Charge Transport Through A Single Molecule of Dibenzo[a,j]coronene on Si(001)-2 × 1: Possible Coulomb Blockade

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Charge transport through single dibenzo[a,j]coronene (C_{32}H_{16}) molecules (DBC) chemisorbed on the Si(001)-2 × 1 surface was investigated by current-voltage (I-V) measurement with scanning tunneling microscopy (STM) at 25°C. The I-V curves taken from two different adsorption structures of the DBC are found to be significantly different. The major DBC species shows periodic steps in the I-V curve, as expected from a possible Coulomb blockade, while the minor DBC species shows a similar I-V curve to the Si substrate. This indicates that the adsorption structure of the chemisorbed DBC molecule to the Si surface governs its conductivity behavior.

Keywords: Scanning tunneling spectroscopies; Electrical transport; Silicon; Aromatics; Nano-electronics and related devices.

Controlling the charge transport properties of single organic molecules is one of the major challenges in the design of molecular electronic devices. Electron transport through organic molecules proceeds via electron tunneling, which is generally dominated by a through-bond super-exchange process [1]. In the super-exchange mechanism, conductance through the molecule decreases exponentially with the length of the molecule [2].

In addition to the super-exchange process, other mechanisms can be operative in determining charge transport through organic molecules located between metal electrodes. Resonant tunneling can occur when the energy of a molecular orbital crosses the Fermi level of the electrodes. In this case, the electronic current shows a step-like increase, as the voltage is swept and the new resonant level is achieved [3-6]. The conductance (dI/dV)/(I/V) vs. voltage curve corresponds to the local-density-of-states (LDOS) of the molecule when resonant tunneling dominates, and this constitutes the basis of scanning tunneling spectroscopy (STS).

The Coulomb blockade phenomenon can also occur in charge transport through a molecule [7-10]. To exhibit a Coulomb blockade, the molecule must couple electronically weakly to the two electrodes [9], so that there are small capacitances at the junctions between the molecule and the electrodes, allowing the molecule to charge up. When a single electron transfers from an electrode to the molecule at low bias voltage, electrostatic interactions prevent another electron from transferring to the molecule until an electron leaves. Thus, electrons flow, one by one, through the molecule. When the bias voltage exceeds a certain threshold, the number of excess electrons that can be localized on the molecule increases from one to two, and at still higher bias voltage it increases from two to three, etc. Then, the I-V curve displays the so-called Coulomb staircase behavior [11, 12].

Scanning tunneling microscopy (STM) [13-16] and conducting probe atomic force microscopy (CP-AFM) [17, 18] have been used to measure the current-voltage (I-V) characteristics through single organic molecules or through self-assembled molecular layers. The scanning probe microscopy techniques allow one to monitor the adsorption structure (STM image) and the I-V characteristics (STS curve) from the same single molecule. Various break junction techniques, such as the mechanically-controllable break junction (MCB) [19-22], or electromigration-induced [23, 24] and lithographically-made break junctions [25, 26] have also been used to measure the I-V characteristics through molecules. In the break junction measurements, molecules can form chemical bonds to both electrodes, but it is not certain how many molecules exist at the break junction [27]. Moreover, some charge transport properties originally attributed to molecules in break junction measurements are also found in the absence of the molecules [28, 29], adding doubt about the reliability of this method for studies of molecular conductivity.

In the present study, charge transport through single dibenzo[a,j]coronene (DBC) molecules on the Si(001)-2 × 1 surface was investigated by I-V measurement with an STM at 25°C. The DBC molecule is a polyaromatic hydrocarbon molecule with nine fused benzene rings. On the Si(001)-2 × 1 surface the DBC molecule forms one major (Type 1) and two minor (Type 2 and 3) adsorption structures [30]. The atomic configurations of these three adsorption structures have been established by comparison of experimental and simulated STM images. We concentrate on the Type 1 and the Type 2 structures in the present study.

Details on the experimental and theoretical methods have been previously reported [30]. An ultra-high vacuum STM (Omicron) and sample crystals cut from p-type boron-doped Si(001) wafers (100 Ω-cm) were used in the present study. The DBC molecules were deposited onto the atomically-clean Si substrate at 25°C, using an electrically heated quartz crucible. All STM observations and I-V curve measurements were carried out at 25°C.

The LDOS calculations were done based on density-functional theory calculations with a plane-wave basis set and the pseudopotential approximation as implemented in Vienna ab initio simulation package (VASP) code [30]. The core orbitals have been represented by non-local opti-
FIG. 1: (a) $I$-$V$ curves and (b) $(dI/dV)/(I/V)$ curves taken on the clean Si(001)-$2 \times 1$ surface and on the major Type 1- and the minor Type 2-DBC structures. Initial set point for the $I$-$V$ measurement is $V_s$ (sample bias) = 1.6 V and $I = 0.07$ nA.

