

C₅₉Si on the Monohydride Si(100):H–(2 × 1) Surface

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We propose the use of the Si atom in the experimentally observed C₅₉Si molecule as a possible way to controllably anchor fullerene molecules on a Si surface, due to the formation of a strong bond to one of the Si surface atoms. All our results are based on ab initio total energy density functional theory, and we obtain that the binding energy is on the order of 2.1 eV, approximately 1.4 eV more stable than a C₆₀ bonded in a similar situation. A possible route to obtain such adsorption via a (C₅₉Si)₂ dimer is examined, and we find the whole process to be exothermic by approximately 0.2 eV.

I. Introduction

C₆₀ and its relatives, collectively known as fullerenes, have attracted wide interest since their discovery in 1985.¹ All this interest, reflected in an enormous amount of both experimental and theoretical studies, has its roots in the unique physical and chemical properties of these molecules, including the great prospects for their applications as new materials. To fully exploit these prospects, one avenue of research has been the doping of fullerenes, with the objective of altering, or in other words, functionalizing these molecules. In particular, the synthesis of the C₅₉Si heterofullerene has been recently reported by different groups,^{2–9} and the properties of this molecule have also been theoretically studied.^{5–15} The interest in this type of system resides in the possibility of the fabrication of nanostructured materials with desired properties, via modification of the electronic structure of the C₆₀ molecule through substitutional doping. The substitution of a carbon by a silicon atom has also been studied in carbon nanotubes.^{16,17} Moreover, this Si atom can be used as a site to anchor other atoms or molecules^{18–20} with the purpose of functionalizing the nanotubes.

For the past few years, molecular electronics has received worldwide attention due to the perspectives of both scientific as well as technological breakthroughs that it will bring.^{21–24} In particular, C₆₀ and other fullerenes have also been used^{25–30} in molecular electronics devices. Considering that (i) Si is the most important material in the electronic industry today and (ii) there is a large amount of knowledge of how to process Si surfaces, the integration of molecular devices with Si has obviously attracted a lot of attention, and many studies along these lines have been reported in the literature.^{31–38} In particular, there has been an increasing interest in functionalizing Si surfaces with fullerenes,^{39–50} either for electron transport properties or even for storage properties, when endohedral fullerenes are considered.^{51,52} The consensus^{46,47,50} is that the C₆₀ is chemisorbed on the Si(100) surface, being preferentially adsorbed at the trenches between two dimer rows, where it binds to four Si dimers, with a C–Si bond strength on the order of 0.5–0.7 eV. However, the interaction of C₆₀ with hydrogen-terminated Si(100) surfaces^{53–55} is weak, having a van der Waals character, and is estimated to be less intense than the C₆₀–C₆₀ interaction.⁵⁴

The advantage of the hydrogen-passivated Si(100) surface is its stability.⁵⁶ It is possible to selectively remove hydrogen from such a passivated surface using a scanning tunneling microscope (STM) and then adsorb, for example, organic molecules at these reactive sites.^{57,58} It would be, therefore, interesting to explore this type of adsorption for fullerenes in hydrogenated Si(100) surfaces. Considering the reactive properties of the Si site in the C₅₉Si molecule, as described above, we here propose, therefore, the use of the Si atom in the C₅₉Si to anchor fullerene molecules on Si surfaces. As discussed below, this will provide a much stronger bond between the fullerene and the surface than the pure C₆₀, which may be useful in the area of nanoelectronics. Moreover, even though we focus on the C₅₉Si system, the ideas presented here are of a more general character and can be applied to other C_mSi molecules or even to more general C_mSi_n fullerenes. In this latter case, the extra Si atoms can even be used as connection knobs between the molecules.

II. Methods

The system we focus on is the monohydride Si(100):H–(2 × 1), where the Si atoms are forming symmetric dimers and there is one hydrogen per Si atom saturating their remaining dangling bonds. We will consider various configurations where in place of one of these hydrogen atoms there would be the adsorption of a C₅₉Si molecule, with the formation of a Si_{surface}–SiC₅₉Si bond. All our results are based on ab initio total energy density functional theory^{59,60} calculations. The exchange–correlation potential was treated through the generalized gradient approximation (GGA) as proposed by Perdew, Burke, and Ernzerhof.⁶¹ The ionic core potentials were represented by nonlocal pseudopotentials,⁶² whereas the spin-polarized Kohn–Sham orbitals were written in terms of a double- ζ numerical basis set plus polarization functions (DZP basis set)⁶³ (SIESTA code⁶⁴). For the self-consistent calculation of the Hamiltonian matrix elements, the charge density was represented in a regular real space grid with mesh spacing of 0.09 Å, which is equivalent to a cutoff of 300 Ry if a plane-wave basis set were being used. Structural optimizations were performed using the conjugate gradient algorithm until all the residual forces were smaller than 0.05 eV/Å. The supercell method with periodic boundary conditions was adopted to represent the system. For the calculations involving a Si(100):H–(2 × 1) surface, we used a supercell with eight atomic layers, eight vacuum layers, and a

