Silicene as a new potential DNA sequencing device

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Abstract
Silicene, a hexagonal buckled 2D allotrope of silicon, shows potential as a platform for numerous new applications, and may allow for easier integration with existing silicon-based microelectronics than graphene. Here, we show that silicene could function as an electrical DNA sequencing device. We investigated the stability of this novel nano-bio system, its electronic properties and the pronounced effects on the transverse electronic transport, i.e., changes in the transmittance and the conductance caused by adsorption of each nucleobase, explored by us through the non-equilibrium Green’s function method. Intriguingly, despite the relatively weak interaction between nucleobases and silicene, significant changes in the transmittance at zero bias are predicted by us, in particular for the two nucleobases cytosine and guanine. Our findings suggest that silicene could be utilized as an integrated-circuit biosensor as part of a lab-on-a-chip device for DNA sequencing.

Keywords: electronic transport, adsorption, nucleobases, 2D material, Dirac material

1. Introduction

It has long been known that, under standard conditions, graphite is the most stable form of carbon while silicon takes on the diamond cubic crystal structure. This natural circumstance is a direct reflection of the greater stability of the sp² hybridization in C and of the sp³ hybridization in Si. Nonetheless, it was theoretically predicted [1–4] and subsequently experimentally confirmed [5–11], that a 2D honeycomb lattice like graphene can also be formed by Si, named silicene. Despite some structural similarities of silicene with graphene, the two differ in a couple of crucial aspects: firstly, the most stable structure of silicene is not planar, but buckled. This feature was described already in its original theoretical prediction [1, 4] and also observed in experiments [7, 10, 11]. Secondly, the method to obtain silicene is rather different from that used originally for graphene [12], in that for silicene one cannot apply the exfoliation method since this allotrope of silicon does not freely exist in nature. Instead, the prevalent method to synthesize silicene is to deposit Si atoms on a metal surface serving as a substrate.

In the present work, we investigate whether silicene could be used for third-generation DNA sequencing [13–19]. Graphene has been extensively studied with this application in mind [20–47]. Nanopores in silicene nanoribbons represent an interesting alternative [48] and might even offer an advantage here over graphene in terms of integrability with existing silicon-based microchip technology. To evaluate its capability for distinguishing the four different nucleobase types of DNA electronically, we investigated the stability, electronic structures and transport properties of silicene with each nucleobase adsorbed on top of silicene. This approach resembles most closely that investigated by the group of KS Kim for 2D-materials, including graphene nanoribbons [25, 26] and very recently also even for silicene nanoribbons [49]. Our results reveal that, although the electronic structure is not drastically changed due to the relatively weak interaction, it might be possible to detect the nucleobase type by...
analyzing subtle changes in the transport properties of the systems.

2. Methods

We combined *ab initio* density functional theory (DFT) [50, 51] as implemented in the SIESTA [52] code with the non-equilibrium Green’s function (NEGF) method from the TranSiesta code [53] to perform electronic transport calculations. To take into account weak dispersive interactions we employed a van der Waals correction [54, 55] to the generalized gradient approximation (PBE-GGA) [56] for the exchange-correlation functional in DFT. For relaxation and also electronic transport calculations in the scattering region, we used a supercell of 20.79 × 20.00 × 36.18 Å, while for the electrodes, the supercell had a size of 20.79 × 20.00 × 12.06 Å. A grid of 6 × 1 × 4 and 64 × 1 × 4 k-points was applied for k-space integration for DFT calculations and for electronic transport calculations in the scattering region, respectively, while for the electrodes this grid was composed of 64 × 1 × 60 k-points, since the transport direction is aligned with the z-axis. Furthermore, double-$\zeta$ polarized basis sets (DZP) and norm-conserving pseudopotentials [57] were used. The conjugate gradient (CG) method was applied to obtain equilibrium structures with residual forces on atoms below 0.01 eV/Å. When calculating relaxed geometries for nucleobases adsorbed on silicene, we tested different starting configurations, in which the molecule was displaced from six different initial configurations which saw the molecule shifted vertically and horizontally parallel to the silicene surface by about 0.25 Å. Also, different starting heights above the silicene sheet were considered, for example, 3.3, 3.0, and 2.5 Å to test whether the resulting relaxed structure would be affected. In all cases, it was found by us that we obtain virtually the same optimized geometry and energy, independent of the particular starting conditions of the force-minimization process.

