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Conduction Pathway of π-Stacked Ethylbenzene Molecular Wires on Si(100)

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Abstract: One of the most important challenges of molecular electronics is to enable systematic fabrication of molecular functional components on well-characterized solid-state substrates in a controlled manner. Recently, experimental techniques were developed to achieve such fabrication where lines of π-stacked ethylbenzene molecules are induced to self-assemble on an H-terminated Si(100) surface at precise locations and along precise directions. In this work, we theoretically analyze charge transport properties of these ethylbenzene wires using a state-of-the-art first-principles technique where density functional theory (DFT) is used within the nonequilibrium Green's function formalism (NEGF). Our device model consists of ethylbenzene stacks bonded to an H-terminated Si(100) surface and bridging two metal leads. The electron transmission spectrum and its associated scattering states as well as the resistance of the molecular wire are determined by the self-consistent NEGF-DFT formalism. The transmission spectrum has a resonance nature for energies around the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the ethylbenzene wires. However, near the Fermi level of the device, which sits inside the HOMO−LUMO gap, the Si substrate is found to play an important role in providing additional pathways for conduction. It has emerged that, within our model system, the transmission peak nearest to the Fermi level corresponds to transport through the Si substrate and not the π-stacked molecular line. The low-bias resistance R is found to increase exponentially with the length of the molecular line n, as $R \sim e^{\beta n}$, indicating a tunneling behavior in conduction. We further found that the exponential scaling has two regimes characterized by two different scaling parameters β: a high value for conduction through the molecular stack in short lines and a lower value for conduction through the substrate in longer lines. Our results suggest that when the conduction of molecular wires bonded to semiconductor substrates is theoretically analyzed, conduction pathways through the substrate need to be taken into account.

1. Introduction

Molecular wires have attracted great attention in chemistry, physics, electrical engineering, and materials science, as they provide an electric conduction pathway at the ultimate size limit.[1] So far, experimental investigations of molecular wires have benefited from scanning probe techniques such as the scanning tunneling microscope (STM). In typical experimental studies, a self-assembled molecular film on a metal surface is approached by a STM tip, forming a metal−molecule−tip geometry for which the tunneling current is measured. Many such measurements[2−10] on molecules such as alkanethiols revealed that electron transport is characterized by an exponential increase of resistance R:

$$R = R_0 e^{\beta n} \tag{1}$$

where n measures the length of the molecule and β is a characteristic inverse length scale. For alkanethiol molecules, the coefficient R_0 is typically in the range of megaohms or more, and $\beta \approx 1$ per carbon atom.[3] Such an exponential increase of resistance is indicative of tunneling behavior, and ballistic electron transport has indeed been confirmed by the measured temperature-independent conductance.[11] The molecules in a metal−molecule−tip setup could be considered as *free-standing*

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if interactions between the molecules are negligible. From the practical point of view, however, any molecular circuitry will most likely involve semiconductor substrates as device support, and it is very important to study charge transport properties in metal−molecule−metal structures on top of semiconductor substrates. It is the purpose of this paper to report such an investigation.

In particular, we focus on the system considered in experiments by Lopinski et al.,[12] who discovered a self-directed chemical growth process in which an H-terminated 2 × 1 Si(100) surface is exposed to styrene molecules. A styrene molecule reacts with a dangling bond, thus chemisorbing onto the surface and abstracting an H atom from an adjacent dimer in the same row. It leaves another dangling bond on this adjacent dimer that can react with a second styrene molecule, which in turn abstracts another H atom from the next dimer, and this process continues, resulting in growth of lines of π-stacked ethylbenzene molecules bonded to the Si surface along the dimer row direction. Piva et al.[13] recently showed experimentally that electron tunneling from a STM tip through an ethylbenzene molecule and into the Si substrate could be regulated by changing the charge state of a nearby dangling bond, thereby demonstrating molecular field-effect control. Due to the $\pi-\pi$ overlap between adjacent molecules, it has been suggested that these ethylbenzene lines could also carry current *along* the molecular stack, that is, parallel to the Si surface such that the line would act as a molecular wire.

Since the ethylbenzene line growth mentioned above occurs on top of a Si substrate, it is not a free-standing molecular wire and therefore it is necessary to investigate effects of the Si atoms on the quantum transport properties of the line. Kirczenow et al.[14] reported such a study using an extended Hückel model where transmission coefficients were calculated at energies near the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the molecules. By comparison to transmission through the substrate, it was determined that, at energies around the HOMO and LUMO levels, conduction occurred mostly through the ethylbenzene molecules with a comparatively small contribution from the Si substrate. Similar calculations were performed by Rochefort et al.[15] using a tight binding model and by Geng et al.[16] using density functional theory (DFT), where a Si(100) surface served as a template for the attachment of the molecules but no Si atoms were included in their transport analysis. Geng et al.,[16] however, suggested that the molecular stack is *not* electronically separate from the substrate. Finally, Liu et al.[17] used DFT to calculate current−voltage ($I-V$) characteristics of stacked benzene molecules without Si. Their results showed that the $I-V$ curve was exponential at low bias, suggesting tunneling-like behavior.

