The origin of the transition voltage of gold–alkanedithiol–gold molecular junctions

An Xiang a,b, Minglang Wang a, Hao Wang a, Hantao Sun a,b, Shimin Hou a,c, Jianhui Liao a,c

a Key Laboratory for the Physics and Chemistry of Nanodevices, Department of Electronics, Peking University, Beijing 100871, China
b Academy for Advanced Interdisciplinary Studies, Peking University, Beijing 100871, China
c Beida Information Research (BIR), Tianjin 300457, China

Article info
Article history:
Received 31 July 2015
In final form 30 November 2015
Available online 14 December 2015

Keywords:
Molecular junction
Electron transport
Transition voltage
Molecule–electrode interface

Abstract
We studied the origin of the transition voltage of octanedithiol (C8DT) molecules sandwiched between two gold electrodes. Au–C8DT–Au molecular junctions were fabricated using the feedback controlled electromigration technique. The conductance measurement and the inelastic electron tunneling spectrum validate that the observed current–voltage characteristics indeed originate from the C8DT molecule in the junction. The transition voltage of Au–C8DT–Au junctions is determined to be about 0.95 V, which cannot be interpreted using the energy difference between the highest occupied molecular orbital or lowest unoccupied molecular orbital of the alkyl chain and the Fermi level of electrodes. Instead, we relate the measured transition voltage to the Au–S bonds, which are about 1.4 eV below the gold Fermi level. Our interpretation is supported by the ultraviolet photoelectron spectroscopy measurements and first-principles quantum transport simulations. These findings provide convincing evidence that the Au–S occupied states play a significant role in the charge transport of Au–alkanedithiol–Au molecular devices.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Understanding the electronic transport properties of single molecules bonded between metal electrodes is of crucial importance for molecular electronics [1,2]. The current–voltage (I–V) characteristics of molecular electronic devices are dominated by the alignment of various molecular energy levels relative to the electrodes Fermi level and their electronic couplings with the conducting states of the electrodes. Transition voltage spectroscopy (TVS), which was firstly introduced by Beebe et al. [3,4], has been demonstrated to be a powerful tool for estimating the energy offset of the molecular orbital closest to the Fermi level of electrodes [5–27]. The transition voltage (Vtrans), at which a minimum appears in the Fowler–Nordheim (F–N) plot of the I–V data, is related to the applied bias voltage that promotes a significant spectral weight of the transmission function into the bias window [28]. Furthermore, the transition voltages for both bias polarities provide useful information about the degree of the junction asymmetry [29,30]. For π-conjugated molecules connected to gold electrodes through Au–S bonds, the transition voltages are consistently measured by different groups [3,4,9,14,17]. The calculated transition voltages of three different asymmetric Au/poly(phenylene) thiol/Au molecular junctions are in quantitative agreement with the experimental values at positive polarity [31]. The origin of the transition voltages can be attributed to the highest occupied molecular orbital (HOMO) of the corresponding poly(phenylene) thiol molecule which contributes a large transmission peak in the junction transmission spectrum [31]. In contrast, the measured transition voltages of saturated alkanedithiol molecules have a broad distribution ranging from 0.7 V to 1.9 V [8,10,13,16,17], though a rather weak dependence on the length of alkyl chains was reported by different research groups [13,17]. Moreover, there is a huge discrepancy between the calculation and experimental values of the transition voltages for alkanedithiol junctions. For instance, the transition voltage of the Au–hexanedithiol–Au junction is calculated to be 2.94 V [32], much larger than the reported experimental value of 1.16 ± 0.15 V [17]. Considering that the energy difference between the closest molecular orbital (HOMO or LUMO (the lowest unoccupied molecular orbital)) of alkane molecules and the Fermi level of gold is larger than 3 eV [33], it is unconvincing to associate the transition voltages of Au–alkanedithiol–Au junctions with the transmission peaks dominated by the HOMO or LUMO of the corresponding alkane molecules. Therefore, how to explain the origin of the transition voltages of Au–alkanedithiol–Au junctions is still a challenge [8,10,13,16,17].
In this article, we investigate the transition voltages of Au–octanedithiol (C8DT)–Au molecular junctions that were fabricated using the feedback controlled electromigration (FCE) method. The inelastic electron tunneling (IET) spectrum obtained simultaneously with the I–V measurement confirms that the C8DT molecule is the pathway for electrons tunneling through the junction, and the origin of the measured transition voltages is interpreted based on the ultraviolet photoelectron spectroscopy (UPS) measurement for the C8DT film on gold substrate and first-principles quantum transport simulations.

