

## Self-assembly of molecular wires on H-terminated Si(100) surfaces driven by London dispersion forces

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First-principles calculations combined with kinetic Monte Carlo simulations are carried out to unambiguously demonstrate the vital role of van der Waals (vdW) interactions in the self-assembly of styrene nanowires on H-terminated Si(100) surfaces. We find that, only with the inclusion of London dispersion forces, accounting for the attractive parts of vdW interactions, are the *effective* intermolecular interactions reversed from repulsive to attractive. Such attractive interactions, in turn, ensure the preferred growth of long wires under physically realistic conditions as observed experimentally. We further propose a cooperative scheme, invoking the application of an electric field and the selective creation of Si dangling bonds, to drastically improve the ordered arrangement of the molecular nanowires. The present paper represents a significant step forward in the fundamental understanding and precise control of molecular self-assembly guided by London dispersion forces.

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As a candidate route for future industrial fabrication techniques, especially for the construction of molecular circuitry, molecular self-assembly<sup>1-3</sup> has been the focus of much fundamental research over the past decades. It is a “bottom-up” approach to materials fabrication in which ordered structures are formed spontaneously as a result of delicate competition between molecule-surface and intermolecular interactions.<sup>4-8</sup> To better understand the microscopic formation mechanisms, it is essential to identify the underlying nature and strength of the interactions dictating the kinetic and dynamic processes involved in molecular self-assembly, so as to gain better control of the fabricated structures.

The growth of styrene nanowires on Si (Ref. 9) offers an ideal platform for elucidating the cooperative role of different molecular interactions controlling the assembly processes. In the experiment, styrene molecules were deposited onto a hydrogen-passivated, (2 × 1) reconstructed Si(100) (H-Si) surface; wires first nucleated at preexisting Si dangling bonds (DBs), then grew longer along the Si dimer rows. At the end of deposition, a large number of the isolated DBs were found to be still present on the surface, coexisting with the long styrene wires.<sup>9</sup> An intriguing chain reaction mechanism was proposed, in which a styrene molecule landing on the surface reacts with an isolated DB and abstracts a hydrogen atom from a neighboring surface site, thereby creating a new DB for the arrival of a second molecule. Such a chain reaction, characterized by local chemical bond formation and breakage, leads to the formation of longer molecular wires. Although many subsequent research efforts<sup>10-16</sup> have been performed for this system, certain crucial aspects remain controversial. For example, conventional density functional theory (DFT) calculations found a repulsive interaction between two chemisorbed styrene molecules on Si(100),<sup>10-12</sup> while hybrid calculations including van der Waals (vdW) effects indicated an attractive interaction.<sup>12,13</sup> Such findings strongly point to

the need for a more accurate description of the intermolecular forces, and revealing the potential role of the ubiquitous vdW forces.

In this Rapid Communication, we use DFT calculations combined with kinetic Monte Carlo (KMC) simulations to investigate the effect of the interstyrene interactions on the growth kinetics and morphological evolution of styrene molecules on the H-Si surfaces. The results unambiguously demonstrate the decisive role of nonlocal vdW interactions in molecular self-assembly. We find that, only with the inclusion of London dispersion forces, accounting for the attractive parts of vdW interactions, are the effective intermolecular interactions reversed from repulsive to attractive. Such attractive interactions, in turn, ensure the preferred growth of long wires as observed experimentally. We also carry out systematic studies of the dependence of wire growth under physically realistic conditions. Based on these results, we propose a scheme, invoking the application of an electric field ( $E$  field) and the selective creation of Si dangling bonds, to drastically improve the quality of the ordered molecular structures.