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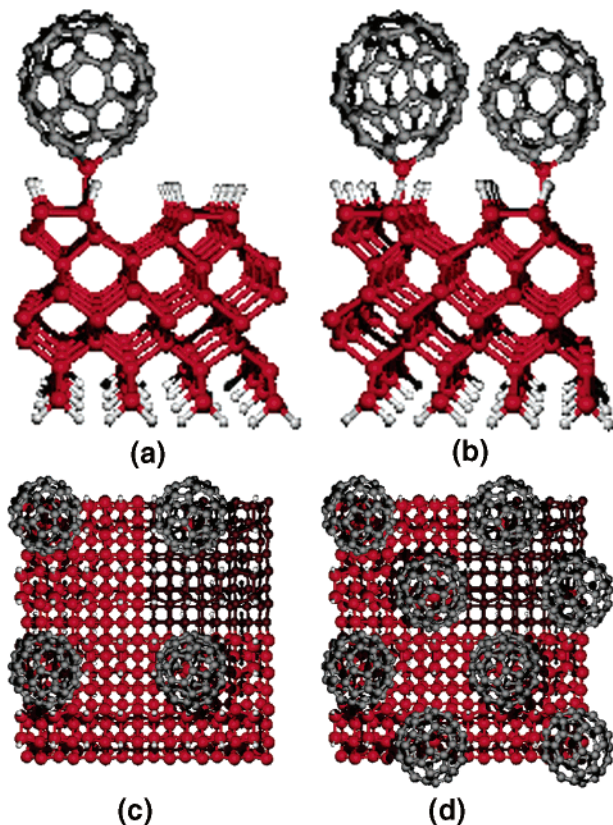


Figure 1. Final equilibrium geometries for the adsorbed $C_{59}Si$ molecules. (a) One $C_{59}Si$ molecule replacing a hydrogen atom in the (4×4) $Si(100):H$ unit cell. (b) Two $C_{59}Si$ molecules replacing hydrogen atoms in the (4×4) $Si(100):H$ unit cell. (c) Top view of the configuration in part a and (d) top view of the configuration in part b. The darker areas in parts c and d indicate the unit cell.

(4×4) surface unit cell (16 Si atoms in each layer). All geometry optimizations were performed without any symmetry constraints, and all atoms in the topmost six silicon layers were allowed to relax, as well as the atoms in the $C_{59}Si$ molecules. The Si atoms in the two bottom layers were held at their bulk positions, and the dangling bonds of the bottom layer were passivated by hydrogen atoms, which were also held fixed throughout the calculations. The hydrogen atoms in the monohydride surface, on the contrary, were allowed to relax. For the Brillouin zone sampling in the surface calculations, a $(2 \times 2 \times 1)$ set was used, where the z -direction is normal to the surface. The binding energies were basis sets superposition error (BSSE)-corrected by the counterpoise method.⁶⁵

III. Results and Discussion

As already mentioned, we are interested in the experimental situation where the molecule $C_{59}Si$ would be bonded, through its Si atom, to one of the Si surface atoms. Hence, in our calculations we have removed one of the hydrogen atoms from the monohydride $Si(100):H-(2 \times 1)$ surface, and the $C_{59}Si$ molecule was placed close to the created Si dangling bond. The system was then allowed to relax, as described above, and the resulting configuration is shown in Figure 1a (lateral view) and in Figure 1c (top view).

In Table 1 we present all the relevant distances. The final $Si(surface)-Si(C_{59}Si)$ bond distance is 2.37 Å. This value is identical to what was obtained previously with non-spin-polarized calculations.⁶⁶ Our calculations give for the pure hydrogenated $Si(100)$ surface a Si–Si dimer interatomic distance of 2.43 Å, a Si–H distance of 1.51 Å, and a Si–Si back-bond

TABLE 1: Relevant Interatomic Distances for the Systems $C_{59}Si-Si(100):H$ and $2(C_{59}Si)-Si(100):H^a$

distances (Å)	$C_{59}Si-Si(100):H$	$2(C_{59}Si)-Si(100):H$
$(Si-Si)_{dimer}$	2.41	2.41
Si–H	1.51	1.51
C–C (HH)	1.42	1.42
C–C (HP)	1.47	1.47
C–Si (HH)	1.84	1.84
C–Si (HP)	1.87	1.87
$Si(C_{59}Si)-Si(surface)$	2.37	2.36

^a See text for details. There are two types of carbon–carbon bonds. The label HH refers to bonds between adjacent hexagons, and the label HP refers to bonds between adjacent hexagons and pentagons.

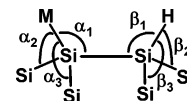


Figure 2. Angles characterizing the local dimer geometry. M could either be a hydrogen atom or a $C_{59}Si$ molecule.

distance of 2.37 Å. From Table 1, we see that the Si–Si bond length for the dimer where the $C_{59}Si$ is attached, $(Si-Si)_{dimer}$, has decreased slightly, by approximately 1%. All the other interatomic distances are basically the same, having changed by less than 1%. There are two types of C–C and C–Si bonds in the $C_{59}Si$ fullerene: the ones between two hexagons, which will be labeled as HH, and the ones between a hexagon and a pentagon, which will be labeled as HP. The C–C (HH) and the C–C (HP) are both very similar to the equivalent distances in the pure C_{60} and in the isolated $C_{59}Si$ and $C_{59}SiH$ molecules.⁶⁶ The C–Si distances, however, are larger than in the isolated $C_{59}Si$ molecule (for the isolated molecule, we have C–Si (HH) = 1.79 Å and C–Si (HP) = 1.84 Å); they are similar, however, to the equivalent distances in the $C_{59}SiH$ molecule.⁶⁶ The binding energy, E_b^{1H} , for the $C_{59}Si$ molecule to the surface is 2.07 eV, defined as

$$E_b^{1H} = -[E_T(Si(100):H + C_{59}Si) - E_T(Si(100):H)_{1H} - E_T(C_{59}Si)]$$

where $E_T(Si(100):H + C_{59}Si)$ is the total energy for the configuration with the $C_{59}Si$ molecule adsorbed on the monohydride $Si(100):H-(2 \times 1)$ surface and $E_T(C_{59}Si)$ and $E_T(Si(100):H)_{1H}$ are the total energies for the isolated $C_{59}Si$ molecule and the monohydride $Si(100):H-(2 \times 1)$ system with one hydrogen removed, respectively. As can be seen, the $C_{59}Si$ forms a rather stable bond on the surface. Comparing with a calculation of the C_{60} molecule adsorbed in a similar geometry, we obtain a binding energy of 0.72 eV, or the adsorbed $C_{59}Si$ molecule is 1.35 eV more stable than C_{60} adsorbed in a similar configuration.

