))$ of the wavefunction, becomes a functional $E[n(\mathbf{r})]$ of the density. Therefore the energy $E[n(\mathbf{r})]$ can now be minimalized with respect to the density $n(\mathbf{r})$ and we can get the energy of the groundstate $E_0(n_0(\mathbf{r}))$ of the system. But this is not that easy when we have interacting electrons in a real potential.This is then transformed to a system, where we have non-interacting, fictitious particles and an effective potential. There the Kohn-Sham-formalism can be used, where we have a one particle wavefunction $\Phi_i(\mathbf{r})$ for which holds: $n_0(\mathbf{r}) = \Sigma_i |\Phi_i(\mathbf{r})|^2$. This leads to the following equations:

$$[-1/2\,\Delta + V_H[n_0](\mathbf{r}) + V_{XC}[n_0](\mathbf{r}) + V_{el}(\mathbf{r}, \{\mathbf{R}_i\})]\,\Phi_i(\mathbf{r}) = \varepsilon_i\Phi_i(\mathbf{r})$$

Here the first term, $-1/2\,\Delta$, stands for the cinetic energy. The second, $V_H[n_0](\mathbf{r})$, describes the interaction between particles and the last term, $V_{el}(\mathbf{r}, \{\mathbf{R}_i\})]$, takes out the electron-electron interaction. So only the exchange-correlation potential $V_{XC}[n_0](\mathbf{r})$ is unknown and it contains all the complexities of the many body system. It is then approximated. For example with the local density approximation (LDA). In the LDA a slowly varying density is assumed, so the inhomogeneous system at a point $\mathbf{r}$ with a local density $n(\mathbf{r})$ is approximated by a homogeneous electron gas with the same density $n(\mathbf{r})$, for which the potential $V_{XC}(\mathbf{r})$ is known as a function of density. Another approximation method is the local spin density approximation (LSDA). As it appears in the following, here is a short explanation. The LDA is not applicable for systems with an external magnetic field, for systems that are polarized or systems, where relativistic effects are important. Because of that a spin-polarized Kohn-Sham theory with the LSDA was developed.

For the calculations, that are performed here, we use a supercell (Fig.1). The supercell
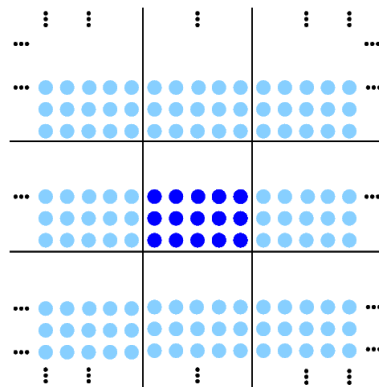

FIG. 1: Supercell

(dark blue in Fig.1) is similar to a unit cell. We use periodic boundary conditions to expand the structure in all directions (as is shown in Fig.1 for two dimensions). So we only need to feed only this one cell with information instaed of needing the information for every single atom of the SiC crystal. The important thing is here, that we need to place a vacuum in the supercell to simulate the surface. The SiC is saturated on one side with Hydrogen atoms, so that it does not effect the interface state on the other side of the SiC, on which the carbon layer(s) is (are) placed.

3. Properties of bulk SiC

In order to perform calculations on a SiC-graphene interface we need to know the properties of the substrate SiC itself to choose the right conditions for the model used in the calculations. Therefore some of the properties of SiC will be mentioned here.