To accurately include the vdW effects, we use the recently developed first-principles vdW density functional (vdW-DF).<sup>17-20</sup> For comparison, the semilocal Perdew-Burke-Ernzerhof (PBE) functional<sup>21</sup> is also used. All the DFT calculations were carried out using the QUANTUM ESPRESSO (QE) simulation package.<sup>22</sup> The computed Si lattice constant is 5.47 Å, consistent with the experimental value of 5.43 Å. To model the substrate, a five-atom-layer slab containing 40 Si atoms and 20 Å of vacuum was used. Both sides of the slab were terminated with H atoms. During relaxation, the bottom Si layer was fixed and all other atoms were allowed to fully relax until the forces on each atom was less than 10<sup>-3</sup> Ry/bohr. A 1 × 2 × 1  $k$ -point mesh was used for the chemisorption configurations, and a single  $k$  point for the styrene dimer in a

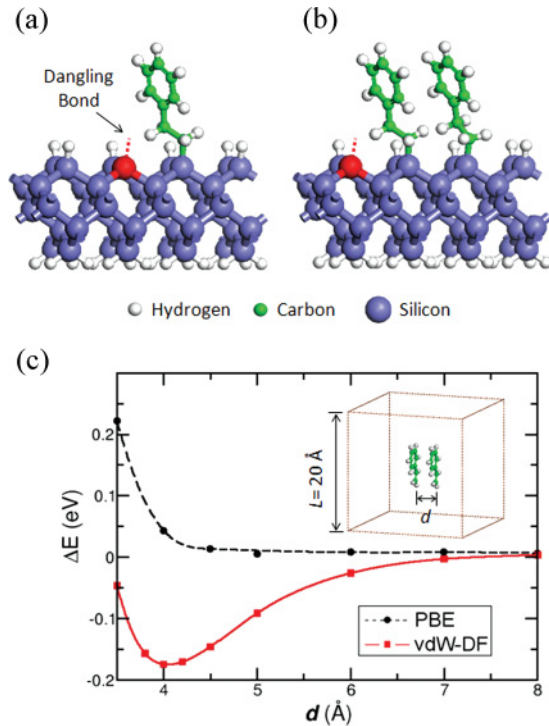


FIG. 1. (Color online) Post H-abstraction configurations of adsorbed styrene (a) monomer and (b) dimer, as obtained from fully relaxed vdW-DF calculations. The PBE calculations gave similar structures with deviations in atomic coordinates of less than 0.1 Å. (c) The interstyrene interaction energies ( $\Delta E$ ) as a function of the separation distance ( $d$ ) in vacuum.

(20 Å)<sup>3</sup> cubic supercell. The plane-wave energy cutoff for all the calculations was 30 Ry.

To simulate the initial stages of wire growth, we compute the adsorption energy for a styrene molecule binding to an isolated DB on the H-Si surface and abstracting a hydrogen atom from a neighboring surface site along the Si dimer row [see Fig. 1(a)]. We denote the energy gained during the initial surface bonding as  $E_{b1} = E_1 - E_{\text{sty}} - E_{\text{sub}}$  where  $E_{\text{sty}}$ ,  $E_{\text{sub}}$ , and  $E_1$  are the corresponding energies of a free styrene molecule, a H-Si substrate with a DB, and the configuration in Fig. 1(a), respectively. For PBE, we obtain  $E_{b1} = -1.04$  eV, while for vdW-DF we obtain  $E_{b1} = -1.03$  eV. The tiny difference in  $E_{b1}$  results from the fact that the styrene molecule is oriented with the benzene ring residing perpendicular to the surface, thereby minimizing any possible vdW interactions with the surface. Figure 1(b) represents the next step in the continued growth of a molecular wire. This configuration results from the adsorption of an additional styrene molecule and subsequent H abstraction at the newly created DB site. The additional energy gain is denoted as  $E_{b2} = E_2 - E_{\text{sty}} - E_1$ , where  $E_2$  is the corresponding energy of the configuration in Fig. 1(b). For PBE,  $E_{b2} = -0.94$  eV is weaker than  $E_{b1}$ . This implies that a styrene dimer is less stable than two isolated styrene monomers by 0.1 eV, hence the interaction between two styrene molecules is effectively repulsive, consistent with Refs. 10 and 11. In other words, a styrene molecule would prefer to remain isolated rather than adsorb at the end of a preexisting wire. In contrast, for vdW-DF,  $E_{b2} =$

$-1.18$  eV, i.e., the binding energy is now enhanced by 0.24 eV, relative to the PBE results. This increase in adsorption energy qualitatively changes the physical picture: A styrene dimer is now more stable than two isolated monomers by 0.15 eV, indicating an effectively attractive intermolecular interaction. As a result, wire growth is more favorable than isolated styrene molecules.