The principal idea of quantum transport calculations is to divide the system under investigation into three parts: two electrodes and a scattering region in between. Defining the boundary as a region where the charge density matches with the bulk electrodes and using localized basis sets, it is possible to write the NEGFs for the scattering region $G(E, V)$ as:

$$G(E, V) = \left[ E \times S_\delta - H_S [\rho] - \Sigma_L(E, V) - \Sigma_R(E, V) \right]^{-1},$$

where $S_\delta$ and $H_S$ are overlap matrix and Hamiltonian, respectively, for the scattering region and $\Sigma_{LR}$ are self-energies that take into account the effect from the left (L) and right (R) electrode onto the central region. The self-energies are given by $\Sigma_a = V_{sa} g_a V_{as}$, where $g_a$ are the surface Green’s functions for the semi-infinite leads and $V_{sa} = V^+_sa$ are the coupling matrix elements between the electrodes and the scattering region. The Hamiltonian can be calculated through a variety of approaches (e.g., using tight-binding methods), but really, $H_S$ is a functional of the electronic density, and for this reason, we used the Hamiltonian obtained from DFT calculations. The charge density is self-consistently calculated via Green’s functions until convergence is achieved at which point the transmission coefficient $T(E)$ can be obtained:

$$T(E) = \prod_L (E - E_m) \prod_R (E_m - E),$$

where the coupling matrices are given by $\Gamma_a = i \left[ \Sigma_a - \Sigma^+_a \right]$, with $\alpha \equiv \{L, R\}$. Further details regarding the methods for calculating electronic transport properties can be found in the literature [53, 58].

3. Pristine silicene

In order to establish the reliability of our computational methods to accurately describe pristine silicene itself, we first carried out a number of benchmark tests concerning the structural and electronic properties of silicene.

Figure 1 shows the fully relaxed supercell for flat and buckled structures in which $\delta$ represents the vertical distortion of the atomic positions from a perfectly planar geometry. The flat structure is found to be metastable in the sense that a small out-of-plane displacement of the atoms would lead to the sheet becoming buckled upon relaxation. Both the hexagonal and parallelepiped unit cells with two and four atoms, respectively, were considered by us (figure 1). The relaxed lattice constant, Si–Si distance, and resulting vertical distortion $\delta$ are listed in figure 1, calculated with the exchange-correlation potential GGA (PBE) and with GGA including van der Waals (vdW) corrections. Our results for the Si–Si distance (2.27 – 2.31 Å) are in excellent agreement with experimental results [10] (2.2 ± 0.1 Å) and with recent theoretical predictions [4] (2.25 Å). For the proper description of pristine silicene, it is of rather little difference whether vdw...
corrections are added to GGA or not. However, since a major goal of our present work is to study the physisorption of DNA nucleobases on silicene, a process in which vdW interactions may be crucial, the conclusion from our benchmark results in figure 1 is that GGA+vdW does indeed yield accurate results for pristine silicene.

We furthermore investigated the energetic properties of pristine silicene, as summarized in figure 2(a). It can be seen that the buckled structure is approximately 0.05 eV/atom more stable than the planar one, in agreement with theoretical predictions [4] and the experimental [10, 11] findings that silicene exists in a buckled configuration. Calculated band structures for the planar and buckled structures are compared in figure 2(b). One can note the similarities with the band structure of graphene, inasmuch as we observe the same crossing of the $\pi$ and $\pi^*$ bands at $K$ and $K'$ points in the Brillouin zone. The main difference between the electronic band structures of the planar and buckled geometries is a varying shift in energy of the respective bands, with the magnitude of the shift smoothly changing as we move through reciprocal space.