Polytypism

Polytypism is a form of polymorphism, which means „many forms". Polymorphism names the phenomenon that a material exists in more than one structural form or arrangement. Polytypism describes the appearance of such different structures, that only differ in the way they are stacked. In Fig.2a the polytypes of SiC are shown. Every polytype has a name referring to some aspect of the structure, that it makes up. So the H in Fig.2a stands for hexagonal whereas the C stands for cubic. The numbers in front of the letters refer to the number of stacking levels that is characteristic for each polytype. To get a better idea we can also take a look at Fig.2b that corresponds to the 4H polytype of SiC, where the yellow balls are silicon- and the grey ones are carbon atoms.
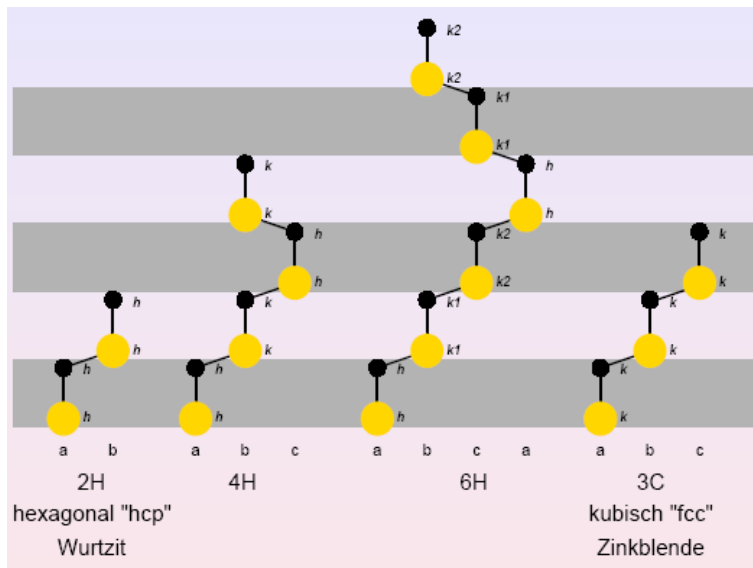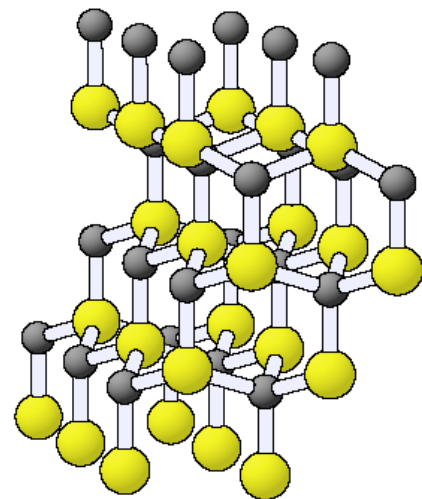

FIG. 2a: different polytypes of SiC   FIG. 2b: 3 dim. image of 4H SiC

Semiconductor and more

Furthermore SiC is an indirect semiconductor with a wide bandgap from 2.39eV up to 3.33eV depending on the different polytypes. This dependence is also illustrated in Fig.3, where different bandstructures appear for different polytypes. (As these bandstructers are calculated with LDA the bandgap is not actually right, see later Mott Hubbard system)
Also to mention is that SiC is among the hardest and most stable materials we know. It is as hard as diamant and it can even be used for medical implants in human bodies, becuase it is chemically inert and does not attack the body. Considering all this properties SiC makes a very good material concerning high temperature,high-frequency and high-power Semiconductor devices.
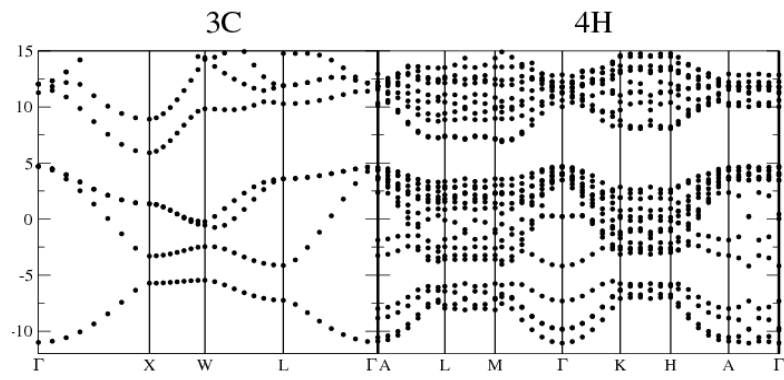
FIG. 3: calculated bandstructure of 3C and 4H SiC

4. Relevant surface reconstructions of SiC

It is clear, that especially the surface and what happens there is important for building up an interface. So a closer look on the surface of SiC is necessary.

First, as was mentioned before, we can look on SiC from two different sides, the Si-terminated and the C-terminated side. The names refer to the sort of atoms, that make up the surface layer of SiC. To look at a surface we can imagine to simply cut the bondings on top of the SiC to get a „plane" surface (See Fig.4). The unsaturated dangling bonds, that now appear on the surface are very reactive, so the question is: How do they rearrange themselves to get into a state with lower energy?
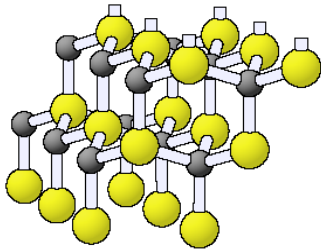