In order to determine the origin of the difference in  $E_{b2}$  obtained above for PBE and vdW-DF, we have calculated the interaction energy ( $\Delta E$ ) between two styrene molecules in vacuum as a function of the separation distance ( $d$ ). The results are contrasted in Fig. 1(c), showing that the styrene-styrene interaction is always repulsive within PBE, but becomes attractive within vdW-DF. In particular, the energy difference at  $d = 4$  Å (roughly the separation on the Si surface) is  $\sim 0.21$  eV, very close to the difference of 0.24 eV in the surface binding energies obtained above. This quantitative comparison strongly indicates that the attractive intermolecular interaction on the surface is indeed due to the dispersion forces.

So far we have established the attractive nature of the interstyrene interaction associated with the vdW force on Si(100), but whether its relatively weak magnitude could indeed play a decisive role under physically realistic nonequilibrium growth conditions remains an open question. This important issue is critically assessed next using kinetic Monte Carlo (KMC) simulations of the growth phenomena, with the relevant activation energies and corresponding rate coefficients calculated within vdW-DF (see Table I). The rates are calculated by  $r = r_0 \exp(-V/k_B T)$ , where  $r_0$ ,  $V$ ,  $k_B$ , and  $T$  are the attempt frequency ( $4.2 \times 10^{10} \text{ s}^{-1}$ ), activation energy, Boltzmann constant, and temperature, respectively. Figure 2 shows the results from the KMC simulations with the growth temperature  $T = 300$  K, deposition rate  $F = 10^{-3}$  monolayers (ML)/s, a styrene coverage of 4%, and a DB concentration of 2%. For simulations based on the PBE activation energies, nearly all the precreated isolated DBs are occupied with adsorbed styrene molecules, and the average length of the wires is only two styrene molecules [Fig. 2(a)]. This is simply a consequence of the intermolecular repulsion that favors isolated styrene molecules over wires. Furthermore, from Figs. 2(c) and 2(d) we see that the rate of wire growth is strongly linked to the fraction of available isolated DBs. In particular, styrene wires do not begin to grow until most of the isolated DB sites have been occupied. In contrast, for simulations based on vdW-DF activation energies, several long wires are formed, with an average length of five molecules. These long wires coexist with a reduced density of isolated

TABLE I.  $V_{\text{diff}}$ ,  $V_{\text{des}}$ ,  $V_{\text{rev1}}$ , and  $V_{\text{rev2}}$  denote the activation energies for a styrene molecule diffusing on the H-Si surface, desorbing to the gas phase, and desorbing to the surface from an isolated DB and a DB at the end of a wire, respectively (Ref. 23).  $V_{\text{diff}}$  and  $V_{\text{des}}$  were taken from Ref. 15;  $V_{\text{res1}}$  and  $V_{\text{res2}}$  were calculated by  $V_{\text{rev1(2)}} = |E_{b1(2)}| + V_{\text{diff}} - V_{\text{des}}$ . (The unit is in eV.)

	$V_{\text{diff}}$	$V_{\text{des}}$	$V_{\text{rev1}}$	$V_{\text{rev2}}$
PBE	0.05	0.34	0.75	0.65
vdW-DF	0.05	0.34	0.74	0.89

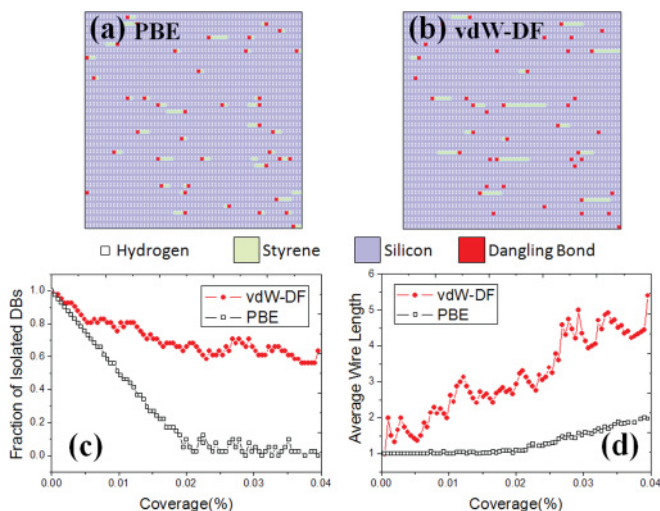


FIG. 2. (Color online) KMC simulations based on (a) PBE and (b) vdW-DF activation energies. The evolutions of (c) and (d) are the fraction of isolated DBs and the average length of the nanowires, respectively.