Using the model illustrated in figure 2(c), we calculated the transmittance for buckled silicene as shown in figure 2(d), exhibiting the characteristic V-shaped curve with straight lines in the vicinity of the Fermi energy, as it is common for Dirac materials.

### 4. Molecular equilibrium configurations

Having established the basic structural and electronic properties of pristine silicene and their accurate description through the computational methods chosen by us in the present study, we now turn our attention to the main focus of this paper, namely the physisorption of DNA nucleobases on silicene and the consequential effects on the electronic conductance properties of this nano-bio hybrid system.

The fully relaxed equilibrium geometries of the four DNA nucleobases adenine, cytosine, guanine, and thymine (abbreviated as A, C, G, and T in the following) physisorbed on silicene are shown in the left panel of figure 3. We first note the larger size of the underlying hexagons formed by the silicon atoms compared to the smaller six- and five-membered rings formed by carbon and nitrogen atoms in the nucleobases. This size mismatch is an important difference to otherwise similar physisorption processes of DNA nucleobases on graphene and boron nitride studied in the past [59–61].

One feature discernible from the side view of figure 3 is that cytosine and guanine have their single oxygen atom located directly above a silicon atom. For thymine with its two oxygen atoms, no such alignment is observed (and for geometrical reasons, it is actually impossible to align both oxygen atoms simultaneously on top of the underlying silicon atoms without inducing drastic deformations in the bond angles or bond lengths of thymine). In terms of the equilibrium distance between nucleobases and silicene, we can distinguish two categories: one category (A and T) in which the closest atomic distance between the two entities is a (non-covalent) Si–H connection with a distance of about $3 \text{Å}$ and a second category (C and G) in which the closest distance is given by a Si–O connection amounting merely to around $2 \text{Å}$. These results are quantitatively summarized in table 2. The correlation between equilibrium distance and binding energy is discussed further below.

### 5. STM fingerprints of DNA nucleobases on silicene

In the right panel of figure 3 we show through a series of simulated images how the four different nucleobases would appear in a scanning tunneling microscope (STM). To calculate the images, we apply the Tersoff–Hamann [63] approach, in which the electronic state of the STM tip is modeled by an s-orbital and the assumption is made that the sample wave-functions near the tip exhibit only small variations. The resulting tunneling current (or rather differential conductance $dI/dV$) is proportional to the local density of states (LDOS) or partial density of charge $\rho(z_0, E_F + V)$ integrated from a specific energy to the Fermi energy ($E_F$), where $z_0$ is the tip height and $E_F$ to $E_F + V$ is the range of energy considered in the LDOS calculation. For filled states, we integrated from $-3 \text{eV}$ to $E_F$ (see partial densities of states, PDOS, in the supplementary data).

Considering the tip to be at the same height for all STM images (we used the same isovalue for LDOS), it is possible to verify that the silicene sheet in the panels for A and T appears in a darker color compared with those for C and G. The explanation is that the bases A and T are further away from silicene than C and G (see table 2). The brightness of the nucleobases are all similar because the distance (tip-nucleobase) is essentially the same for all.

Now we discuss the correlation of the STM images with the equilibrium geometries. For adenine the final structure (see top and side views in the left panel of figure 3) is less tilted compared to the other nucleobases (C, G, and T), and therefore both rings of this nucleobase are clearly discernible in the STM image. The methyl group (CH$_3$) has one hydrogen pointing up, which is thus the closest atom to the STM tip and hence appears as the brightest spot in this region. The amine group (NH$_2$) does not possess such a bright signature, because it is somewhat lower in height compared to the H atom from the CH$_3$ group. We also identify the two hydrogen atoms bonded to carbon atoms, as two small bulges. For guanine the