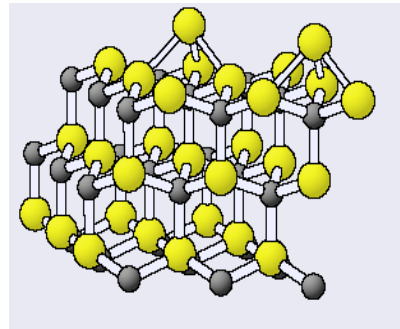*FIG. 4: unreconstructed SiC , Si-terminated side*

FIG. 5: $\sqrt{3}\times\sqrt{3}$ R30° reconstruction

The answer to this question is called surface reconstruction. A surface reconstruction is a mechanism, that happens at a surface and leads to a new structure. To better understanding there now follows an example. If we take unsaturated SiC, as in Fig.4, a possible surface reconstruction is the so called $\sqrt{3}\times\sqrt{3}$ R30° reconstruction, that is shown in Fig. 5. There each Si-adatom undergoes three bondings. As a result afterwards only two unsaturated bonds (per surface unit cell) instead of 3 are left. That is of course energetically more favourable.

The name of the reconstruction ($\sqrt{3}\times\sqrt{3}$ R30°) simply describes the geometry of the „new" unit cell after the reconstruction, with respect to the old unit cell. This is illustrated in Fig.6. The old unit cell is given in dark red and the new unit cell in red. The new one is rotated by 30° with respect to the old one and the basis vectors are $\sqrt{3}$ times longer than the ones of the old unit cell, hence the name $\sqrt{3}\times\sqrt{3}$ R30° .
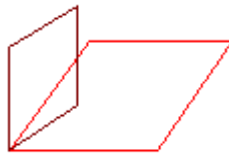

FIG. 6: Scetch of unit cell structures

But there are a lot more reconstructions and of course they appear on both sides of SiC, the Si-faced and the C-faced side. A few of them are mentioned in the following, but these aren't the only reconstructions of SiC.

Now we want to consider want happens with the surface state. So we have a look at some different calculations of the structure of the interface state. We see the results on Fig.7. For the simplest calculation (LDA) we get only one surface state (dashed line in Fig.7), but if we consider the spinand use the LSDA, we get a splitting of that state in an occupied and an empty state (dash and point line). For even more difficult calculations (quasiparticle corrections) the split gets even wider (line). This splitting is due to a so called Mott-Hubbard system and the lines with the widest split correspond to it. A Mott-Hubbard system is a system with the necessary prior conditions: low interaction between neighbour orbitals and strong selfinteraction, which is characterized by the Hubbard parameter U. This results then in a split of an energy state in one occupied and one empty state. They are then separated by the Hubbard parameter U. Of course the empty state cannot be
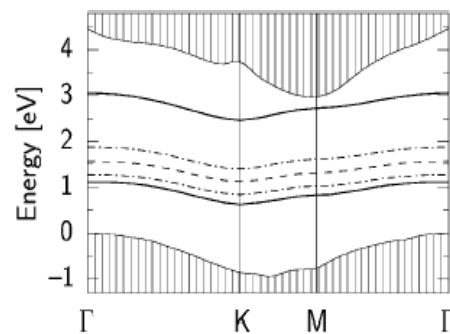

FIG. 7: calculations of the surface state of SiC. shaded regions are projected bulkstates.

measured directly, but it can be calculated and with indirect methods it can also be measured experimentally [4]. So for SiC we have such a splitting of the surface state that is already seen in the local spin density approximation (Fig.7 dash and point line).

5. Production of SiC/Graphene

It was already said in the motivation, that annealing at elevated temperatures leads to a SiC/Graphene interface. But the geometric structure of the interface remains unclear, as there are different surface reconstructions observed by experimental groups. In the following the different reconstructions, that were observed at different temperatures will be discussed shortly .