As a reference, we calculated the disilene binding energy, i.e., the energy required to break Si_2H_6 into two SiH_3 . We obtained a value of 3.2 eV, which should be compared to an experimental value of 3.5 eV. This means that we are probably underestimating the binding energies by something on the order of 8%. The local dimer geometry can be characterized by the angles shown in Figure 2. For a regular dimer on the surface ($M = H$ in Figure 2), we obtain $\alpha_1 = \beta_1 = 110^\circ 85'$ and $\alpha_2 = \alpha_3 = \beta_2 = \beta_3 = 112^\circ 95'$. For the dimer where $M = C_{59}Si$ in Figure 2, we obtain $\alpha_1 = 95^\circ 91'$, $\alpha_2 = 118^\circ 7'$, $\alpha_3 = 119^\circ 2'$, $\beta_1 = 109^\circ 93'$, $\beta_2 = 111^\circ 30'$, and $\beta_3 = 112^\circ 03'$. Therefore, the fullerene tends to be in a more upright position, as can be also seen in Figure 1a.

In Figure 3 we present the band structure for this system. We see that there are many almost dispersionless bands close

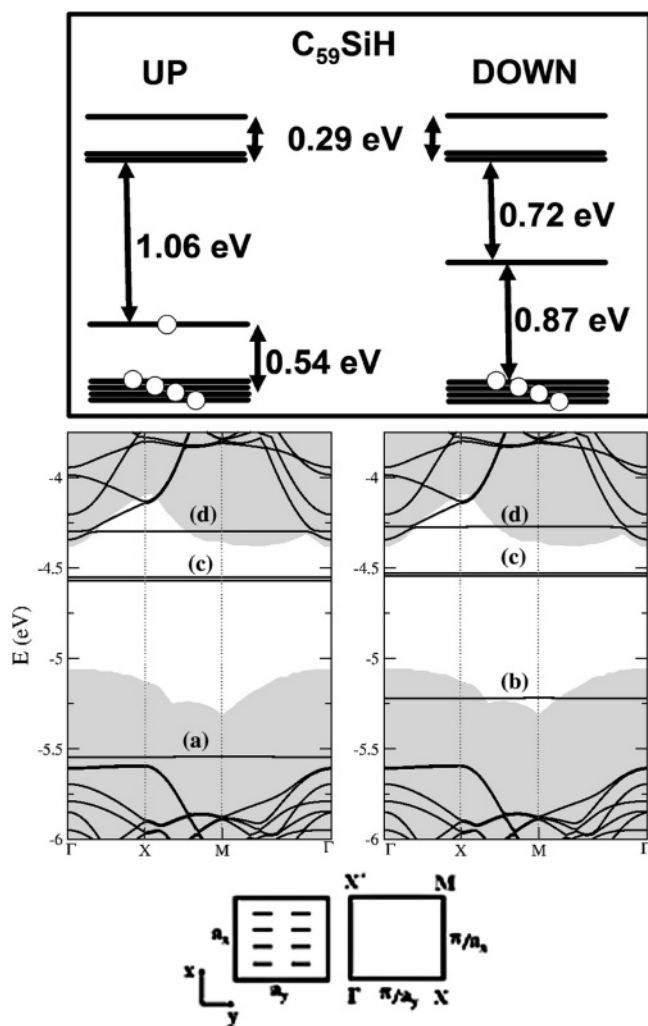


Figure 3. Electronic structure for the isolated C₅₉SiH molecule and the band structure for the system (C₅₉Si)-Si(100):H. The top panel presents a schematic structure of the molecular orbitals for the C₅₉SiH molecule close to the HOMO-LUMO gap. The small white dots represent the level occupation by an electron. The middle left (right) panel presents the majority (minority) spin bands for the (C₅₉Si)-Si(100):H. The shaded regions are the projected bulk band structure whereas the lines are the slab band structure. The a through d marked bands are discussed in the text. The bottom panel shows the real space unit cell and the corresponding Brillouin zone.

to the gap region, which are all related to the fullerene. The one marked by the letter a is fully occupied, and the ones marked by the letters b-d are all empty. For an isolated C₆₀ molecule, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are 5-fold and 3-fold degenerate, respectively. This is a result of the icosahedral symmetry of the molecule. For the isolated C₅₉Si, however, as there is a symmetry reduction, there is a lifting of the C₆₀ HOMO and LUMO degeneracies. The five C₆₀ degenerate HOMO orbitals split in four closely spaced levels and another one at a higher energy of approximately 0.1 eV.⁶⁶ The three C₆₀ LUMO levels now result in two closely spaced levels and another one at a lower energy of approximately 0.3 eV. This means that our calculated HOMO-LUMO gap decreases from 1.6 eV to approximately 1.2 eV. Upon bonding to a hydrogen atom, forming the C₅₉SiH molecule, there is the introduction of an extra electron and a level below the C₅₉Si HOMO. This leads to the formation of bonding and antibonding orbitals and a σ -like Si-H bond. As a result, as shown in Figure 3, the system now has total spin of $1/2$, and there are four occupied