DBs [Fig. 2(b)]. Such a strong preference for long wires is consistent with experimental observations.<sup>9</sup> The defining feature is the net attractive interactions between the styrene molecules, promoting wire growth during the initial nucleation stages [Figs. 2(c) and 2(d)]. In other words, although the dispersion forces are relatively weak in magnitude compared with the total chemisorption energy, they critically influence the kinetic processes of the molecules and their self-assembly on the surfaces.

Next we examine the evolution of the wire growth at different temperatures. At the relatively low temperature of  $T = 250$  K, even with the inclusion of dispersion forces, fewer isolated DBs survive and the wires are shorter [Fig. 3(a)]. This is because once a styrene molecule is chemisorbed at a DB site it is unable to desorb at this low temperature; therefore, it cannot differentiate between an isolated DB site and a DB site next to an adsorbed styrene molecule. Upon increasing  $T$  to 350 K, the simulation results indicate that the isolated styrene molecules can more readily desorb from isolated DBs and are able to better sample the surface. This allows for a greater chance of finding the more favorable DB sites, i.e., sites with a lower desorption probability, giving rise to the preferred growth of longer styrene wires [Fig. 3(b)]. However, this enhanced lengthening of wires by the growth temperature is not monotonous. At  $T = 400$  K, only a low equilibrium coverage of molecules can be established, due to more frequent molecular desorption from the surface [Fig. 3(c)]. In this case, the barriers to desorb from both isolated DBs and DBs adjacent to styrene molecules are easily overcome; therefore, very few wires are formed, and those that do form are short and unstable, shrinking and evaporating in a relatively short period of time, again very similar to experimental observations.<sup>16</sup> Similar observations were also obtained by varying the deposition rate ( $F$ ) alone, with the high  $F$  results corresponding to the low  $T$  cases.

Although long molecular wires can be grown on the surfaces, as is evident from experiment and our simulations, the

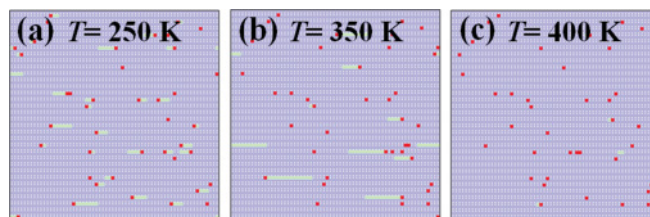


FIG. 3. (Color online) Growth patterns obtained at the constant deposition rate  $F = 10^{-3}$  ML/s and growth temperatures of (a) 250, (b) 350, and (c) 400 K.

ordering of these wires is far from ideal. This is especially true when considering potential applications where the ability to deposit highly ordered patterns is crucial for device operation. One major obstacle is the lack of control with regard to a predefined wire growth direction. Once a styrene molecule has been adsorbed at an isolated DB, it can abstract a hydrogen atom from either side along the Si dimer row direction, translating into an ambiguity in the wire growth direction. This ambiguity is, again, clearly visible in both experiment and our simulations.

To overcome this obstacle, we propose taking advantage of the polar nature of the styrene molecules through the application of an external  $E$  field parallel to the Si surface. When the first molecule is adsorbed at an isolated DB site, it tilts toward the surface before H abstraction [Fig. 4(a)] with the tilt angle either to the left or right along the dimer row. It is natural to expect that the tilt direction will be correlated with the side on which a H is abstracted and by extrapolation the direction along which the wire would grow. Therefore, by applying an external field that couples to the dipole moment of the molecules, it should be possible to collectively orient them all toward a preferred direction. We have computed the total dipole moment of an adsorbed styrene molecule parallel to the surface to be 0.58 D. Therefore, the application of an  $E$  field of  $0.5$  V/Å would result in an energy difference of 0.06 eV between the two tilt directions. Correspondingly, the wires would be  $\sim 10$  times more likely to head for the designated direction at room temperature.