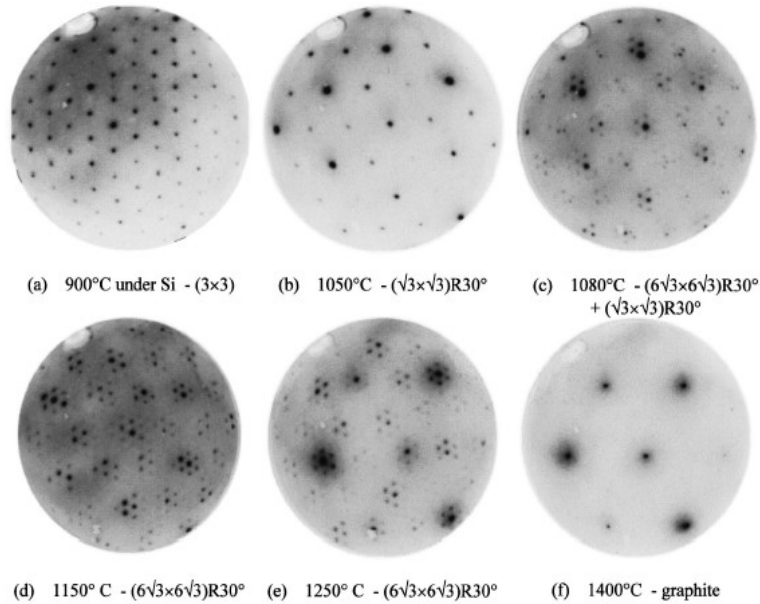In Fig.8 pictures from low energy electron diffraction (LEED) are shown [2].

(a) 900°C under Si - (3×3)   (b) 1050°C - (√3×√3)R30°   (c) 1080°C - (6√3×6√3)R30° + (√3×√3)R30°

(d) 1150° C - (6√3×6√3)R30°   (e) 1250° C - (6√3×6√3)R30°   (f) 1400°C - graphite

FIG. 8: Different reconstructions observed at different temperatures [2]

As we can see the temperature ranges from 900°C up to 1400°C. But within this range we see different diffraction patterns. At the highest temperature there is the pattern of pure graphite visible, in the lower regions there are various patterns, that belong to different reconstructions. Their names are written underneath the according LEED pattern. The $\sqrt{3}\times\sqrt{3}$ $R30°$ reconstruction, that was mentioned before, appears at a temperature of 1050°C, but then is replaced by a mixture of $\sqrt{3}\times\sqrt{3}$ $R30°$ and $6\sqrt{3}\times6\sqrt{3}$ $R30°$,that finally becomes a $6\sqrt{3}\times6\sqrt{3}$ $R30°$ C-rich structure. This reconstruction is especially worth mentioning as it might be the natural realization of the reconstruction, that happens at the interface SiC/Graphene, due to the fact, that 13 times the lattice constant of graphene almost exactly fits $6\sqrt{3}$ times the lattice constant of SiC.

6. Model interface

As the actual interface is unclear, a model interface was investigated.
The 1x1 6H-SiC polytype was used because this type is actually the type most often used in experiments. The supercell contained 6 bi-layers of SiC and one or two carbon monolayers and a vacuum interval of up to 15 Å. The graphene layer (carbon mono layer) was placed on top of the unreconstructed 6H-SiC and we got a lateral $\sqrt{3} \times \sqrt{3}$ $R30°$ elementary cell on the interface as can be seen in Fig.9. But in this model the graphene layer needs to be stretched about 8%, because of a lattice mismatch between graphene and SiC. The stretching does only effect the total bandwidth (it changes from 19.1eV to 17.3eV), it does not effect the electronic structure close to the Fermi level. As also can be seen in Fig.9 the interface unit cell contains three surface atoms of SiC and four elementary unit cells of graphene [3].
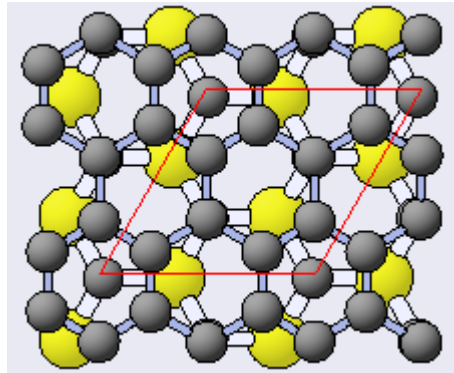

FIG. 9: C-terminated side with one graphene layer on top. Elementary cell is marked red.

