Electrical characteristics of layered palladium alkanethiolates by conducting atomic force microscopy

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Current-voltage measurements on individual Pd(II) alkanethiolate nanostructures of varying bilayer thicknesses (hexyl to hexadecyl) employing conducting atomic force microscopy have shown the presence of a low current region near zero bias, the width of which increases with the bilayer thickness. The resistance in this region varies exponentially with the bilayer thickness with a low decay parameter value of 0.2 ± 0.04 Å^{-1} indicating a long-range nonresonant tunneling through the alkyl chains. The changeover from low current to high current with increasing bias is accompanied by a negative differential resistance feature, which arises due to Pd–S charge transfer. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2828340]

Inorganic-organic hybrids constitute an emerging class of materials with synergistic combination of properties of the constituent inorganic and organic components.[1] While the inorganic framework can provide a wide range of potentially useful properties, electronic, magnetic, mechanical, and thermal, the organic counterpart may impart special attributes—fluorescence efficiency, polarizability, plasticity, as well as structural diversity. Metal alkanethiolates are interesting that the inorganic backbone of metal-sulfur-metal linkage is separated by alkylchains to form a lamellar bilayer structure with the bilayer thickness varying systematically with the alkylchain length. Extensive studies have been carried out in the literature on the structures of Ag, Cd, Cu, and Pd alkanethiolates.[2–4] They have also been used as precursors to obtain metal and metal sulfide nanostructures.[5] Among them, palladium(II) alkanethiolates (PdSR) are unique that they are soluble in organic media and their liquid crystalline properties can be programed by self-assembly in organic media.[4,6] Given the structure of the Pd thiolate bilayer with close Pd–Pd distances (3.11 Å as against 2.74 Å in Pd metal), one is tempted to consider the set of Pd–S–Pd backbones as evenly spaced one dimensional conductors with an intervening medium of the hydrocarbon chains. Recently, there is an interesting report on the electronic structure of the toroidal compounds of palladium thiolates whose exceptional stability is attributed to the delocalization of π bonding orbitals of Pd–S distributed throughout the Pd ring.[7] We considered it interesting to investigate the electrical behavior of PdSRs of different bilayer thicknesses, especially with a high spatial resolution offered by conducting atomic force microscopy (C-AFM).[8] As such, experimental studies on metal thiolates are rare, the only example being a bulk measurement on nickel thiolate.[9] C-AFM is particularly useful in our study of

PdSRs as in these compounds, though x-ray crystalline, the stacking extension is typically limited to a few hundred nanometers at varied orientations. We have analyzed the microstructure using AFM images and collected current-voltage (*I-V*) characteristics from different bilayers. Our study has shown that the *I-V* data contain a low current region near zero bias, the width of which varies proportionally with the alkyl chain length and a negative differential resistance feature (NDR) followed by a higher current region.

Palladium alkanethiolates were prepared according to the procedure reported earlier.[4] Briefly, palladium acetate was mixed with an excess of alkanethiol in toluene to get a viscous orange colored solution. A series of long chain Pd(II) alkanethiolates, hexyl, octyl, decyl, dodecyl, and hexadecylthiolates was prepared. For C-AFM studies, the recrystallized thiolate was redispersed in toluene and drop cast on a highly oriented pyrolytic graphite (HOPG) substrate and annealed to improve crystallinity. Imaging and *I-V* measurements were simultaneously performed employing a multimode atomic force microscope powered with a Nanoscope IV controller (Digital Instruments, Santa Barbara) and Keithley 236 multimeter, the details of which can be found elsewhere.[10]

A representative AFM image of the lamellar solid of PdSC$_{12}$ is shown in Fig. 1 along with a schematic of the bilayer structure. Bundles of elongated features extending over several hundreds of nanometers are the lamellar bilayers that have been subjected to study the *I-V* characteristics. Each feature has a width of ~40 nm, which correspond to a bundle of ten units (each unit being 3.6 nm). Due to the poor resolution of the gold-coated tip, the individual units could not be seen in the AFM image, although our earlier STM study has revealed the essential nanostructure.[6]