| Structure | $a$ (Å) | $d_{\text{Si-Si}}$ (Å) | $\delta$ (Å) | $a$ (Å) | $d_{\text{Si-Si}}$ (Å) | $\delta$ (Å) |
|-----------|--------|---------------------|----------|--------|---------------------|----------|
| Planar    | 3.945  | 2.27                | 0.00     | 3.995  | 2.30                | 0.00     |
| Buckled   | 3.949  | 2.27                | 0.46     | 4.002  | 2.31                | 0.51     |
Figure 2. Pristine silicene properties are shown: (a) total energy as a function of the lattice constant, illustrating the relatively higher stability of buckled silicene compared to the planar allotrope; (b) band dispersion of planar and buckled configurations; (c) computational model for quantum transport calculations showing the leads, the buffer region, and the scattering region; and (d) electronic transport as a function of energy for the more stable buckled configuration.

Figure 3. The left panel shows top views and side views of the fully relaxed geometries for the four different nucleobases (A, C, G, and T) physisorbed on a buckled silicene sheet. The hexagonal network of Si atoms is drawn in salmon color, C atoms are represented as green spheres, N atoms in blue, O atoms in red, and H atoms in white. The right panel shows the nucleobase fingerprints on silicene as they would appear in an image recorded by a scanning tunneling microscope (STM). The STM images were generated with the WSxM software [62] from our DFT calculations using the Tersoff–Hamann approximation for filled states. STM fingerprints for each nucleobase are shown twice for clarity, once with the atomic structure superimposed and once without it. The hexagonal patterns of dots to the lower left in each image is meant to help locating the Si atoms from the buckled silicene sheet which are either extended upwards (blue dots) or downwards (red dots) from the plane.
Table 2. For each nucleobase (A, C, G, and T) the closest pair of atoms between the silicene sheet (Si) and the base (either H or O) are given along with their respective distance in Å. The corresponding binding ($E_b$) energies were calculated by performing a vertical energy scan (see figure 4) and are given in eV as the energy relative to infinitely far separated nucleobase and silicene sheet. Negative binding energies thus indicate stable configurations.

| Nucleobase | Closest atoms | distance Si-base | $E_b$ |
|------------|---------------|-----------------|-------|
| A          | Si–H          | 3.065           | −0.604|
| C          | Si–O          | 2.039           | −0.881|
| G          | Si–O          | 1.990           | −0.774|
| T          | Si–H          | 3.070           | −0.601|

equilibrium geometry is tilted (see side view, left panel of figure 3), and because of that, it is more difficult to recognize the rings as in the case of adenine. However, the methyl group is pointing up and thus has one of its H atoms appear as the brightest spot, similar to the adenine case. The oxygen atom is pointing down towards the substrate and the corresponding intensity is therefore less bright. Cytosine possesses the same tilted equilibrium geometry as guanine (see side view, left panel of figure 3) and a similar interpretation is therefore possible here. The main differences are the two hydrogen atoms pointing up at the same side of the molecule. These two hydrogen atoms appear as a large bright spot on the right side of the right side of cytosine. Finally, for thymine we observe two bright spots due to the two CH$_3$ groups. The two oxygen atoms are pointing slightly down and the brightness is therefore less strong for them. These nucleobase fingerprints could be an important guide for experimentalists trying to identify via STM the four DNA nucleobases adsorbed on silicene.

6. Interaction strengths

To explore the correlation between equilibrium height of the DNA nucleobases above the silicene substrate and the associated binding energy, we carried out a vertical height scan of the energy for the combined system (figure 4). The binding energy was calculated from the difference in energy between the minimum of the fitted curve and the asymptotic limit for large distances (table 2). Cytosine is found to exhibit the strongest binding, followed closely by guanine. Adenine and thymine are both bound about equally strong with the lowest overall binding energies. Clearly, the lower binding energies are found for those two nucleobases (A and T) that are furthest away from silicene, as it could be expected.