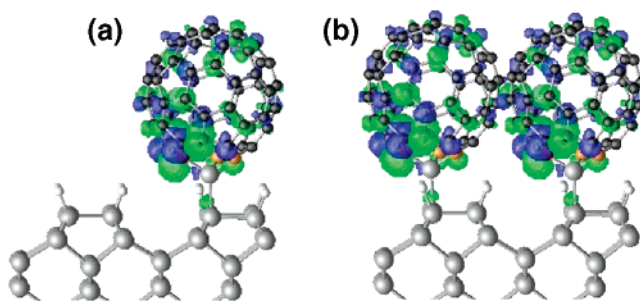


Figure 4. Isosurfaces for the net local magnetization $m(\mathbf{r}) = \rho_{\uparrow}(\mathbf{r}) - \rho_{\downarrow}(\mathbf{r})$ for the (a) (C₅₉Si)-Si(100):H, and (b) 2(C₅₉Si)-Si(100):H. The green surface corresponds to net \uparrow spins at a value of $\rho_{\uparrow}(\mathbf{r}) - \rho_{\downarrow}(\mathbf{r}) = +0.001$ e/bohr³, and the blue surface to \downarrow spins at $\rho_{\uparrow}(\mathbf{r}) - \rho_{\downarrow}(\mathbf{r}) = -0.001$ e/bohr³. The gray spheres denote Si atoms, the small white spheres denote hydrogen atoms, and the black ones represent the C atoms. The orange and red spheres represent the C atoms that are nearest neighbors to the Si in the C₅₉Si molecules.

closely spaced levels below the HOMO, with equivalent, almost degenerate four levels at approximately the same energy for the minority spins. The LUMO is spin down and has the same character as the spin up HOMO. The original triply degenerate C₆₀ LUMO orbitals have similar energies for both spin channels, and they split in two almost degenerate levels and a third one at approximately 0.29 eV higher in energy. In Figure 3 it is possible to see the similarities between the band structure for the (C₅₉Si)-Si(100):H system and the level structure for the isolated C₅₉SiH. The four occupied levels below the HOMO for the C₅₉SiH generate four bands, for each spin channel, which are not shown in Figure 3, but that are located at approximately 0.6 eV below band a. The splitting between the occupied band (a) and the unoccupied band (b) is 0.35 eV, and between bands a and c it is 1.0 eV. Finally, the splitting between bands c and d is 0.3 eV. All these values are very similar to the level splittings for the C₅₉SiH molecule.

A consequence of this band structure is that the system has a nonzero total spin, as it also occurs for the isolated C₅₉SiH molecule.⁶⁶ From the majority (spin up) and minority (spin down) charge densities, $\rho_{\uparrow}(\mathbf{r})$ and $\rho_{\downarrow}(\mathbf{r})$, respectively, we can obtain the net local magnetization $m(\mathbf{r}) = \rho_{\uparrow}(\mathbf{r}) - \rho_{\downarrow}(\mathbf{r})$. We plot $m(\mathbf{r})$ for the (C₅₉Si)-Si(100):H system in Figure 4a. As can be seen, $m(\mathbf{r})$ is nonzero only at the fullerene and around the Si atom from the dimer where the C₅₉Si is attached. The net magnetization has a clear p-orbital character at each C atom, alternating signs throughout the fullerene cage. It has, however, a larger value at the three C atoms that are nearest neighbors to the Si atom in the C₅₉Si molecule. This is related to the character of the levels marked by the letter a in Figure 3. They are more localized around these three carbon atoms, leading therefore to this behavior for $m(\mathbf{r})$. The empty states marked by the letter b in Figure 3 have a similar character. The c and d levels, however, are more delocalized over the entire cage, resembling more the lowest unoccupied level in the C₆₀ molecule, as discussed above. As the characters of these levels are also similar in the 2(C₅₉Si)-Si(100):H system, we simply show a figure of them below, when we discuss the higher coverage situation.

For our supercell geometry, i.e., a (4 × 4) surface unit cell and only one adsorbed C₅₉Si, the smallest distance between carbon atoms in adjacent C₅₉Si molecules is 8.5 Å, whereas this same distance in our C₆₀ bulk solid⁶⁷ is around 3.4 Å. Therefore, we expect the interaction between the C₅₉Si molecules in our system to be rather weak; i.e., they can be basically considered to be isolated from each other. This is confirmed by the essentially flat bands presented in Figure 3.

We, therefore, also considered another system with a higher surface coverage, where the smallest distance between carbon atoms in adjacent $C_{59}Si$ would be more similar to the distance between two C_{60} in the bulk. In this case, we used the previous supercell with a (4×4) -Si(100):H- (2×1) surface unit cell, but with two instead of one adsorbed $C_{59}Si$. The final relaxed geometry is presented in Figure 1b (side view) and Figure 1d (top view). The smallest distance between carbon atoms in adjacent $C_{59}Si$ molecules is, now, 3.9 Å, and the final bond lengths are given in Table 1. As can be seen, all the distances are very similar to the situation with only one adsorbed fullerene per (4×4) unit cell. This indicates that the interaction between the molecules is of a very weak nature, as already expected. Regarding the angles displayed in Figure 2, we have for the two dimers where the $C_{59}Si$ are bonded: $\alpha_1 = 94^\circ 67'$, $\alpha_2 = 119^\circ 2'$, $\alpha_3 = 119^\circ 4'$, $\beta_1 = 108^\circ 84'$, $\beta_2 = 111^\circ 96'$, and $\beta_3 = 112^\circ 4'$, again all very similar to the system $(C_{59}Si)$ -Si(100):H, with the largest changes being on the order of 1° .