7. Results of the calculations and discussion

In order to compare the results of the calculation with the spectrum of graphene, which was experimentally observed, here a few words about graphene first.
Graphene has a unique electronic bandstructure with a conic point shown in Fig.10. Around this point graphene has a linear dispersion and therefore ballistic transport is possible. Furthermore graphene becomes semimetallic, because the Fermilevel runs exactly through the conic point. The conic point is located at the K Point of the two
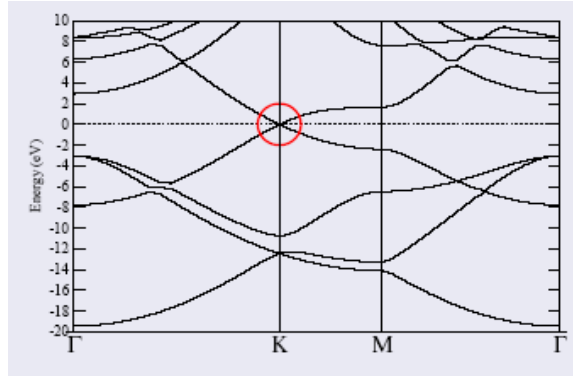

FIG. 10: Electronic structure of graphene, with the conic point marked by a red circle.

dimensional brillouin zone.
Now to the results of the calculation. We start with the first layer of carbon, that was located on the Si-terminated side of 1x1 6H-SiC. Again the interface unit cell is made up by a $\sqrt{3} \times \sqrt{3}$ $R30°$ reconstruction, as also is visible in Fig.9. The graphene is covalently bonded to the SiC with a bond length of 2.0Å. This bonding releases an energy of 0.72eV per graphene unit cell. That amount of energy makes also clear, that the bonding is covalent.
On the C-terminated side there is almost the same picture. Again we have a covalent bonding between the graphene and the SiC. Here the bondlength is slightly shorter than on the Si-terminated side. It is 1.87Å, that is actually the same bond length as in SiC itself. There is a released energy of 0.6eV. Still high enougth to point out the covalent character of the bonding.
Taking a look at the calculated bandstructures on these two sides for one graphene layer, we get the results shown in Fig.11a and 11b.
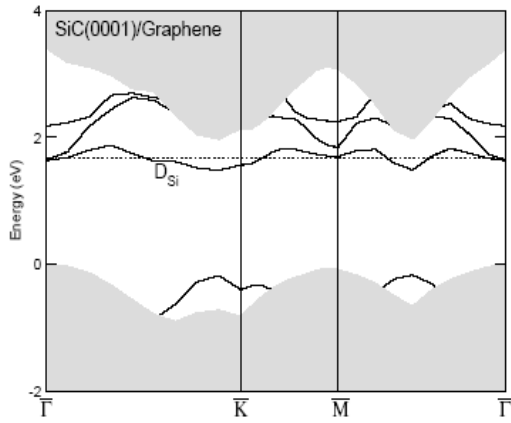
FIG. 11a: calulation of the bandstructure of SiC/Graphene on the Si-terminated side [3]
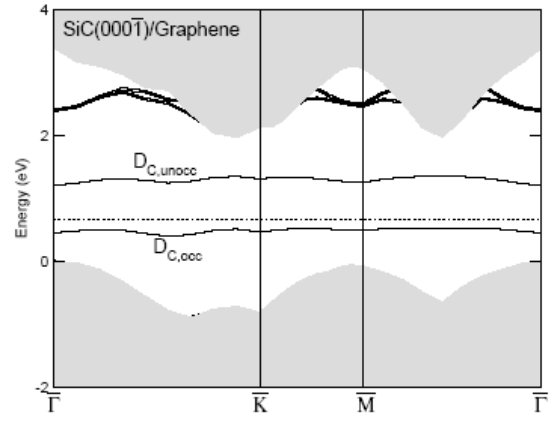
FIG. 11b: calculation of the bandstructure of SiC/graphene on the C-terminated side [3]

The shaded regions on the pictures are the projected conduction and valence bands of SiC. The lines are the true surface or interface states. As we can see on both pictures, there does not appear a conic point as in the graphene spectrum. This means that the covalent bonding of the layer changes the spectrum drastically as might also do the dangling bond in the middle of the carbon rings. On the Si-terminated side (Fig.11a) we make out a single metallic state D_{si}. Here the Fermi level is pinned by this metallic state. In contrast to this on the C-terminated side we find a splitting of the state in one $D_{C,occ}$ occupied state and one $D_{C,unocc}$ unoccupied state. This is an effect similar to the one for SiC explained above (see „SiC: surface reconstruction"), but it is much more complicated. It only gets visible in the LSDA not in the LDA. Because of this effect the surface on the C-terminated side becomes semiconducting. But nevertheless no graphene characteristic properties are found with only one graphene layer.