7. Charge density redistribution

To better understand the processes occurring at the electronic structure level when a nucleobase interacts with silicene, we calculated how the charge density of the system changes when these two entities are brought together. Mathematically, the change in charge density is simply expressed as

$$\Delta \rho(\vec{r}) = \rho_{\text{Si-base}}(\vec{r}) - \rho_{\text{Si}}(\vec{r}) - \rho_{\text{base}}(\vec{r}).$$

In figure 5 we plot the resulting isosurfaces of the calculated charge density difference in space for the four nucleobases physisorbed on silicene. Blue color indicates that $\Delta \rho(\vec{r})$ possesses a negative value, meaning that electronic charge density has increased in this region under the physisorption/chemisorption processes, while red color means that $\Delta \rho(\vec{r})$ is of positive value, indicating that the electronic charge density has decreased in this region. It can be seen quite clearly from these plots that for adenine and thymine interacting with silicene (figures 5(a) and (d)), charge redistribution is concentrated mainly to the nucleobase part and in a trivial manner: a shift distributed uniformly over the whole area of the nucleobase, which could be interpreted as an electrostatic repulsion (electronic charge density shifting away from the silicene sheet). The interaction of adenine and thymine with silicene could thus be characterized as weak and purely non-covalent. However, the situation is radically different for the cases of cytosine and guanine interacting with silicene. Here, we notice a complex redistribution of charge density both in the nucleobase part and in the silicene substrate (figures 5(b) and (c)). The respective insets in panels (b) and (c) of the figure clearly show that the major charge density redistribution occurs along the connection between the single oxygen atom of these two nucleobases and a Si atom of silicene, suggesting the formation of a weak bond of partially covalent nature. In other words; cytosine and guanine appear to be at least weakly chemisorbed on silicene, while adenine and thymine are merely physisorbed (no sign of covalent interaction). It is interesting to note that S Kilina et al [64] observed similar behavior for nucleobases adsorbed on a Cu(111) surface.

What is common for cytosine and guanine, the two bases that interact more strongly with silicene, is that they each possess one oxygen atom (figure 3). It is via this oxygen atom that they form a quasi-covalent bond with a Si atom in silicene. The two nucleobases which are found by us not to interact strongly with silicene, adenine and thymine, possess either no oxygen atom (adenine) or two oxygen atoms (thymine). In the former case, it is trivially obvious that where there is no oxygen atom, no oxygen-mediated interaction between nucleobase and silicene can take place. For thymine, on the other hand, forming two covalent bonds simultaneously with Si atoms through its two oxygen atoms is not possible for simple geometric reasons without enforcing any drastic distortions of the bond angles or bond lengths in the nucleobase.

8. Quantum transport properties

We finally come to the question whether silicene may possess any functionality for DNA sequencing. Stated in a more specific way, we need to assess how the electronic transport properties of silicene will be affected when the four different nucleobases are physisorbed on its surface.

The energy-resolved transmittance $T(E)$ indicates the probability of an electron to be transmitted from one electrode
Figure 4. Energy variation as a function of the height distance between a nucleobase and the silicene sheet is plotted for each of the four nucleobases: (a) adenine; (b) cytosine; (c) guanine; (d) thymine. Colored symbols indicate calculated data points; black dashed lines represent a best fit of the data, with a Lennard-Jones type potential for the long-range behavior.

Figure 5. The change in electronic charge density is plotted, calculated as the difference between the charge density of the total system (silicene + nucleobase) and that of each constituent part (silicene, nucleobase) separately. Blue color indicates a negative difference in the charge density; red color indicates a positive difference in the charge density. The main panels show isosurfaces for a value of 0.001 electron × bohr$^{-3}$ while the insets show the same charge density difference data plotted for a larger isosurface value of 0.03 electron × bohr$^{-3}$ and viewed from a different perspective. (a) Adenine; (b) cytosine; (c) guanine; (d) thymine.
Figure 6. The plot shows the zero-bias transmission of silicene with and without nucleobases on top as a function of the electron energy, with the Fermi level for the whole system aligned to 0 on the horizontal axis. The curve in black color represents the transmittance for pristine silicene without any nucleobases present while the other colors (red, orange, green, and blue) refer respectively to the transmission for each nucleobase (A, C, G, and T, in that precise order) physisorbed or chemisorbed on top of silicene. The larger panel to the left shows the overall data while the two smaller panels to the right present a focused view of the same data for selected energy intervals of interest. The significance of the dashed vertical lines is discussed in the main text.