2. Experimental and calculation methods

2.1. Fabrication of device structures

Conventional photolithography and electron beam fabrication (5 nm Ti/40 nm Au) were used to define the macroscopic bonding pads on silicon wafer with 500 nm SiO2. Then, 30 nm aluminum was deposited and oxidized naturally in air to form ~3–5 nm AlOx as dielectric layer. Lastly, a suspending PMMA mask was patterned on PMMA/MMMA double layer resist by electron beam lithography (EBL), followed by angle evaporation (20 nm Au without adhesion layer) on the top of AlOx layer. As a result, gold bowtie structures with a constriction (~100 nm in width) at the center were formed on the alumina layer.

2.2. Fabrication of molecular junctions

Devices were first cleaned by oxygen plasma to get rid of any organic residues on the electrode surface. Then, the self-assembled monolayer (SAM) of C8DT was formed on the gold surface by immersing the sample in ~1 mM C8DT solution in ethanol. The C8DT 97% used in this study was purchased from Sigma–Aldrich Company and the ethanol 99.7% was purchased from Beijing Institute of Chemical Reagents. To keep the molecules from oxidation in air, an argon environment was used for the self-assembly process. Normally, we immersed the devices in the dilute C8DT solution overnight to ensure the formation of dense SAM. Subsequently, devices were rinsed in pure ethanol and blow dried with nitrogen (99.99%) gun. Immediately after this, devices were wire bonded and transferred to the low temperature cryostat. The device was mounted on the sample holder in a vacuum chamber (~5E–5 mbar). The initial resistance of an as-prepared device was measured at low bias (±50 mV). Then, FCE was performed to generate a nanogap in gold nanowire of each device at 4.2 K and single or very few C8DT molecules bridged the gap through the Au–S bonds [34,35].

2.3. Electronic measurements

All the devices were characterized by scanning electron microscopy (SEM, FEI Quanta 600). We measured I–V curves of devices during electromigration in a cryostat (Oxford Ins., OptistatAC-V). The I–V curves were measured using a data acquisition board (National Instruments, PCI 6281) together with a homemade LabVIEW program. A current amplifier (Keithley 428) was used to convert the current to voltage. The temperature of device was controlled by the temperature controller (ITC, Model 503). The IET spectrum was measured using a Lock-in amplifier (Stanford Research Systems 830) to directly obtain the second harmonic signal (d2I/dV2) at 4.2 K with an AC modulation of 9 mV at 77.77 Hz, and the time constant was set to 3 s. When sweeping the bias voltage from –0.2 V to 0.2 V with a step size of 1 mV, we measured each d2I/dV2 point 1000 times and averaged them for the IETS demonstration.

2.4. Theoretical calculations

We use the SIESTA code to study the atomic structure of Au–C8DT–Au molecular junctions. SIESTA is an efficient density functional theory (DFT) package, which makes use of improved Troullier–Martins pseudopotentials for the atomic cores and adopts a finite-range numerical orbital basis set to expand the wave functions of the valence electrons [36,37]. While a double-zeta plus polarization (DZP) basis set is used for H, C, S and Au atoms at the electrode surface, a single-zeta plus polarization (SZP) basis is used for Au atoms in the bulk. Geometry optimization is performed by standard conjugate gradient relaxation until the atomic forces are smaller than 0.03 eV Å–1, and the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) to the exchange and correlation functional is used to account for the electron–electron interaction [38]. The electronic transport properties of the Au–C8DT–Au molecular junctions are calculated using the SMEAGOL package, which is a practical implementation of the NEGF + DFT approach and employs SIESTA as the DFT platform [39–41]. Here NEGF is the acronym for non-equilibrium Green’s function. Because the molecular levels calculated by using local or semi-local exchange and correlation functionals are usually too high in energy due to the self-interaction error [42], the atomic self-interaction correction (ASIC) scheme is used to deal with the alignment problem in the transport calculations [43,44]. The ASIC corrections are only applied to H, C and S atoms in the C8DT molecule, but not to Au in the electrodes as the self-interaction error for metals is small. We use an equivalent cutoff of 200 Ryd for the real space grid. The charge density is integrated over 36 energy points along the semi-circle, 36 along the line in the complex plane, 240 along the real axis, while 36 poles are used for the Fermi function (the electronic temperature is 25 meV). We always consider periodic boundary conditions in the plane transverse to the transport. The unit cell of the extended molecule comprises the C8DT molecule and ten Au(1 1 1) atomic layers with a (3 × 3) in plane supercell. The I–V curve of the junction is calculated as