A typical *I-V* curve obtained from PdSC$_6$ is shown in Fig. 2(a). Clearly, the *I-V* curve exhibits a non-Ohmic behavior and is asymmetric. The current is low close to zero bias

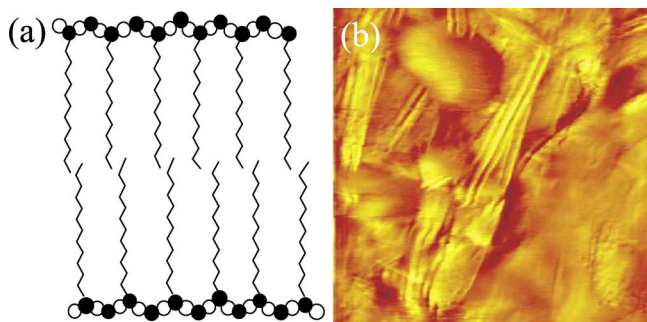a)Author to whom correspondence should be addressed. Electronic mail: kulkarni@jncasr.ac.in.

FIG. 1. (Color online) (a) A schematic of PdSC$_{12}$, which self-assembles in organic media to form lamellar bilayer structures. (b) AFM topography of PdSC$_{12}$ deposited on HOPG. The elongated features represent bilayers. Image size is $1.6 \times 1.6 \ \mu m^2$.

FIG. 3. A semilog plot of the resistance of Pd-alkanethiolate bilayers against the actual bilayer thickness [d(001) spacing from powder x-ray diffraction data[4]]. The intercept of the linear fit gives R_0, the contact resistance, as 5.9 kΩ.

and increases almost linearly with bias voltage up to ± 0.2 V [see the inset below Fig. 2(a)] beyond which there is a sudden rise in the current, especially in positive bias. Similarly, the variation in the current in the high bias region is roughly linear but with a higher slope. The different linear regimes in the spectrum are marked by the dotted lines. At the crossover region (+0.46 V), we observe a small but well-defined peak, corresponding to a NDR feature.

The I-V characteristics for bilayers with increasing chain lengths (PdSC$_8$ and PdSC$_{16}$) are given in Figs. 2(b) and 2(c). It is clearly seen that the overall current decreases with increasing chain length of the thiolate. The low current region near zero bias lies between +0.4 and −0.5 V in PdSC$_6$ [Fig. 2(a)], while in PdSC$_{16}$ [Fig. 2(c)], it lies between ± 0.75 V. Accordingly, the NDR feature is shifted to a higher bias

value (+0.8 V), but with a diminished intensity appearing like a shoulder in the crossover region. The width of the low current region varies proportionally with the bilayer thickness, as can be seen from Fig. 2(d).

A linear I-V with low current around the zero bias is akin to the transport behavior of alkanethiols.[11–16] The most common situation for long-range electron transport, as encountered in donor-bridge-acceptor assemblies and metal-insulator-metal junctions, is where the Fermi level of the electrodes occurs in the middle of the highest occupied molecular orbital/lowest unoccupied molecular orbital gap for the organic molecule and in this situation, coherent nonresonant tunneling, also known as superexchange tunneling, is the mechanism of electron transport.[16–18] For alkanes up to a certain length and for low voltages, the current through the junction is given by

$$I = I_0 e^{-\beta d}, \tag{1}$$

where d is the length of the molecular bridge (chain length) and β is an energy-dependent decay parameter characterizing the molecule.[16–18] Hence, in nonresonant tunneling regime, the current falls off exponentially with increasing distance or chain length. β is a measure of the tunneling efficiency through the alkyl chains, a higher value indicating lower tunneling efficiency.[19] Measurements on self-assembled monolayers of alkanethiol junctions by various techniques employing Hg drop electrodes[13,16] and C-AFM (Refs. 19 and 20) with varying chain lengths have estimated a β value of 1 ± 0.1 Å^{-1}, indicating a lower tunneling efficiency. For conjugated systems with high tunneling efficiency, β is found to be small, 0.4 ± 0.2 Å^{-1}.[21,22]