to the other via the scattering region in between. When analyzing in the following the changes in the zero-bias T(E) function upon adsorption of the nucleobases on silicene, it is important to remember the results of the equilibrium binding geometries presented above, which led us to identify two groups of nucleobases in terms of their silicene-nucleobase distance: group I (A and T) with a larger distance between silicene and nucleobase and weaker coupling, and group II (C and G) with shorter distances and stronger coupling between the sole oxygen atom from the respective nucleobases and a protruding silicon atom in the buckled silicene sheet.

Figure 6 shows plots of the energy-resolved transmission for pristine silicene as well as for silicene with one of each of the four nucleobases adsorbed on top of it. For group I we note that the resulting change in transmission is quite small for almost the entire range of energy, while for group II a considerable reduction in transmission compared to pristine silicene is found (for energies below about −0.3 eV relative to the Fermi energy, as well as for energies above +0.4 eV and even more pronounced above +0.6 eV). As expected, group II shows the larger change in transmittance due to the strong coupling with silicene, as seen from the charge density difference plots (cf figure 5). Group I exhibits a much smaller decrease in the transmittance due to weaker interaction with silicene. Based on the resulting large overall difference in transmission behavior one can thus rather easily distinguish between group I and group II, i.e., differentiate between having adenine or thymine physisorbed versus cytosine or guanine.

To clearly demonstrate that the diminution of the transmittance for C and G is due to the strong coupling between the oxygen atom from the nucleobase and silicene, we performed a transport calculation in a minimalistic model system consisting of an OH group bonded with silicene (at the same distance as was found for guanine and cytosine binding to silicene, i.e., about 2 Å). The transmittance change for silicene when OH is bound to it is shown in the figure S2 of the supplementary data (for comparison, the transmittance plots of C and G have also been reproduced there from figure 6). We see that the addition of an OH group to silicene overall generates the same trend in the transmission profile as that found for C and G, thus confirming that the reduction in transmittance originates from the binding of oxygen to silicene.

The two groups, I and II, are thus seen to be easily distinguishable based on their very different overall transmittance. However, as we shall show in the following, it might be possible to go further and even differentiate within each group between the two respective constituting nucleobases. Analyzing the electronic properties (see plots of PDOS in figure S1 of the supplementary data), we find for all nucleobases that the nucleobase states are located relatively far from the Fermi energy, in the sense that the electronic signatures from the nucleobases start from ±1.0 eV above/below $E_F$ and because of that we can expect pronounced changes in the transmission for energies above +1.0 eV or below −1.0 eV.

Two energy values have been marked by dashed lines in figure 6 and the following discussion concentrates on transport properties at these two energies. For $E = −1.26$ eV we first note a drastic decrease in transmission for the nucleobase A, followed by a lesser decrease for G and C, and a relatively small decrease relative to pristine silicene for T. This can be seen more clearly in the magnified inset of 6 on the right upper panel. If one were to measure therefore the conductance of a properly gated silicene device (with the gate voltage tuned such that the Fermi energy were shifted down by −1.26 eV), one would obtain significantly different results for A and T, as well as for the group constituted by C and G. For the second energy of interest, $E = +1.0$ eV, we find (cf 6 right lower panel) that A and T exhibit virtually no difference.
in transmission relative to pristine silicene, while C and G show a significant difference and, more importantly, are rather different from each other also, due to a pronounced dip in the transmission spectrum of the nucleobase C. Thus, a conductance measurement in a silicene device gated so that the Fermi energy were shifted upwards by +1.0 eV should reveal a strong reduction in conductance for C, less of a reduction for the nucleobase G, and virtually no reduction in conductance for the nucleobases A and T. Combined measurements, therefore, in which conductances are recorded both for gate voltages of −1.26 V and +1.0 V should, in principle, distinguish fully between A, C, G, and T.