\[ I(V) = \frac{2e}{h} \int_{-\infty}^{\infty} T(V, E) \left| f(E - \mu_L) - f(E - \mu_R) \right| dE, \]

where \( T(V, E) \) is the bias V dependent transmission coefficient of the junction, \( f(E) \) is the Fermi function, \( \mu_{L/R} = E_F \pm \frac{e}{2} V/2 \) is the local Fermi level of the left/right gold electrode. The transition voltage is obtained from the minimum appearing in the F–N plot of the I–V data, i.e. a plot of \( \ln(I/V^2) \) against \( 1/V \). Then, the total transmission coefficient \( T(V, E) \) of the junction is evaluated as

\[ T(V, E) = \frac{1}{\Omega_{2DBZ}} \int_{2DBZ} T(K, V, E) dK, \]

where \( \Omega_{2DBZ} = \Omega_2 \times \Omega_{2DBZ} \) is the area of the two-dimensional Brillouin zone (2DBZ) in the transverse directions. The k-dependent transmission coefficient \( T(K, V, E) \) is obtained as

\[ T(K, V, E) = Tr [\Gamma_1 G_{se} \Gamma_2 G_{se}], \]

where \( G_{se} \) is the retarded Green’s function matrix of the extended molecule and \( \Gamma_{1,2} \) is the broadening function matrix describing the interaction of the extended molecule with the left (right) electrode. Here, we calculate the transmission coefficient by sampling \( 4 \times 4 \) k-points in the transverse 2DBZ.

3. Results and discussion

Since the transition voltages of Au–alkanedithiol–Au junctions show a rather weak dependence on the length of alkyl chains [13,17], we choose C8DT as the representative. Fig. 1(a) shows the SEM image of the electrode pair separated by a tiny gap gener-
I images. The low-bias conductance is extracted from the least-square curves and in some cases are even rather large at high bias voltages. However, the maximum current scatters in a quantitative different (see Fig. S1 in the Supplementary Material) [45].

The current always increases linearly at low bias and goes up rapidly at high bias. This indicates that we are indeed measuring C8DT molecules rather than any other artifacts. To do this, we measured the conductance and the IET spectra of Au–C8DT–Au junctions fabricated with the electromigration method [8,13]. Compared with the conductance histogram of Au–C8DT–Au junction method where three conductance peaks are always constructed using the scanning tunneling microscopy (STM) break transition voltages at positive and negative bias polarities are 0.96 ± 0.23 V and −0.95 ± 0.25 V, respectively. The TVS analysis provides information about the energy level alignment and the junction symmetry. The transition voltages characterize the energy difference between the dominating molecular level and the Fermi level. The most probable conductance value determined from Gaussian fitting (blue line) is (5.1 ± 0.6) × 10^−5 G₀. The insert shows a typical I–V curve of the Au–C8DT–Au molecular junction in the low-bias region. (c) The representative IET spectrum of a Au–C8DT–Au junction. The peaks at positive polarity labeled by short red lines and highlighted by color shadow are assigned to specific internal vibration modes of Au–C8DT–Au molecular junctions. The dips at negative polarity are also highlighted and labeled for comparison. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Now, we look at the transition voltages of Au–C8DT–Au junctions. Fig. 2(a) shows the F–N plot of a typical I–V curve. Two obvious inflections marked by blue arrows appear in the F–N plots at both positive and negative polarities. The absolute values of the two transition voltages are both 1.09 V for this junction. Fig. 2(b) shows the statistical distribution analysis of the transition voltages obtained from all the I–V data. The most probable values for the transition voltages at positive and negative bias polarities are 0.96 ± 0.23 V and −0.95 ± 0.25 V, respectively. The TVS analysis provides information about the energy level alignment and the junction symmetry. The transition voltages characterize the energy difference between the dominating molecular level and the Fermi level. The most probable conductance value determined from Gaussian fitting (blue line) is (5.1 ± 0.6) × 10^−5 G₀. The insert shows a typical I–V curve of the Au–C8DT–Au molecular junction. The peaks at positive polarity labeled by short red lines and highlighted by color shadow are assigned to specific internal vibration modes of Au–C8DT–Au molecular junctions. The dips at negative polarity are also highlighted and labeled for comparison. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Another more direct evidence can be provided by measuring the IET spectra of molecular junctions. IET spectroscopy has been widely accepted as a characterization technique to identify the existence of the desired molecule in the junction. Fig. 1(c) shows a representative IET spectrum for Au–C8DT–Au molecular junctions. Compared with infrared, Raman and high-resolution electron energy loss spectra reported in the literature [48–50], the peaks in the IET spectrum shown in Fig. 1(c) can be assigned to specific vibration modes as following: (I) the Au–S stretching mode ν (Au–S) at around 38 meV; (II) the C–S stretching mode ν(C–S) at 87 meV; (III) the C–H rocking mode δ(CH₂) at 109 meV; (IV) the C–C stretching mode ν(C–C) at 129 meV; (V) the C–H out-of-plane wagging and twisting mode γ(CH₂) at 167 meV; (VI) the C–H scissoring mode δ(CH₂) at 185 meV. Besides these six characteristic peaks which are often observed in the IET spectra of Au–alkanedithiol–Au junctions [51–55], the double-peak structure at around 10 meV should be the zero-bias feature [56] and the peak at about 63 meV can be assigned to the Au–S–C stretching mode ν(Au–S–C) [52]. The IET spectrum is further validated by the anti-symmetric behavior. The absolute values of the peak positions at positive bias polarity are very close to those of the corresponding dips at negative bias polarity (see Table S1 in the Supplementary Material) [45], in spite of some difference in the intensity of peaks. Thus, the IET spectra also suggest that the measured I–V characteristics are indeed dominated by the C8DT molecules other than adsorbents or vacuum tunneling.
level of electrodes. The similar absolute values of the transition voltages for both bias polarities suggest that the C8DT molecule binds almost symmetrically to the two gold electrodes. This indicates that the C8DT molecule tends to form similar Au–S bonds at two molecule–electrode interfaces [47,57].