FIG. 2: Calculated LDOS curves for the clean Si(001)-c(4 x 2) surface, Type 1- and Type 2-DBC structures. In the last two cases only the contribution of adsorbed molecule is represented. The calculated LDOS have been shifted so that the Fermi energy corresponds to the zero of energy.

mized ultrasoft pseudopotentials (USPPs) similar to those introduced by Vanderbilt. The electron exchange correlation effects have been represented by the PW91 generalized gradient approximation (GGA) of Perdew, et al.

Figure 1(a) shows $I$-$V$ curves taken on the clean Si(001) surface and on DBC molecules adsorbed as the major Type 1 and the minor Type 2 structures. STM tips were first cleaned by applying bias voltage pulses of up to ±10 V, before starting to take the $I$-$V$ curves on the DBC molecules in every experiment. The tip cleaning was repeated until the STM tips could reproduce the previously-reported $I$-$V$ curve on the clean Si(001)-$2 \times 1$ substrate [31-34], which is shown as the black lowest curve in Fig. 1(a). Then, more than one hundred $I$-$V$ curves using several Si samples were averaged for each $I$-$V$ curve in Fig. 1(a). The $I$-$V$ curves for the clean Si surface and for the Type 2-DBC structure are similar, but that for the Type 1-DBC structure is strikingly different, displaying a series of periodic steps, as indicated by red arrow heads in Fig. 1(a). All features are independent of the dopant in the Si substrate: they are reproducible on both $p$-type (100 $\Omega$-cm) and $n$-type (10 $\Omega$-cm) Si substrates (not shown here).

The difference is clearer in the $(dI/dV)/(I/V)$ curves shown in Fig. 1(b). The $(dI/dV)/(I/V)$ curves for the

FIG. 3: Schematic of (a) the metal-molecule-semiconductor junction in the STM geometry, and (b) equivalent circuit for the Coulomb staircase.
FIG. 4: (a)-(c) the $I-V$ and (a')-(c') the $(dI/dV) - V$ curves for the clean Si, the Type 1- and the Type 2-DBC structures before and after the tip crashing.

clean Si(001) surface and for the Type 2-DBC structure both display prominent features near $-1 \text{ V}$ and $+1 \text{ V}$ consistent with that reported previously for the clean Si (001) surface [31–34]. Meanwhile, the $(dI/dV)/(I/V)$ curve for the Type 1-DBC structure in Fig. 1(b) shows three equally spaced peaks between $-1.5$ and $0.5 \text{ V}$, but no peaks near $-1 \text{ V}$ and $+1 \text{ V}$.

As mentioned in the Introduction, either resonant tunneling or Coulomb blockade can cause periodic steps in an $I-V$ curve. Similar periodic steps have been observed in the MCB measurements of the $I-V$ curve of the bisthioeterthiophene 2,5”-bis(acetylthio)-5,2’5’,2”-terthienyl (T3) molecule located between gold electrodes [20]. In that case, the steps were explained in terms of resonant tunneling. On the other hand, features in the $I-V$ curve through a (E,E) 1,4 bis4 (E) 4 (tert-butylthio)styrilbenzene (OPV5) molecule located between gold electrodes produced by the lithographically-made break junction method, have been attributed to the Coulomb blockade [26]. In both the T3 and OPV5 cases, Au-S chemical bonds were assumed to form between the molecule and the gold electrodes.

In order to investigate qualitatively the possibility of resonant tunneling causing some or all of the $I-V$ curves shown in Fig. 1, very simple LDOS calculations were done for the Type 1- and Type 2-DBC structures as well as for the bare Si(001)-c(4 × 2) surface. Details like tip-induced molecular level shift, compensation for smaller calculated band gaps, or contribution of the LDOS from the Si substrates were not considered in the present study, which will be investigated in future. The resulting curves are displayed in Fig. 2. For the Type 1 and Type 2-DBC structures, the LDOS contributed from only the adsorbed molecule are reported. For the clean Si(001) substrate,
that while the experiments were done at room temperature, the calculations give a weak peak near +0.3 eV and intense peaks near −0.5 and +1.0 eV, as indicated by bars, which is qualitatively consistent with experiment in Fig. 1(b) that shows two peaks around −1 V and +1 V. The calculated structure derives primarily from the π and π∗ orbitals of the silicon surface dimers. It is relevant to note that while the experiments were done at room temperature on the 2 × 1 reconstruction, the calculations correspond to 0 K and to the c(4 × 2) reconstruction.

For the Type 2-DBC structure, the calculated LDOS of the adsorbed molecule displays peaks at −0.5 and +0.6 eV. This is a much smaller splitting than that in the experimentally observed I-V curve, suggesting that the observed structure may not be dominated by the energy levels of the adsorbed molecule. It is noted here that calculated LDOS may show smaller band gaps in general, which was not compensated in the present calculations. The similarity of experimental I-V curves for the Type-2 DBC structure and for the bare Si surface rather suggests that the structure in the I-V curve of the Type-2 DBC structure derives primarily from the π and π∗ orbitals of the Si dimers. It is speculated that the mixing between the orbitals localized on the adsorbed molecule and those associated with the nearby Si dimers could act so as to promote the tunneling into the orbitals of the Si dimers.