The binding energy per molecule, E_b^{2H} , for the coverage of two $C_{59}Si$ molecules in a (4×4) surface unit cell, is defined as

$$E_b^{2H} = -[E_T(\text{Si}(100):\text{H} + 2C_{59}\text{Si}) - E_T(\text{Si}(100):\text{H})_{2H} - E_T(2C_{59}\text{Si})]/2$$

where $E_T(\text{Si}(100):\text{H} + 2C_{59}\text{Si})$ is the total energy for the configuration with the two $C_{59}Si$ molecules adsorbed on the monohydride Si(100):H- (2×1) surface and $E_T(2C_{59}\text{Si})$ and $E_T(\text{Si}(100):\text{H})_{2H}$ are the total energies for two isolated $C_{59}Si$ molecules and the monohydride Si(100):H- (2×1) system with two hydrogen atoms removed, respectively. We obtain a value of $E_b^{2H} = 2.10$ eV, very similar but slightly larger in modulus than E_b^{1H} . If we consider that the cohesive energy that we obtain⁶⁷ for the bulk C_{60} is 0.18 eV, then this gives a value for the fullerene–fullerene interaction (0.18/6, due to the 12 nearest neighbors) of something on the order of 0.03 eV. From $E_b^{2H} = 2.10$ eV and $E_b^{1H} = 2.07$ eV and the fact that each molecule has four nearest neighbors, we would obtain for the interaction energy between the adsorbed $C_{59}Si$ molecules something on the order of 0.015 eV. Considering that the distance between the $C_{59}Si$ molecules is larger than the distance between C_{60} molecules in the bulk and the precision of our calculation, the increase in the binding energy in the higher coverage case seems to indicate an attractive interaction between the fullerenes. This would mean that in the real system the gain in energy would be on the order⁶⁷ of 0.15 eV.

In Figure 5 we present the band structure for the $2(C_{59}Si)$ -Si(100):H system. A comparison between Figures 3 and 5 indicates that the electronic structures for the higher and lower coverage are rather similar, with the presence of narrow bands close to the bulk band gap, marked with the letters a–d. As these bands have a fullerene character, as shown in Figure 6, there are twice as many of these bands in Figure 5 as in Figure 3. The character of all these bands has already been discussed above. Again, only the a band is fully occupied in Figure 5. As previously, this means that the system has a nonzero total spin, as can be seen in Figure 4b. The net local magnetization, $m(\mathbf{r})$, in this case is very similar to the lower coverage situation, with a nonzero $m(\mathbf{r})$ only at the fullerene and around the Si atom from the dimer where the $C_{59}Si$ is attached. As the total spin for each fullerene is $1/2$, we have investigated a possible coupling between these spins. We have performed a calculation with total spin 1 (result shown in Figures 4b and 5) and total spin 0 (broken symmetry case, with each fullerene still having a nonzero net

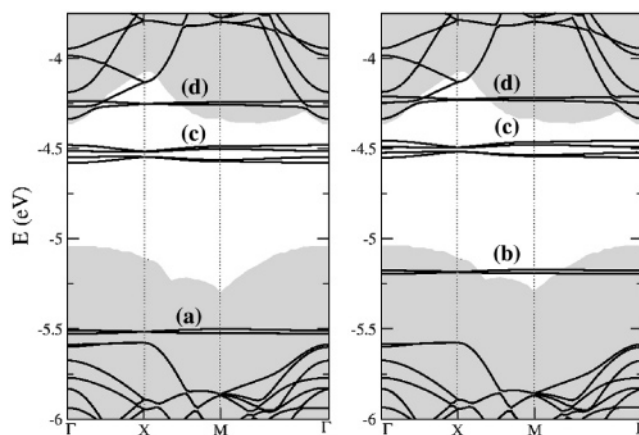


Figure 5. Band structure for the system $2(C_{59}Si)$ -Si(100):H. The left (right) panel presents the majority (minority) spin bands. The shaded regions are the projected bulk band structure whereas the lines are the slab band structure. The unit cell and the corresponding Brillouin zone are the same as shown in Figure 3. The a through d marked bands are discussed in the text (see Figure 6).