While these theoretical investigations yielded a good deal of information about transport through π-stacked molecules, there remain several issues that need to be carefully addressed. These include how transport properties of the π-stacked rings at energies near the Fermi level of the device are influenced by the Si(100) substrate; origin of the transmission spectrum and assignment of transmission peaks to specific molecular orbitals (MOs); molecular length dependence of the resistance and whether eq 1 holds for this system; and, for theoretical interest, effect of the number of Si layers included in a transport analysis. These issues are best addressed by self-consistent first-principles methods where the molecular stack, metal contacts, and Si substrate are treated on an equal footing. In the rest of the paper we shall address these issues using a state-of-the-art technique by carrying out DFT self-consistent analysis within the Keldysh nonequilibrium Green's function (NEGF)[18,19] formalism. We found it is possible to have a conduction pathway entirely through the Si substrate and not the π-stacked molecular line. The low-bias resistance R is found to increase exponentially with the length n of the molecular line as in eq 1, but the exponential scaling has two regimes characterized by two different scaling parameters β: a high value of β for conduction through the molecular stack when the molecular line is short and a much lower value of β for conduction through the substrate for longer lines. Our results suggest that the Si substrate plays an important role for charge conduction in the π-stacked ethylbenzene molecular line; namely, for lines longer than a few molecules, the resistance scaling at the Fermi level can be dominated by the Si substrate. Therefore, in order to theoretically understand quantum transport through molecular wires fabricated on top of a semiconductor substrate, the role of the substrate needs to be included in the analysis.

The rest of the paper is organized as follows. Section 2 presents theoretical method and calculation details, Section 3 discusses results, and Section 4 provides a short summary.

2. Theoretical Method

The system we study consists of π-stacked aromatic rings bridging two Al leads in a two-probe transport structure, and the aromatic rings are bonded to a Si substrate via an alkyl chain. The length of the π-stack is determined by the number of molecules n. Figure 1a shows a system where $n = 4$. The different molecules in the stack as well as their associated Si atoms are shown in Figure 1b−h. These are (b) benzene rings, labeled as *n*benz; (c) ethylbenzene molecules, labeled as *n*eb; (d−g) ethylbenzene molecules on varying numbers, X, of Si layers, labeled as *n*eb*X*Si; and (h) two ethylbenzene molecules on four layers of Si with a gap separating them, labeled as *n*gap4Si, where n is the sum of two ethylbenzene molecules and the number of spaces in the gap. The reason to study structure *n*gap4Si will become apparent below. Similar structures as that of Figure 1 but containing $n = 1-8$ units were also studied [$n = 3-8$ for case h with the gap].

The geometry optimizations were carried out with the Gaussian program[20] on all of the above systems using the B3LYP[21,22] functional, guided by experimental STM images.[12] The geometry of a single benzene molecule was optimized with the 6-31G(d) basis and the structure was repeated at 3.84 Å for

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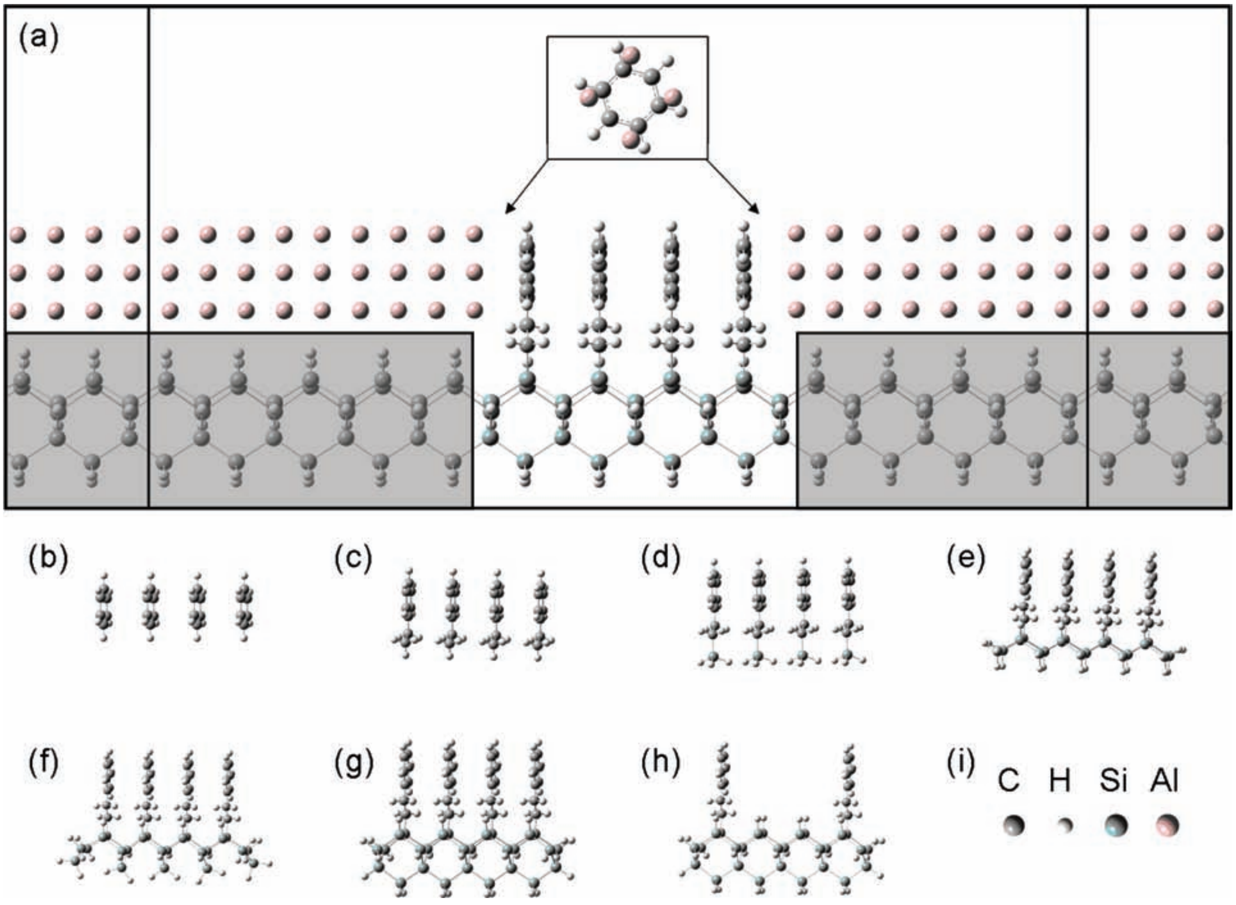