The calculated LDOS for the Type 1-DBC structure displays prominent peaks near −1.4, −0.5, and +0.8 eV around the Fermi level, which seems to agree with the experimental I-V curve shown in Fig. 1(b). However, the calculated LDOS resemble somewhat each other for the Type 1- and Type 2-DBC structures. For example, there are four similar large peaks in both LDOS curves, as indicated by bars in Fig. 2. Meanwhile, these two LDOS curves for the Type 1- and Type 2-DBC structures are largely different from that for the clean Si(001) substrate. This is different from the experimental result, where the (dI/dV)/(I/V) curves for the clean Si(001) and for the Type 2-DBC structure are relatively similar, but that for the Type 1-DBC structure is strikingly different. Thus, it is not sure whether the periodic structure in the I-V curve of the type 1-DBC structure might arise from the energy levels of the adsorbed molecule or not.

Another possibility is also explored that the structure in the I-V curve of the type 1-DBC species arises from a Coulomb blockade rather than from resonant tunneling. Figure 3 shows schematic drawings of (a) the metal-molecule-semiconductor junction in the STM geometry, and (b) the equivalent circuit for the Coulomb staircase. The capacitances between the molecule and the substrate and between the molecule and the STM tip are designated C1 and C2, respectively. According to the standard theory of the Coulomb staircase, the period of the steps in the I-V curve is given by e/C2, where the resistance R2 >> R1 [11, 12]. This led us to carry out an experiment in which the STM tip was crashed into the surface before the I-V measurements were made. The motivation here is that the crashing the STM tip into the Si substrate should change the tip shape, especially the curvature at the very apex of the STM tip, thereby changing C2, and the step spacing.

Figure 4 shows (a)-(c) the I-V and (a′)-(c′) the (dI/dV)-V curves for the clean Si, the Type 1- and the Type 2-DBC structures before and after the tip crashing. The two I-V and the (dI/dV)-V curves for the clean Si surface are basically the same before and after the tip crashing as shown in Fig. 4(a) and (a′), which indicates that the STM tip after crashing into the surface still detects the Si surface states. Moreover, STM images of the Type 1- and the Type 2-DBC structures before and after the tip crashing remained nearly the same, as shown in Fig. 5. For the Type 2-DBC structure, the two curves before and after the tip crashing are also basically the same as shown in Fig. 4(c) and (c′). However, the Type 1-DBC conductivity behavior changed significantly following the tip crashing, as shown in Fig. 4(b). In the (dI/dV)-V curves in Fig. 4(b′), the period of the steps was changed from ∼1.0 V to ∼1.4 V by crashing the tip onto the surface, which corresponds to a change of the C2 value from 1.8 × 10−19 F to 1.2 × 10−19 F in the standard theory [11, 12]. The error bars in Fig. 4(b′) are standard deviations (2σ) of the peak maxima derived from 231 I-V curves measured before and 72 I-V curves measured after the STM tip crash. The results of the tip crashing experiments are consistent with the Coulomb blockade explanation for the periodic steps in the I-V curve of the Type 1-DBC structure. However, in order for the Coulomb blockade to appear, there must be a tunneling barrier (and capacitance C1 of the order of ∼10−19 F) between the molecule and the Si substrate, and it is difficult to reconcile theoretically such a capacitance of this magnitude for the Type 1-DBC molecule given that it has the six Si-C covalent chemical bonds between the molecule and the Si substrate, as shown in Fig. 3(a) [30]. It may be possible that the altered spacing in the I-V curve of the type 1-DBC structure after tip crashing is a consequence of interference between different pathways for tunneling involving the modified tip [35].

In discussing the Coulomb blockade possibility, it is assumed that the excess charge accumulates on the ad
sorbed molecule. However, there is another possibility that the excess charge accumulates on the Si dimers adjacent to the molecule. This could occur, for example, because these Si dimers are in a different environment than those on the bare Si surface, as a result of the presence of the DBC molecule. It is noted also that the physical separation of the Si dimers at different ends of the adsorbed molecule, combined with dielectric screening, could make the Coulomb repulsion between the localized charges at the edges of the DBC adsorption site quite small.

In summary, we have studied charge transport through single DBC molecules with different adsorption structures on the Si(001)-2 × 1 surface. The minor Type 2-DBC structure shows periodic steps in its I-V curve similar to that for the clean Si(001) substrate. On the other hand, the major Type 1-DBC structure shows periodic steps in its I-V curve, as expected from a possible Coulomb blockade. It is not clear at present whether the periodic steps originate from a Coulomb blockade effect, or from resonant tunneling through the energy levels of the adsorbed molecule. The idea of charge storage on Si dimer sites neighboring the adsorbed DBC molecule is postulated for the Coulomb blockade possibility. Although the physical mechanism of the charge transport in the Type 1- and Type 2-DBC structures on the Si(001) substrate is not clear at present, it is very intriguing that different adsorption structures of the molecule on the surface causes a profound influence on its charge transport behavior.

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