So we come to the second layer of graphene. The second layer is placed in AB stacking. Here we have on both sides a weak bonding only by van der Waals forces. The distance is 3.3Å, almost the same as in graphite, where it is 3.35Å. The calculation method we used, the local spin density approximation (LSDA), does not take into account van der Waals forces, but still it produces reasonable results for interlayer distances in van der Waals crystals. Now again we calculated the bandstructures for both sides,the Si-terminated and the C-terminated side, as can be seen on Fig.12a and 12b.
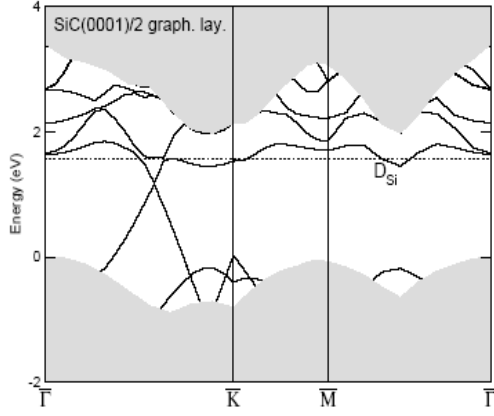
FIG. 12a: calculation of the bandstructure of SiC/2 graphene layers on the Si-terminated side [3]
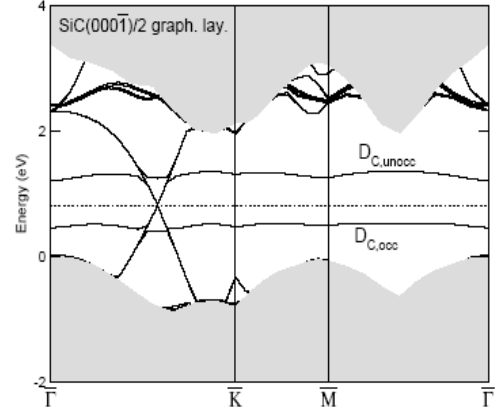
FIG.12b: calculation of the bandstructure of SiC/2 graphene layers on the C-terminated side [3]

Here it is obvious that we have a conic point on both sides. The fact that this point is not located at the K point of the brillouin zone is easily explained. It is due to the new interface unit cell, that of course has an other geometry as the graphene unit cell. The appearence of the conic point shows that the second layer is acting almost like a free standing graphene layer. But on the Si-terminated side we see that the Fermilevel is still pinned by the metallic state D_{si} and therefore the Fermilevel does not run exacly through the conic point but is above it. This makes the graphene n-doped, as we have a charge flow from the substrate to the graphene layer. On the C-terminated side the Fermilevel runs exactly through the conic point and so we get a semimetallic/semiconducting interface.

In order to find an explanation for the non-splitting of the metallic D_{si} state. We consider the charge density of the interface state at Fermi energy. The result is illustrated in Fig.13.
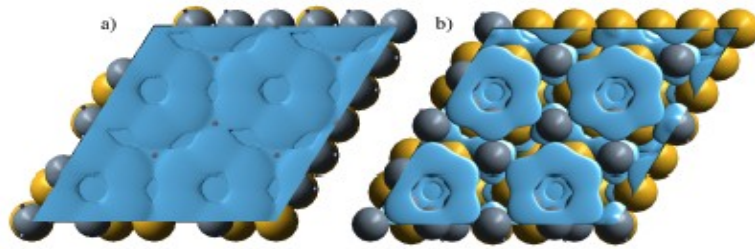

FIG. 13: charge density of the interface state at fermi energy at
a) Si-terminated and b) C-terminated side [3]

Only one graphene layer is placed above the SiC in this picture. As we can see on the Si-terminated side the charge density is delocalized over the whole interface. In contrast to that on the C-terminated side we find a localized density, that is only smeard over the carbon ring above the unsaturated C bond. But this actually corresponds to the splitting and non splitting of the interface state, as localisation favors spin polarisation we get the split in case b). But we do not get it on the Si side, as it is spin-degenerate.

8. Conclusion

In conclusion we calculated the interface between unreconstructed 6H-SiC surfaces and carbon layers with ab initio density-functional theory. We find differences between the Si-terminated and the C-terminated side in the electronic structures. The Si-terminated side is metallic while the C-terminated side is semiconducting. The electronic structure of graphene, namly the conic point, appears only with the second carbon layer. So the first sheet, that is covalently bound to the SiC, acts like a buffer layer between the SiC and the graphene layers. Therefore the Graphene-like structure that was measured experimentally must be due to more than one Graphene sheet.

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