The stated goal of our study is to test the hypothesis whether a silicene-based device in contact with individual nucleobases from a single-stranded nucleic acid molecule could in principle be used to electrically sequence DNA. It is useful to discuss in this context the sensitivity $S = \left| \frac{g(V_g)}{g_0} \right|$ of such a hypothetical silicene-based sensor, where $g$ refers to the conductance of the device with a nucleobase adsorbed, and $g_0$ is the pristine device conductance. For a small bias voltage, the conductance can be defined [25] as $g(V_g) = \frac{2e^2}{h}BE(V = \mu)$, where $h$ is Planck’s constant and $\mu = E_F - eV_g$ is the chemical potential. We assume the presence of a gate voltage ($V_{g_{\text{eff}}}$) capable to tune the chemical potential to the resonances in the transmission spectrum discussed in the preceding paragraph.

The resulting sensitivity histograms in figure 7 demonstrate that a distinction between the four nucleobases might be possible if the combined conductance data from measurements at two gate voltages (specifically −1.26 V and +1.00 V) is available. Thus, at $V_g = -1.26$ V the silicene device possesses a sensitivity spectrum that should allow to distinguish the nucleobase A from T and from the group of C and G. At $V_g = +1.0$ V, we note that the silicene device exhibits large sensitivity towards C and G, while having small sensitivity towards A and T, allowing in principle to distinguish nucleobase C from G, and from the group of A and T. The low sensitivity of silicene towards the nucleobase T could be regarded as problematic, as it might appear impossible to distinguish the appearance of a T in the DNA sequence from a ‘no signal’ event corresponding to pristine silicene. However, it might still be possible to detect T by taking into account the duration of such a ‘silence’ in the electronic data which would be presumably shorter for the intermittence between two adjacent nucleotides as compared to the passage of a whole nucleotide.

Finally, we note that in an experiment to test our predictions, silicene would presumably be required to rest on top of a supporting substrate. The effect of this substrate on the electronic structure and transport properties of silicene might be pronounced and depends in detail on the nature of the substrate and the resulting strength of interaction with silicene. However, even though the presence of a substrate may therefore shift the reference transmission function of pristine silicene, we still expect that the relative changes calculated here when nucleobases adsorb on silicene supported by a substrate might be similar to the ones presented in this article, so that the overall conclusions of our work would not change. This assumption remains to be tested with calculations explicitly considering the effect of a substrate on the sensing capabilities of silicene.

9. Conclusions

In summary, we have presented here a comprehensive theoretical study about the interaction between DNA nucleobases and silicene, and discussed a possible emerging application as a biosensor. Our computational results demonstrate that adenine and thymine are physisorbed on silicene, whereas cytosine and guanine are weakly chemisorbed through the formation of a Si–O bond. We also investigated how the electronic transport properties of silicene are affected by the adsorption of DNA, demonstrating that it certainly appears possible to distinguish an electronic signal due to the strong interaction of cytosine and guanine with silicene from the weaker interaction of adenine and thymine. When considering the application of a gate voltage to effectively shift the Fermi energy of the system, one can even argue that for specific energies, the transmission of the nucleobases differs from that of pristine silicene in a characteristic manner, and a distinction of all four nucleobases might be achievable. This result indicates that silicene is a promising candidate for applications as a DNA sequencing device.

How could an actual device be constructed then out of silicene to sequence DNA? Clearly, a large (infinite) silicene sheet, as simulated here by us, would not be able to electrically sequence DNA. Rather, it is necessary to cut out a narrow strip, i.e., a silicene nanoribbon, and span it over a microfluidic channel through which single-stranded DNA is pulled. The individual nucleotides from the DNA molecule can then briefly get in contact with the silicene nanoribbon in the sequence in which they occur in the polymer and thereby characteristically affect the conductance of the silicene nanoribbon according to the sensitivities calculated in the present work. This approach is very much analogous to the working device idea pioneered by Professor Kwang-Soo Kim and his group [25].
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