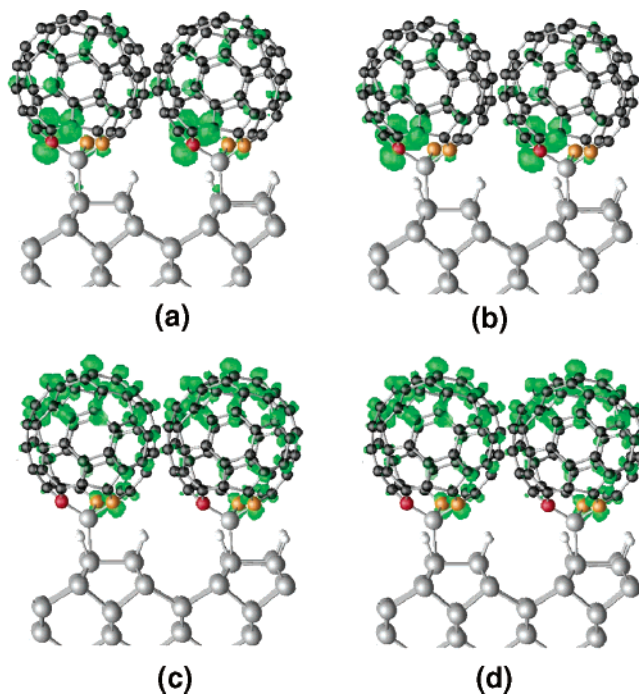


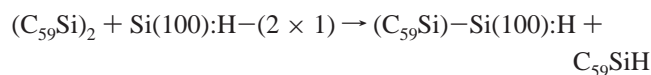
Figure 6. Charge density isosurfaces (0.001 e/bohr^3). Each isosurface from a through d corresponds to the bands marked in Figure 5, respectively. The gray spheres denote Si atoms, the small white spheres denote hydrogen atoms, and the black ones represent the C atoms. The orange and red spheres represent the C atoms that are nearest neighbors to the Si in the $C_{59}Si$ molecules.

magnetization). The energy difference between these two configurations was on the order of 0.01 eV (higher spin lower in energy). Even though this number would indicate a tendency for a ferromagnetic coupling, the result is within our accuracy limit and should, thus, be taken with caution.

The main difference between the bands in Figures 3 and 5 is an increase in the dispersion of the fullerene-related bands, which is now around 0.1 eV. For the solid of C_{60} we obtain a dispersion for the HOMO- and LUMO-derived bands on the order of 0.3 eV. As in this solid each molecule has 12 first nearest neighbors, as compared to 4 in the present case, these numbers are consistent with a picture where the fullerenes are interacting with each in the higher coverage regime. As the experimental value for the band dispersion in bulk C_{60} is around

0.5 eV (our smaller value is related to a larger lattice parameter⁶⁷ due to the GGA), we thus expect for this system a dispersion more on the order of 0.2 eV.

Finally, let us discuss some possibilities to experimentally obtain the systems describe here. It is clear that to have the C₅₉Si molecule bonded through its Si atom to a surface Si atom, there is the need to generate Si dangling bonds by hydrogen desorption. One possible way of to obtain this system experimentally^{57,58} would be via a STM tip. Another way, however, would be through an appropriate surface reaction. We here propose the use of the (C₅₉Si)₂ molecule. Even though this molecule has not been experimentally described yet, we have studied⁶⁹ its properties and have predicted that it has a binding energy of 1.63 eV with respect to dissociation as two isolated C₅₉Si molecules. This molecule could be a convenient way to bring the C₅₉Si into contact with the Si(100) surface. We look into a possible scenario where the (C₅₉Si)₂ would collide with the surface and react in such a way that one C₅₉Si would end up bound to the surface and the other would fly away as a C₅₉-SiH. Schematically, this reaction is described as



We obtain that this reaction is exothermic by approximately 0.2 eV, suggesting that this might be a viable process.

IV. Conclusions

In summary, we have studied the adsorption of substitutionally doped fullerenes C₅₉Si onto a monohydride Si(100) surface. We find that these molecules are adsorbed with the formation of strong C₅₉Si-Si_{surface} bonds, which is a possible way to obtain a very stable layer of fullerenes on a Si surface. This is similar to what has been experimentally obtained via the azafullerene, C₅₉N, molecule.⁷⁰ Assuming that this adsorption process has been successfully realized, many possibilities can be envisaged, such as functionalization of the adsorbed fullerenes,⁷¹ electron doping of the fullerene monolayer,⁷² or even their use in quantum computing^{73,74} or transport through a magnetic molecule,⁷⁶ if endohedral N-doping is considered. Moreover, all these studies can be investigated either as a function of coverage or as a function of doping (or both).