An in-depth insight into the energy level alignment in Au–C8DT–Au junctions can be obtained by analyzing the I–V curves with the single-level tunneling model [58–60], in which the current through the junction can be calculated using Eq. (1) with the transmission coefficient approximated by a Lorentzian function

$$T(V, E) = \frac{4\Gamma_L \Gamma_R}{E^2 - (\epsilon_0 + \Gamma_L \Gamma_R E^2)^2 + (\Gamma_L + \Gamma_R)^2}$$

(4)

Here, $\epsilon_0$ is the molecular level position and $\Gamma_L$ ($\Gamma_R$) is its coupling strength to the left (right) electrode. Fig. 2(c) shows the I–V curve in a linear scale, which is the same data set as that in Fig. 2(a). The blue line is the fitting curve from the single-level tunneling model. From the fitting, the energy offset $\epsilon_0$ of the molecule level closest to the Fermi level of electrodes and its coupling strengths ($\Gamma_L$ and $\Gamma_R$) to two electrodes can be extracted [59]. For this specific junction, the molecular level dominating the low-bias conductance is 0.91 eV away from the Fermi level of the electrode and it couples almost equally to the left and right electrodes ($\Gamma_L = 5.3$ meV and $\Gamma_R = 4.9$ meV). Fig. 2(d) shows the histogram of the energy offset for all measured Au–C8DT–Au junctions. The most probable value for $\epsilon_0$ is $0.83 \pm 0.16$ eV.

It should be pointed out that our measured values (~0.95 V) of $V_{\text{trans}}$ are very close to the reported values (1.1 ± 0.07 V) for “suspended-wire” Au–C9DT–Au junctions [10] and those (1.10 ± 0.32 V) for Au–C8DT–Au junctions with the low conductance values which are fabricated using the STM break-junction method [17]. In contrast, our measured values differ by a factor of two with those (~1.93 V) reported by Song and coworkers [8,13], though we both fabricated Au–C8DT–Au junctions using the electromigration method and the low-bias conductance values are also similar. In order to explain this surprising result, we investigate the relation of the low-bias conductance with the energy level alignment and the molecule–electrode coupling strengths.

As shown in Fig. S2 of the Supplementary Material [45], there is almost no correlation between the low-bias conductance and the energy position of the conducting level while the low-bias conductance strongly depends on the coupling strengths. Considering that the formation of molecular junctions in the electromigration method is a probabilistic event, we believe that the junction structures fabricated in our experiments should be markedly different from those reported by Song et al. and thus the measured $V_{\text{trans}}$ values are different significantly. Since the lower values of $V_{\text{trans}}$ are obtained from hundreds of molecular junctions [17], these kinds of junctions should be formed more frequently. Therefore, we focus on the origin of these relatively lower $V_{\text{trans}}$ values in Au–C8DT–Au molecular junctions.

The energy offset determined from $V_{\text{trans}}$ is much lower than the energy difference between the HOMO or LUMO of alkyl chains and the gold Fermi level [33]. We also notice that a filled state at ~1.4 eV below the Fermi level of gold has been reproducibly observed in scanning tunneling spectroscopy of octanethiol molecules adsorbed on the Au(111) surface in the standing-up phase [61]. The filled state is attributed to the Au–S bonds localized at the molecule–substrate interface. It seems reasonable to relate the occurrence of a transition voltage in the F–N plot of Au–C8DT–Au junctions to the tail of the Au–S state entering the bias window.