Figure 1. (a) Two-probe transport structure. Semi-infinite leads extending to ±∞ (left and right boxes) are bridged by the ethylbenzene line in the scattering region (center box). The atoms in the shaded region were excluded from calculations for simplicity, and dangling bonds were capped with H atoms. (Inset) Arrangement of the four lead atoms closest to the molecule from a view along the lead. (b−h) Subset ($n = 4$) of stacked ring structures: (b) benzene rings, labeled *n*benz; (c) ethylbenzene molecules, *n*eb; (d−g) ethylbenzene molecules on $X = 1$, 2, 3, and 4 layers of Si, labeled *n*eb*X*Si; (h) two ethylbenzene molecules with a gap separating them on four layers of Si (here n is the sum of two molecules plus the number of spaces in the gap), labeled *n*gap4Si. (i) Legend for the different atoms.

1−8 units, corresponding to the separation between dimers on the H-terminated Si(100) 2 × 1 reconstructed surface.[23] The ethylbenzene structure was optimized in the same manner by constraining the ethyl C atoms to the same plane as the ring C atoms. The ethylbenzene molecular structure was optimized with the same basis set on a 1-layer Si surface composed of two dimer rows with three dimers in each row. All dangling bonds on the Si atoms were capped with H atoms. The Si coordinates were frozen and the ethylbenzene molecule was constrained to be perpendicular to the surface. The structures containing 1−4 layers of Si were then built with this optimized ethylbenzene structure, which was frozen along with the first layer of Si dimer atoms while all other Si atoms and capping H atoms were allowed to relax with the B3LYP/3-21G method. The smaller basis set was used in this case because the bigger systems (i.e., 8eb4Si) were rather computationally intensive. However, comparison of the optimized structures with the 6-31G(d) and 3-21G bases yielded very similar results. The structures containing only two ethylbenzene molecules but a varying number of dimers in between (as shown in Figure 1h) were optimized in the same manner.

The optimized structures were used to bridge two Al(100) leads, as shown in Figure 1a. In this work, we model the leads as nanowires with 3 × 3 cross section. The ring-lead orientation was determined by representing each lead with its first plane of (four) atoms in their bulk positions and placing one benzene molecule between the two leads. The benzene molecule was allowed to relax in between the leads and the lead−lead separation was optimized with the Gaussian program. The lowest energy lead plane to ring plane distance was found to be 2.8 Å, and this optimized lead−ring orientation was used for all systems (inset of Figure 1a). The leads were then extended from these structures by simply placing Al atoms at their face-centered cubic (fcc) bulk positions. The general system for which transport calculations were performed consists of three parts: a left lead, a scattering region, and a right lead (see Figure 1a). The leads repeat to $z = \pm\infty$ while the scattering region contains the ethylbenzene line on the Si surface and a portion of each lead. In the transport analysis, we have excluded the atoms in the shaded region in Figure 1a to eliminate the possibility of direct transmission through the substrate and to reduce the prohibitively large NEGF-DFT computation required if these shaded regions were included. Dangling bonds were capped with H atoms. Because the purpose of this work is to understand whether the conduction pathway is through the molecular stack or through Si atoms, by excluding the shaded regions we therefore assumed that the leads are electrically insulated from the substrate and their only connection is to the aromatic rings.

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A recently developed quantum transport technique[18,19] that is based on the real-space, Keldysh nonequilibrium Green's function (NEGF) formalism combined self-consistently with density functional theory (DFT) was used to analyze the two-probe system. The basic idea of the real-space NEGF-DFT formalism is to calculate the Hamiltonian and electronic structure of the two-probe transport structure by DFT; determine the nonequilibrium statistical properties of the scattering region by NEGF; and deal with the transport boundary conditions by real-space numerical procedures. We refer interested readers to refs 18 and 19 for details of our NEGF-DFT implementation. Very briefly, we calculate the retarded Green's function at energy E by directly inverting the Hamiltonian matrix:[24]

$$G(E) = [(E + i\eta)S - H - \Sigma_1 - \Sigma_2]^{-1} \qquad (2)$$

where H and S are the Hamiltonian and overlap matrices for the scattering region as determined by DFT. η is a positive infinitesimal and $\Sigma_{1,2}$ are self-energies that account for the effect of the left and right leads on the scattering region. The self-energy is a complex quantity with its real part representing a shift of the energy levels and its imaginary part representing their broadening, which can be represented by the linewidth matrix:

$$\Gamma_{1,2} = i(\Sigma_{1,2} - \Sigma_{1,2}^{\dagger}) \qquad (3)$$

The self-energy is calculated within our NEGF-DFT formalism by an iterative technique.[25] From these quantities, the electronic density matrix can be obtained as

$$\rho = \frac{1}{2\pi}\int_{-\infty}^{\infty} [f(E,\mu_1)G\Gamma_1G^{\dagger} + f(E,\mu_2)G\Gamma_2G^{\dagger}]\, \mathrm{d}E \qquad (4)$$

where $\mu_{1,2}$ are the electrochemical potentials of the left and right electrodes and $f(E,\mu)$ is the Fermi−Dirac function that describes the population for a given energy and electrochemical potential. The density obtained from the above equation is used in a subsequent DFT iteration step and the cycle is repeated until self-consistency. The transmission function is then obtained from the Green's function as

$$T(E) = \mathrm{Tr}(\Gamma_1G\Gamma_2G^{\dagger}) \qquad (5)$$

which represents the probability that an electron with a given energy E transmits from one lead, through the scattering region, into the other lead. The electric current is obtained from the transmission coefficient,[26] and in the limit of zero temperature it is given by

$$I = \frac{2\mathrm{e}}{h}\int_{\mu_1}^{\mu_2} T(E)\, \mathrm{d}E = \frac{2\mathrm{e}}{h}\int_{\mu_1}^{\mu_2} \mathrm{Tr}(\Gamma_1G\Gamma_2G^{\dagger})\, \mathrm{d}E. \qquad (6)$$