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References and Notes

- (1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.
- (2) Kimura, T.; Sugai, T.; Shinohara, H. *Chem. Phys. Lett.* **1996**, *256*, 269.
- (3) Fye, J. L.; Jarrold, M. J. *Phys. Chem. A* **1997**, *101*, 1836.
- (4) Pellarin, M.; Ray, C.; Mélinon, P.; Lermé, J.; Vialle, J. L.; Kéghélian, P.; Perez, A.; Broyer, M. *Chem. Phys. Lett.* **1997**, *277*, 96.
- (5) Ray, C.; Pellarin, M.; Lermé, J.; Vialle, J. L.; Broyer, M.; Blase, X.; Mélinon, P.; Kéghélian, P.; Perez, A. *Phys. Rev. Lett.* **1998**, *80*, 5365.
- (6) Pellarin, M.; Ray, C.; Lermé, J.; Vialle, J. L.; Broyer, M.; Blase, X.; Kéghélian, P.; Mélinon, P.; Perez, A. *J. Chem. Phys.* **1999**, *110*, 6927.
- (7) Pellarin, M.; Ray, C.; Lermé, J.; Vialle, J. L.; Broyer, M.; Blase, X.; Kéghélian, P.; Mélinon, P.; Perez, A. *Eur. Phys. J. D* **1999**, *9*, 49.
- (8) Billas, I. M. L.; Tast, F.; Branz, W.; Malinowski, N.; Heinebrodt, M.; Martin, T. P.; Boero, M.; Massobrio, C.; Parrinello, M. *Eur. Phys. J. D* **1999**, *9*, 337.
- (9) Billas, I. M. L.; Massobrio, C.; Boero, M.; Parrinello, M.; Branz, W.; Tast, F.; Malinowski, N.; Heinebrodt, M.; Martin, T. P. *J. Chem. Phys.* **1999**, *111*, 6787.
- (10) Guirado-Lopez, R. *Phys. Rev. B* **2002**, *65*, 165421.
- (11) Fu, C.-C.; Weissmann, M.; Machado, M.; Ordejón, P. *Phys. Rev. B* **2001**, *63*, 085411.
- (12) Fu, C.-C.; Fava, J.; Weht, R.; Weissmann, M. *Phys. Rev. B* **2002**, *66*, 045405.
- (13) Marcos, P. A.; Alonso, J. A.; Molina, L. M.; Rubio, A.; López, M. J. *J. Chem. Phys.* **2003**, *119*, 1127.
- (14) Marcos, P. A.; Alonso, J. A.; López, M. J. *J. Chem. Phys.* **2005**, *123*, 204323.
- (15) Simeon, T. M.; Yanov, I.; Leszczynski, J. *Int. J. Quantum Chem.* **2005**, *105*, 429.
- (16) Baierle, R. J.; Fagan, S. B.; Mota, R.; da Silva, A. J. R.; Fazzio, A. *Phys. Rev. B* **2001**, *64*, 085413.
- (17) Fagan, S. B.; Mota, R.; da Silva, A. J. R.; Fazzio, A. *Nano Lett.* **2004**, *4*, 975.
- (18) Fagan, S. B.; da Silva, A. J. R.; Mota, R.; Baierle, R. J.; Fazzio, A. *Phys. Rev. B* **2003**, *67*, 033405.
- (19) Fagan, S. B.; Mota, R.; Baierle, R. J.; da Silva, A. J. R.; Fazzio, A. *Mater. Charact.* **2003**, *50*, 183.
- (20) Fagan, S. B.; Mota, R.; Baierle, R. J.; da Silva, A. J. R.; Fazzio, A. *Diamond Relat. Mater.* **2003**, *12*, 861.
- (21) *Introducing Molecular Electronics*; Cuniberti, G.; Fagas, G.; Richter, K. Eds.; Springer: Berlin, 2005.
- (22) *Molecular Nanoelectronics*; Reed, M. A.; Lee, T., Eds.; American Scientific Publishers: Stevenson Ranch, CA, 2003.
- (23) Nitzan, A.; Ratner, M. A. *Science* **2003**, *300*, 1384–1389.
- (24) Joachim, C.; Ratner, M. A. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 8801–8808.
- (25) Park, H.; Park, J.; Lim, A. K. L.; Anderson, E. H.; Alivisatos, A. P.; McEuen, P. L. *Nature* **2000**, *407*, 57.
- (26) Palacio, J. J.; Pérez-Jiménez, A. J.; Louis, E.; Vergés, J. A. *Phys. Rev. B* **2001**, *64*, 115411.
- (27) Taylor, J.; Guo, H.; Wang, J. *Phys. Rev. B* **2001**, *63*, 121104.
- (28) Stadler, R.; Ami, S.; Forshaw, M.; Joachim, C. *Nanotechnology* **2001**, *12*, 350.
- (29) Yu, L. H.; Natelson, D. *Nano Lett.* **2004**, *4*, 79.
- (30) Pasupathy, A. N.; Park, J.; Chang, C.; Soldatov, A. V.; Lebedkin, S.; Bialczak, R. C.; Grose, J. E.; Donev, L. A. K.; Sethna, J. P.; Ralph, D. C.; McEuen, P. L. *Nano Lett.* **2005**, *5*, 203.
- (31) Wolkow, R. A. *Annu. Rev. Phys. Chem.* **1999**, *50*, 413.
- (32) Hersam, M. C.; Guisinger, N. P.; Lyding, J. W. *Nanotechnology* **2000**, *11*, 70.
- (33) Bent, S. F. *Surf. Sci.* **2002**, *500*, 879.
- (34) Buriak, J. M. *Chem. Rev.* **2002**, *102*, 1271.
- (35) Filler, M. A.; Bent, S. F. *Prog. Surf. Sci.* **2003**, *73*, 1.
- (36) Guisinger, N. P.; Greene, M. E.; Basu, R.; Baluch, A. S.; Hersam, M. C. *Nano Lett.* **2004**, *4*, 22.
- (37) Rakshit, T.; Liang, G.-C.; Ghosh, A. W.; Datta, S. *Nano Lett.* **2004**, *4*, 1803.
- (38) Guisinger, N. P.; Yoder, N. L.; Hersam, M. C. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 8838.
- (39) Moriarty, P.; Upward, M. D.; Dunn, A. W.; Ma, Y.-R.; Beton, P. H.; Teehan, D. *Phys. Rev. B* **1998**, *57*, 362.
- (40) Suto, S.; Sakamoto, K.; Kondo, D.; Wakita, T.; Kimura, A.; Kakizaki, A.; Hu, C.-W.; Kasuya, A. *Surf. Sci.* **1999**, *438*, 242.
- (41) De Seta, M.; Sanvito, D.; Evangelisti, F. *Phys. Rev. B* **1999**, *59*, 9878.
- (42) Feng, W.; Miller, B. *Langmuir* **1999**, *15*, 3152.
- (43) Dunn, A. W.; Svensson, E. D.; Dekker, C. *Surf. Sci.* **2002**, *498*, 237.
- (44) Kageshima, M.; Ogiso, H.; Tokumoto, H. *Surf. Sci.* **2002**, *517*, L557.
- (45) Godwin, P. D.; Kenny, S. D.; Smith, R. *Surf. Sci.* **2003**, *529*, 237.
- (46) Hobbs, C.; Kantorovich, L. *Nanotechnology* **2004**, *15*, S1.
- (47) Keeling, D. L.; Humphry, M. J.; Fawcett, R. H.; Beton, P. H.; Hobbs, C.; Kantorovich, L. *Phys. Rev. Lett.* **2005**, *94*, 146104.
- (48) Liang, G.-C.; Ghosh, A. W. *Phys. Rev. Lett.* **2005**, *95*, 076403.
- (49) Cheng, C.-P.; Pi, T.-W.; Ouyang, C.-P.; Wen, J.-F. *J. Vac. Sci. Technol., B* **2005**, *23*, 1018.
- (50) Hobbs, C.; Kantorovich, L.; Gale, J. D. *Surf. Sci.* **2005**, *591*, 45.
- (51) Godwin, P. D.; Kenny, S. D.; Smith, R.; Belbruno, J. *Surf. Sci.* **2001**, *490*, 409.
- (52) Butcher, M. J.; Nolan, J. W.; Hunt, M. R. C.; Beton, P. H.; Dunsch, L.; Kuran, P.; Georgi, P.; Dennis, T. J. S. *Phys. Rev. B* **2003**, *67*, 125413.
- (53) Schmidt, J.; Hunt, M. R. C.; Miao, P.; Palmer, R. E. *Phys. Rev. B* **1997**, *56*, 9918.
- (54) Sanvito, D.; De Seta, M.; Evangelisti, F. *Surf. Sci.* **2000**, *452*, 191.
- (55) Oura, K.; Lifshits, V. G.; Saranin, A. A.; Zotov, A. V.; Katayama, M. *Surf. Sci. Rep.* **1999**, *35*, 1.
- (56) Hersam, M. C.; Guisinger, N. P.; Lyding, J. W.; Thompson, D. S.; Moore, J. S. *Appl. Phys. Lett.* **2001**, *78*, 886.
- (57) Abeln, G. C.; Hersam, M. C.; Thompson, D. S.; Hwang, S.-T.; Choi, H.; Moore, J. S.; Lyding, J. W. *J. Vac. Sci. Technol., B* **1998**, *16*, 3874.