To support this hypothesis experimentally, we measured the UPS spectrum of C8DT monolayer self-assembled on a gold substrate. Fig. 3(a) shows the UPS spectra measured from a C8DT monolayer (red curve) and a bare gold substrate (green curve). Compared with the bare gold surface, the C8DT monolayer on gold substrate presents a broad peak at about 1.4 ± 0.3 eV below the Fermi level, which is referred to as the Au–S state. This is in excellent agreement with the spectral feature observed for octanethiol adsorbed on a gold substrate [62]. To further illustrate the contributions of the Au–S states to the transition voltages of Au–C8DT–Au junctions, we present schematic pictures of the energy level alignment in Au–C8DT–Au junctions at zero and finite bias in Fig. 3(b) and (c) [63]. At zero bias, the broadened energy levels of the two Au–S bonds locate much closer to the Fermi level of electrodes than the HOMO and LUMO of the alkyl chain (Fig. 3(b)). When a finite bias is applied to the junction, the local Fermi levels of the left and right electrodes together with the Au–S states are moving upwards or downwards. At a specific bias, a significant weight of one Au–S state enters the bias window. Consequently, the electric current through the junction increases rapidly, leading to the presence of an inflection in the F–N plot. The same situation will happen when applying an opposite bias.

Our hypothesis is also supported by theoretical simulations. We investigate the role of the Au–S bonds in the TVS of Au–C8DT–Au junctions employing the NEGF + DFT approach. The optimized atomic structure of the Au–C8DT–Au junction model is shown in Fig. 4(a), in which one C8DT molecule is assumed to bind symmetrically to the two gold electrodes at the adatom site of the Au(111) surface through the Au–S bonds with a bond length of 2.321 Å. Fig. 4(b) shows the calculated I–V curve and the corresponding F–N plots for both bias polarities. Here the empirical scale factor $\alpha$, which is a measure of the deviation of the ASIC potential from the exact SiC one, is set to be 0.50, thus that the HOMO of the C8DT molecule in the gas phase can be shifted downward to ~7.60 eV (i.e., it is much close to the negative of the ionization potential [7.64 eV] calculated at the PBE/6-311 + G(d,p) level). As one can clearly see, the current increases linearly at low bias but then increases rapidly after the bias exceeds 0.7 V. Correspondingly, a well-defined minimum appears in the F–N plot and the transition voltage is determined to be 1.1 V independent on the

![Fig. 3](image-url)
The bias-dependent transmission spectra of the Au–C8DT–Au junction. The spectra of Au–C8DT–Au junctions. Inset: the corresponding I/C2

The LDOS of the S atom and the Au adatom projected onto their atomic orbitals. Fig. 5.

In summary, we have investigated the origin of transition voltages of Au–C8DT–Au molecular junctions fabricated using the FCE method. The transition voltages of these Au–C8DT–Au junctions are measured to be ~0.95 V and depend weakly on the bias polarity. Our NEGF + DFT calculations for the junction model in which one C8DT molecule is connected to two gold electrodes at the adatom site of the Au(111) surface through the Au–S bond deliver a transition voltage of 1.1 V, in good agreement with the experimental value. Bias-dependent transmission spectra reveal that the occurrence of transition voltage in Au–C8DT–Au junctions is directly related to the bias-induced shift of the transmission peak dominated by the Au–S bonds localized at the molecule–electrode interfaces. These occupied states contributed by the Au–S bonds are further confirmed by the UPS measurements on C8DT molecules adsorbed on gold substrate. Our findings not only provide an explanation to the origin of transition voltages of Au–alkanethiol–Au junctions but also demonstrate the important role of the molecule–electrode interfaces in electron conduction of molecular devices.

Conflict of interest

We have no conflict of interest in this paper.

Acknowledgments

This project is supported by the National Natural Science Foundation of China (Nos. 61321001 and 21573014) and the MOST of China (Nos. 2011CB933001 and 2013CB933404).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemphys.2015.11.010.

References

See Supplementary Material for the measured I–V curves of 17 Au–C8DT–Au molecular junctions, the comparison of the peak positions in the IET spectrum (Fig. 1c) at positive bias polarity with those of the corresponding dips at negative bias polarity and the relation of the low-bias conductance of Au–C8DT–Au junctions with the energy level alignment and the molecule-electrode coupling strengths.