In the NEGF-DFT calculations, we used norm-conserving pseudopotentials[27] to describe the atomic core, used double-ζ polarized numerical orbitals to expand all physical quantities, and the exchange−correlation was treated at the local density approximation level.[28]

3. Results and Discussion

3.1. Transmission Spectra and Scattering States. Figure 2 shows the calculated transmission spectra for six different systems having four π-stacked aromatic rings in the scattering region (see Figure 1). The energy axis is relative to the Fermi energy of the Al electrodes which was calculated to be $E_F = -3.9$ eV (shifted to $E_F = 0$ in the figure). The transmission spectrum is dominated by sharp peaks away from the Fermi level.[29] By calculating the scattering states associated with these peaks and projecting them onto the MOs, we have determined which MOs are responsible for each peak. The MO analysis includes all except the Al atoms in the scattering region, and the MOs that dominate each peak are assigned in the figure (see Figure 2 caption). Since the transmission close to the Fermi level is nearly zero, it is dominated by the tails from the transmission peaks. This analysis will yield insight into the nature of low bias conductance.

The transmission spectrum through four π-stacked benzene rings (4benz, no substrate) is shown in Figure 2a. There is a large band gap of approximately 4 eV separating a pair of occupied peaks (assigned to occupied MOs) from a pair of unoccupied peaks (assigned to unoccupied MOs), which compares well with the results of Kirczenow et al.[14] and Geng et al.,[16] who reported 4.1 eV for their calculated band gap. These peaks are all due to transmission through MOs on the rings, as expected since there is no substrate present. Note that the Fermi level is nearer to the unoccupied peak centered at 1.9 eV than to the occupied peak centered at −2.6 eV. Therefore, for this system and at low bias, transmission through unoccupied MOs would dominate transport. In previous work,[30] two of us showed that low-bias transmission through a benzenedithiol molecule bridging two metal leads occurred through the HOMO when it was bonded to Au leads and through the LUMO when it was bonded to Al leads. Therefore, the Fermi level alignment inside the HOMO−LUMO gap depends on the material details of both the molecules and the leads.

Figure 2b shows the transmission spectrum through four π-stacked ethylbenzene molecules (4eb). For the occupied peaks, hybridization of MOs on the ring with those of the ethyl tail causes the two peaks to split into four, which is clear from comparing the labels in Figure 2 panels a and b. The same is also true for the unoccupied peaks, but there also appears to be a new peak near 1.2 eV. In fact, this peak is also present in the pure benzene case (Figure 2a) where a tiny feature can be found at this energy. This feature is enhanced in Figure 2b due to the presence of the ethyl tail. As for Figure 2a, the unoccupied peaks are nearer to E_F than the occupied peaks so the former are expected to dominate transport at low bias.

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(28) In our numerical calculations, the LCAO basis sets had the following atomic radial cut-offs (in au): C 5.67, H 5.63, Si 3.01, and Al 7.10. For real space grids, at least 3 grid points for each au were used. One hundred k-points for sampling in the z-direction were used in generating the electronic structure of the leads. Since we used quasi-one-dimensional nanowires to model the leads, no k-sampling was necessary for the x- and y-directions.

(29) Note that although the peaks appear sharp in this wide energy range of −3 to +3 eV, their width at half-maximum varies from 0.04 to 0.1 eV. This is larger than the energy scale of room temperature, so including further Fermi level smearing by room temperature will not significantly change the transmission spectra.