- (58) Lopinski, G. P.; Wayner, D. D. M.; Wolkow, R. A. *Nature* **2000**, 406, 48.
- (59) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, 136, B864.
- (60) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, 140, A1133.
- (61) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, 77, 3865.
- (62) Troullier, N.; Martins, J. L. *Phys. Rev. B* **1991**, 43, 1993.
- (63) Artacho, E.; Sánchez-Portal, D.; Ordejón, P.; García, A.; Soler, J. M. *Phys. Status Solidi B* **1999**, 215, 809 and references therein.
- (64) Soler, J. M.; Artacho, E.; Gale, J. D.; García, A.; Junquera, J.; Ordejón, P.; Sánchez-Portal, D. *J. Phys.: Condens. Matter* **2002**, 14, 2745.
- (65) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, 19, 553.
- (66) Zanella, I.; Fazzio, A.; da Silva, A. J. R. *Int. J. Quantum Chem.* **2005**, 103, 557.
- (67) It is well-known that the GGA approximation for systems such as graphite, fullerenes and carbon nanotubes tends to give too large a distance between the component units. In our case, the smallest distance between carbon atoms in adjacent C₆₀ molecules in a bulk solid is 3.4 Å, which should be compared to the experimental value of approximately 3.0 Å. We used a face-centered cubic (FCC) solid with one C₆₀ molecule per unit cell. For this system we obtained a cohesive energy of 0.18 eV. This is almost smaller by a factor of 10 when compared to the experimental cohesive energy⁶⁸ of approximately 1.7 eV. This is caused by both the larger fullerene–fullerene distance and a deficiency of the GGA to properly describe the nature of the intermolecular interaction. This error, however, does not alter our main conclusions such as the order of magnitude of the binding energies and level structure, which do not depend sensitively on the interaction between C₅₉Si molecules. However, the dispersion of the bands a–d in Figure 5 will be underestimated as well as the energy gain related to the higher coverage regime.
- (68) Pan, C.; Sampson, P.; Chai, Y.; Hauge, R. H.; Margrave, J. L. *J. Phys. Chem.* **1991**, 95, 2944.
- (69) Zanella, I.; da Silva, A. J. R. *Chem. Phys. Lett.* submitted for publication.
- (70) Butcher, M. J.; Jones, F. H.; Beton, P. H.; Moriarty, P.; Cotier, B. N.; Upward, M. D.; Prassides, K.; Kordatos, K.; Tagmatarchis, N.; Wudl, F.; Dhanak, V.; Johal, T. K.; Crotti, C.; Comicioli, C.; Ottaviani, C. *Phys. Rev. Lett.* **1999**, 83, 3478.
- (71) Upward, M. D.; Moriarty, P.; Beton, P. H.; Birkett, P. R.; Kroto, H. W.; Walton, D. R. M.; Taylor, R. *Surf. Sci.* **1998**, 405, L526.
- (72) Yang, W. L.; Brouet, V.; Zhou, X. J.; Choi, H. J.; Louie, S. G.; Cohen, M. L.; Kellar, A.; Bogdanov, P. V.; Lanzara, A.; Goldoni, A.; Parmigiani, F.; Hussain, Z.; Shen, Z.-X. *Science* **2003**, 300, 303.
- (73) Harneit, W. *Phys. Rev. A* **2002**, 65, 032322.
- (74) Mehring, M.; Scherer, W.; Weidinger, A. *Phys. Rev. Lett.* **2004**, 93, 206603.
- (75) Elste, F.; Timm, C. *Phys. Rev. Lett.* **2005**, 71, 155403.