To explore quantitatively the effect of the external field, we have further simulated the growth of wires from DBs arranged in ordered lines of varying densities as shown in Figs. 4(b)–4(e). In Fig. 4(b), we see that, as before, without the

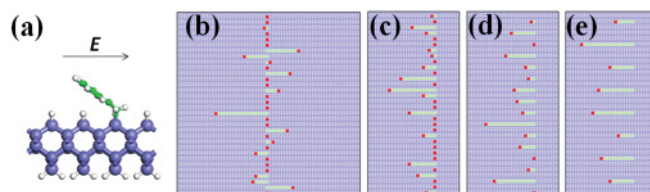


FIG. 4. (Color online) (a) Optimized configuration of the first chemisorbed styrene molecule before H abstraction. The arrow denotes the direction of the external  $E$  field. (b) Growth pattern in the absence of an external  $E$  field. (c)–(e) Growth patterns under the influence of an  $E$  field starting from 32, 16, and 8 DBs, respectively. All simulations were performed at  $T = 300$  K and  $F = 10^{-3}$  ML/s.

application of an external  $E$  field the wires show no preference to a particular growth direction. In contrast, the selective creation of DBs, mimicking the effect of an  $E$  field, leads to a dramatic improvement in the ordering and uniformity of the wires [Figs. 4(c)–4(e)]. Recently, an experimental work<sup>24</sup> has achieved directed growth of 3-trifluoromethyl styrene wires perpendicular to the Si dimer rows with the application of an  $E$  field. The molecule used in this experiment possesses a much larger dipole moment (over 3 D) than styrene; therefore, the magnitude of the  $E$  field applied in the experiment is much weaker than that in our present model study. In addition, we note that the directed growth is perpendicular to the Si dimer rows, which is expected to encounter a higher-energy barrier for H abstraction than that along the dimer rows. Despite all these differences, on a principle level, the experimental success<sup>24</sup> offers supporting evidence on the practicability and generality of the proposal presented in this study to control the direction in molecular self-assembly with the application of an external  $E$  field.

Before closing, we note that, as mentioned earlier, the attractive nature of the interstyrene interactions on Si(100) has also been revealed using second-order Møller-Plesset (MP2) theory.<sup>12</sup> Although we have not used other implementations of vdW interactions, such as the dispersion corrected DFT schemes of Grimme<sup>25</sup> (DFT-D) and Tkatchenko and Scheffler<sup>26</sup> (DFT-TS) to carry out a comparative study of the same styrene systems on Si(100), we can gain a helpful estimate on the relative differences using another widely studied system, a benzene dimer. This benchmark system has been widely studied within the schemes of vdW-DF,<sup>27</sup> MP2,<sup>28</sup> DFT-D,<sup>25</sup> and vdW-TS,<sup>29</sup> and the results show that the intermolecular attractions are all of the order of 0.1 eV. We therefore expect that the decisive role of the vdW effects as exploited in our

combined vdW-DF and KMC studies is a generic property of the systems. In particular, the small quantitative differences between the different schemes will not alter the central findings of the present paper.

In summary, we have revealed the crucial role of London dispersion forces on the self-assembly of styrene wires on the H-Si(100) surfaces. If the dispersion forces are neglected, such as in conventional DFT calculations using the PBE functional, the effective interstyrene interactions are repulsive, which is clearly in disagreement with experimental observations. In contrast, with the inclusion of London dispersion forces, as described by the vdW-DF formalism, the effective intermolecular interaction is reversed to be attractive in nature, thereby promoting the preferred growth of long wires under physically realistic conditions. Furthermore, we have proposed a cooperative scheme, invoking the application of an external  $E$  field and the selective creation of DBs, to substantially improve the ordering of molecular patterns. The present paper not only uncovers the underlying intermolecular forces driving molecular self-assembly at silicon surfaces, but also points to directions for achieving major advances in manipulating molecular patterns for different functionalities.

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- <sup>23</sup>Due to the large energy gain associated with chemical adsorption, we have neglected the surface diffusion anisotropy of a styrene molecule and the extra activation energy of a diffusing molecule from a H site to a DB site. We have also neglected the activation energy for H abstraction and the energy difference for the configurations before and after H abstraction, and our test simulations indicate that such approximations do not affect the central physical picture explored in this paper.
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