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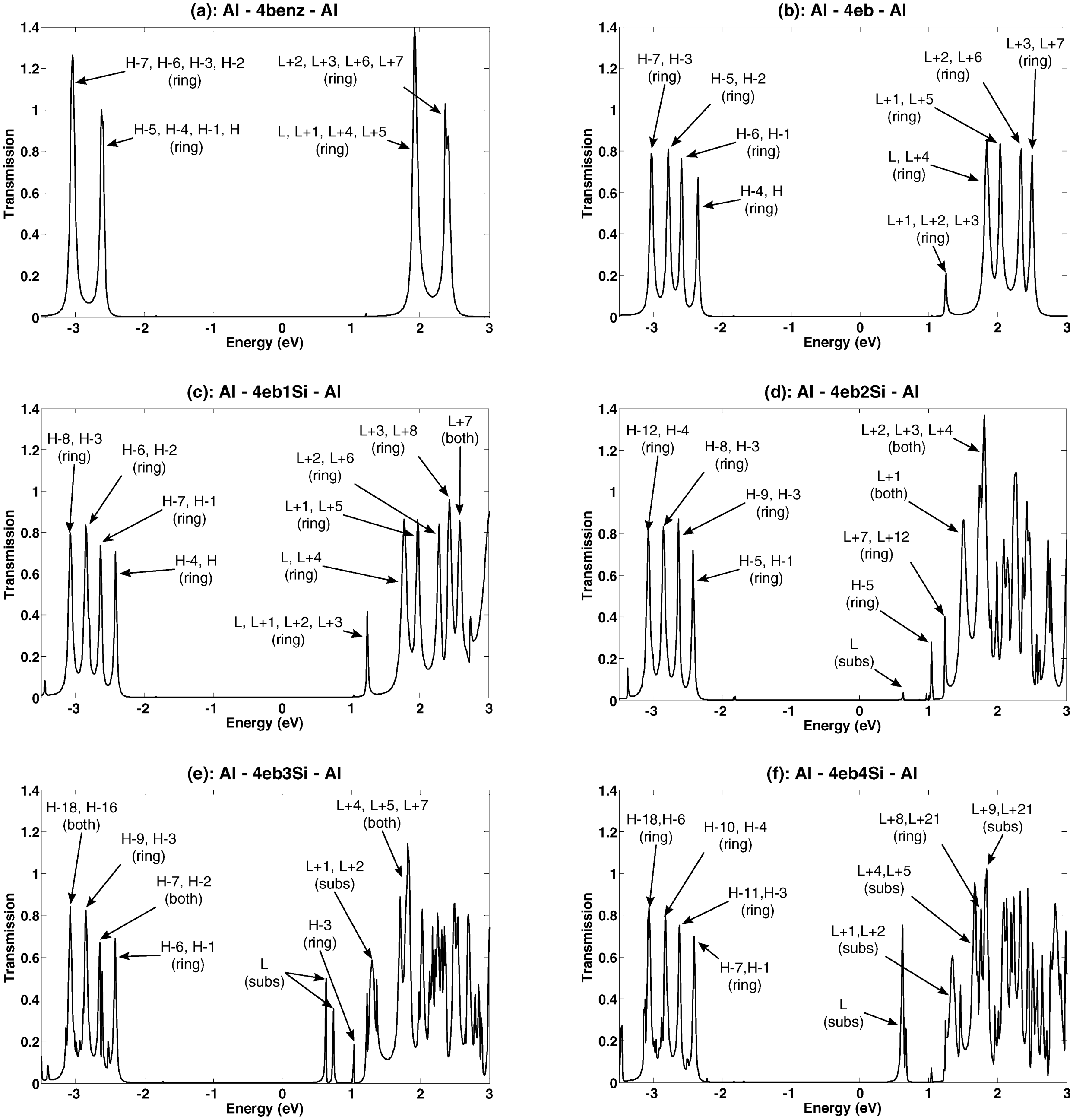

Figure 2. Transmission spectra for six sets of four π-stacked aromatic rings (structures shown in Figure 1b−g) inside the scattering region (Figure 1a). The peaks are assigned to the MOs of the subsystem (all atoms excluding Al) through which transmission is occurring at that energy. The occupied MOs are labeled as H for HOMO (highest occupied molecular orbital), H − 1 for HOMO − 1, and so on. Similarly, the unoccupied MOs are labeled as L for LUMO (lowest unoccupied molecular orbital), L + 1 for LUMO + 1 and so on. The labels also include whether the MO is localized over the π-stacked rings (ring), over the Si substrate (subs), or whether it is delocalized over both rings and substrate (both). The energy axis is relative to the Fermi level of the leads, which was calculated to be $E_F = -3.9$ eV.

We now investigate what happens when Si substrate layers are present. To do so, we systematically add Si layers beneath the ethylbenzene molecules. The transmission through four ethylbenzene molecules bonded to one layer of Si atoms (4eb1Si) is shown in Figure 2c. The occupied peaks are nearly identical in shape and position to those for the ethylbenzene system (Figure 2b). There is, however, a subtle difference in the labeling of the peaks: note that H − 5 is absent in Figure 2c. For the present system of ethylbenzene bonded to one layer of Si, H − 5 is a MO localized on the Si atoms and does not contribute to transmission, hence the lack of the H − 5 peak in the transmission spectrum. The occupied peaks correspond to the same MOs localized on the ethylbenzene molecules as in Figure 2b. The unoccupied peaks are similar to those for ethylbenzene with the exception that there is an additional peak labeled L + 7, which corresponds to transmission through a MO delocalized over both the rings and the Si atoms. There is no transmission entirely through the substrate since the Si atoms are not actually bonded together.

Figure 2d shows the transmission spectrum through four ethylbenzene molecules bonded to two layers of Si (4eb2Si). As above, the occupied peaks are similar to those of Figure 2 panels c and b. On the unoccupied side, there is substantial hybridization between the MOs of the ring and substrate as manifested in the L + 1/L + 2, L + 3, and L + 4 peaks that involve transmission through MOs delocalized over both the

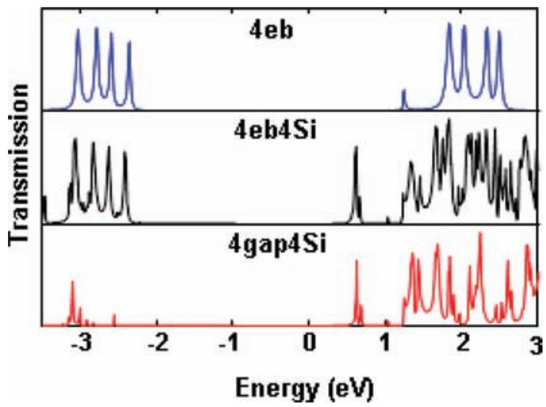

Figure 3. Transmission spectra of 4eb (structure in Figure 1c), 4eb4Si (Figure 1g), and 4gap4Si (Figure 1h). Note that for the 4gap4Si system, the two middle molecules are absent and the transmission pathway through the molecules is blocked by the vacuum gap. The peaks in the 4gap4Si curve are entirely due to transport through the Si substrate.

ring and Si atoms. There is also a tiny peak near 0.6 eV that is entirely due to transmission through a MO on Si. This conductance pathway now exists since the Si atoms are bonded together, providing a conduit for electron transport through the substrate.

Figure 2 panels e and f show the transmission through four ethylbenzene molecules on three layers of Si (4eb3Si) and four layers of Si (4eb4Si), respectively. As in Figure 2b−d, the occupied MOs are essentially the same and are entirely due to transport through MOs of the molecules. For these two systems, there are unoccupied transmission peaks due to transmission through the Si substrate, the molecular rings, and some through both. Note that the peak near 0.6 eV due to transmission through the substrate is substantially enhanced as more Si layers are included. This is reasonable since the cross section of the conduction pathway increases with additional Si layers. Results in Figure 2c−f strongly suggest the existence of hybridization between the ethylbenzene molecules and the Si atoms underneath, and this hybridization leads to a transport pathway entirely through the substrate.

To further confirm this interesting result, we have also considered a system where the middle two ethylbenzene molecules are removed, leaving a vacuum gap and thereby blocking the pathway through the stacked rings (structure in Figure 1h). Figure 3 plots the transmission spectrum for this system (referred to as 4gap4Si), together with the results for 4eb4Si and 4eb (i.e., Figure 2 panels f and b, respectively). It is clear that the peak for the 4eb4Si system at 0.6 eV remains essentially the same after removal of the two middle ethylbenzene molecules in 4gap4Si. The same is also true for many of the features in the range from 1.1 to 1.7 eV for which the Si substrate contributes to transmission. This is further evidence that transmission at these energies takes place through the substrate. Note that on the occupied side the reverse is true: the large transmission peaks match very well for 4eb4Si and 4eb while the transmission through 4gap4Si is comparatively small. This confirms that these peaks correspond to transmission through the molecules. Note that Kirczenow et al.[14] also found a small amount of transmission through the substrate but at energies near the occupied peaks instead of the unoccupied peaks. Their calculation was only done at energies near the HOMO and LUMO energies of the π-stacked molecules. Perhaps their model would have also demonstrated substantial conductance through the substrate if transmission in between these HOMO and LUMO energies was calculated.

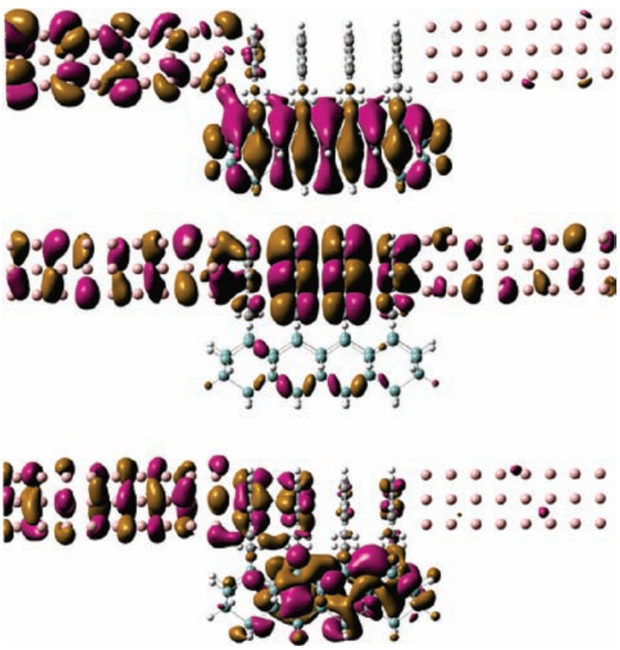

Figure 4. Norm of the scattering state wave functions for the 4eb4Si system corresponding to three different peaks in the transmission spectrum of Figure 2f. (Top) Scattering state corresponding to the peak at 0.6 eV showing transmission entirely through the substrate; (middle) scattering state showing transmission through the benzene rings corresponding to the peak at −2.4 eV; (bottom) scattering state showing transmission through both the substrate and the benzene rings corresponding to the peak at 1.8 eV.

The norm of the scattering state wave functions for different transmission peaks through 4eb4Si (structure in Figure 2f) are plotted in Figure 4. They nicely show three different modes of transmission through the system. These include transmission through the substrate at 0.6 eV (top), transmission through the rings at −2.4 eV (middle), and transmission through both the substrate and the rings at 1.8 eV (bottom).

These results demonstrate that the substrate to which a molecular line is attached can play an important role not only as a structural support but also as a transmission pathway. In particular, for the π-stacked ethylbenzene line on Si(100) in our model, the transmission peak nearest to E_F corresponds to transmission entirely through the substrate. This suggests that a substantial fraction of current flows through the Si substrate. For molecular electronics it is important to understand, control, and even possibly exploit this phenomenon. As stated above, selecting electrodes such that their Fermi level is closer to the HOMO of the molecules may reduce conduction through the substrate. Just as low work function electrodes are recognized as necessary for efficient electron injection into organic light-emitting diodes, suitably matched electrode material will be required to efficiently and selectively inject into silicon surface-bound multimolecular units. To the extent that such ideal leads are approached, molecular specific transport will be achieved and transport in that realm will exhibit good conductance.

Another approach to reduce conduction through the substrate may be to use alkylbenzene molecules with longer alkane tails, as was also suggested by Rochefort and Beausoleil.[31] In fact, allyl benzene (3 C atoms in the tail) lines have been successfully

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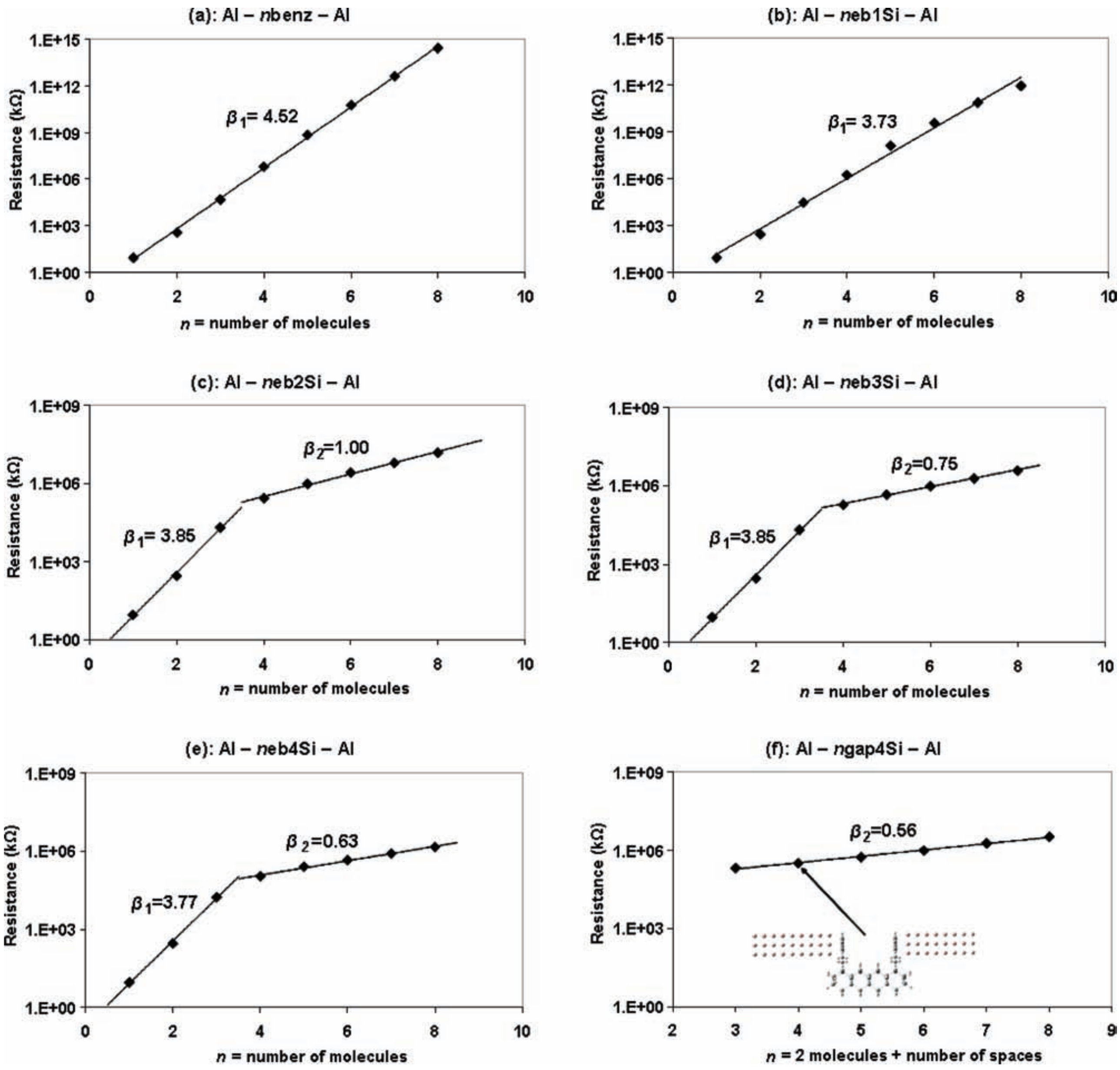

Figure 5. Semilogarithmic plots of zero-bias resistance for the systems shown in Figure 1b,d−h as a function of the number of molecular units. Straight lines are exponential fits ($R \sim e^{\beta n}$) to the calculated data (◆) and their slopes give the scaling parameter β. Note that in several cases there are two regimes with different slopes. The higher slope corresponds to transmission through the rings and the lower slope corresponds to transmission through the substrate (see also β values in Table 1).

grown on a Si(100) surface in an analogous fashion to that of styrene.[32] Yet another alternative may be to use substituent groups on the ethylbenzene molecules in order to shift the MO energies relative to E_F, as proposed by Geng et al.[16] Using electron-donating substituent groups would raise the HOMO energy and bring it closer to E_F, thus increasing its participation in low bias conductance. A fourth approach may be to shift the substrate peak at 0.6 eV away from the Fermi level. At least two ways in which this might be achieved are: to use a gate voltage to alter the electronic properties of the substrate or to use dipole fields from substituent groups on ethylbenzene molecules to tune the transport characteristics of the underlying substrate, as shown by one of us recently.[33] The latter could be the subject of further studies.

On the other hand, this phenomenon may be useful if it opens up a conductance channel within the substrate, directly below the molecular line. It is conceivable that such an approach could also be used to control the surface states of the Si(100) surface by judiciously selecting the molecular units that attach to it. At this point, it is not clear if the channel would be localized directly below the attached molecules, or if it would be present

Table 1. Exponential Scaling Factors β per Molecule[a]

set	transmission through rings, β_1	transmission through substrate, β_2
*n*benz	4.52 (1.18)	N/A
*n*eb1Si	3.73 (0.97)	N/A
*n*eb2Si	3.85 (1.00)	1.00 (0.26)
*n*eb3Si	3.85 (1.00)	0.75 (0.20)
*n*eb4Si	3.77 (0.98)	0.63 (0.16)
*n*gap4Si	N/A	0.56 (0.15)

[a] Values are from Figure 5 and are separated into those resulting from transmission through the rings and transmission through the substrate.[34] Corresponding β values per angstrom are given in parentheses.

throughout the entire Si surface. The Si slab model used in these calculations to mimic a surface was not thick enough to make definite statements, but this is certainly an avenue worth pursuing with further studies.

3.2. Resistance Scaling. As mentioned above, the zero-bias conductance is given by $G = T_{E_F}G_0$, where T_{E_F} is the transmission at the Fermi energy and $G_0 = 2e^2/h$ is the conductance quantum. The zero-bias resistance is obtained as $R = 1/G$, and Figure 5a–e are semilogarithmic plots of R as a function of the number of molecular units n in the π-stack on top of varying numbers of Si layers. Figure 5f is for a system where there are only two molecules (one at each lead) and there is a vacuum gap separating them. The resistance is found to exponentially increase with n, indicating tunneling-type transport, namely, $R \sim e^{\beta n}$, where β is an inverse length scale factor. The straight lines in Figure 5 are fit to the calculated data points, and the scaling parameter β is obtained from the slope.

For the case of ethylbenzene molecules on 2, 3, or 4 layers of Si, there are two regimes with different slopes from 1–3 molecules and 4–8 molecules, which we will discuss below. The scaling parameters β are summarized in Table 1. For comparison, note that for the resistance of alkanes, $\beta \sim 1$ per carbon atom[3] (each carbon unit corresponding to a distance of ~1 Å) and this would translate to $\beta \sim 3.5$ per molecular unit in our case. Of course, the systems differ in that conduction through alkanes occurs through C–C single bonds, while for the systems studied here it is through the π-stacked system as well as through the Si substrate. Note that, as discussed in the previous section, transport through benzene rings (Figure 5a) and ethylbenzene molecules on one layer of Si (Figure 5b) occurs only through the molecules. For these two systems, R scales with only one β with values of 4.52 and 3.73, respectively. The difference arises because the ethyl tail has a slight modulating effect on the benzene ring.

Most interesting are situations with thicker Si layers as shown in Figure 5c–e, where two β values are found for the scaling, indicating two regimes of tunneling behavior. In the first regime, for shorter lines with $n = 1-3$, we found $\beta = 3.85$, 3.85, and 3.77 for 2, 3, and 4 layers of Si, respectively. These values are close to each other regardless of the number of Si layers and they are also similar to that of ethylbenzene lines on one layer of Si. This result strongly suggests that for short lines of 1–3 molecules, transmission through the stacked rings dominates at low bias. In the second regime, which is for longer lines with $n = 4-8$, the scaling parameter β changes to a different value that depends on the number of Si layers, suggesting that transmission through the substrate dominates for longer lines. These scaling parameters are $\beta = 1.00$, 0.75, and 0.63 for 2, 3, and 4 Si layers, respectively. The decrease of β with more Si layers is also reasonable, since for more Si layers the conducting pathway is wider and thus the resistance should be lower. Finally, Figure 5f is for systems having all molecules removed except the two nearest to the leads: for these systems transmission is entirely through the Si and we found $\beta = 0.56$.

These results suggest that low-bias transmission consists of two competing mechanisms: transmission through the rings versus transmission through the substrate. While the Si pathway is ultimately favored in longer lines, the metal leads connect to the substrate through relatively poor molecular links (alkane tails of the two terminal molecules in a line). Because of this, the through-molecule conduction channel can dominate at very short lengths, but that channel becomes insignificant in lines with more than three molecules due to the large associated β. However, this length scale is not a universal value but it will depend on many system details such as the doping level of Si, the molecular species, the leads, etc. In addition, we note that thermal fluctuations will result in deviations from the particular structures studied in this work. However, because the molecules are tethered at a separation determined by the dimer spacing of Si(100), which happens to be very similar to the intermolecular spacing of stacked benzene molecules, we do not expect the deviations to be so significant as to qualitatively affect the tunneling behavior and the conduction pathways reported here.

4. Summary

We have calculated quantum transport properties of π-stacked ethylbenzene molecules bonded to a Si surface from atomic first principles. By systematically increasing the number of Si layers included in the analysis, we found that there is substantial transport at low bias through the substrate once two or more layers of the substrate are included. This was revealed from a transmission peak due to transport through the substrate that was nearer to the Fermi level than the peaks corresponding to transport through the molecular line. Analysis of the scattering states of this peak confirmed that transport at low bias would indeed occur through the substrate. We also studied the low bias resistance as a function of the number of units of π-stacked molecules on varying numbers of Si layers. This revealed that transport occurred through a tunneling-type mechanism where resistance increased exponentially with the number of molecules. Two competing low-bias transport mechanisms were observed, characterized by two different values of the scaling parameters β: through the molecules and through the substrate. Our results strongly suggest that quantum transport through molecules bonded to a substrate behaves rather differently than that without a substrate.

The promise of the hybrid molecule–silicon approach to molecular electronics lies in the familiar local and dynamic control over silicon conductivity through field and dopant concentration control *combined with* the tremendously varied palette of functionality that can be installed in molecules. This work highlights some of the challenges but also the prospects for such a hybrid system. It also suggests that first-principles theoretical analysis of such hybrid device structures should include substrate atoms on an equal footing with the molecules.

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Supporting Information Available: Complete ref 20 and absolute energies and optimized geometries of all calculated structures. This information is available free of charge via the Internet at http://pubs.acs.org.

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(32) Unpublished result.

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(34) Note that transport through the rings is not possible for 2-*n*eb4si and transport through the substrate is not possible for *n*benz and *n*eb1Si.