In this study, the resistance of the thiolate bilayer is calculated from the linear regime of the low bias region in the I-V curve [see inset of Fig. 2(a)]. For nonresonant tunneling,[19]

$$R = R_0 e^{\beta d}, \tag{2}$$

which follows directly from Eq. (1), d being bilayer thickness. A semilog plot of the resistance versus bilayer thickness (Fig. 3) ranging from hexyl to hexadecane thiolates gives a linear variation, clearly indicating that the exponential dependence of resistance on bilayer thickness β, as calculated from the slope of the plot in Fig. 3, is 0.2 ± 0.04 Å^{-1}.
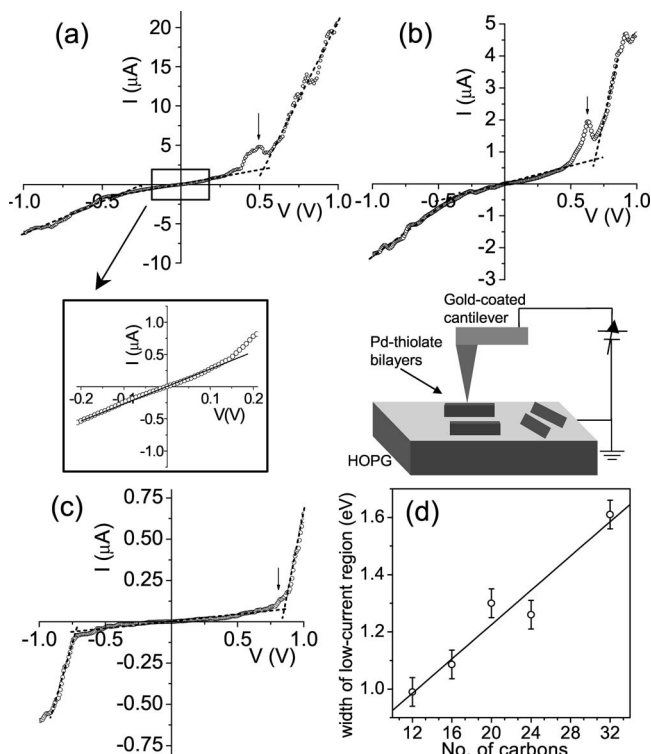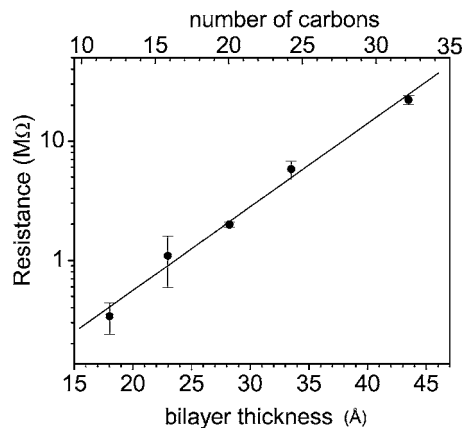

FIG. 2. I-V characteristics of PdSRs with increasing bilayer thickness from C-AFM (a) PdSC$_6$, (b) PdSC$_8$, and (c) PdSC$_{16}$. (d) Influence of chain length on the width of the low current region. The box below (a) gives a zoomed in view of the rectangular region marked. The different linear regimes are indicated by dotted lines. The arrows indicate NDR positions. A schematic of the configuration employed for C-AFM is also given.
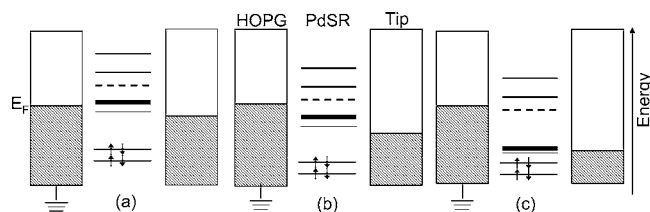
FIG. 4. A schematic energy level diagram showing different regimes of tunneling in PdSR; E_F denotes the Fermi level, the solid lines represent (depending on thickness) conducting states of varying strengths. The dashed line stands for a localized state. (a) V_{tip} is less positive; largely nonresonant tunneling, (b) V_{tip} is medium; resonant tunneling, and (c) V_{tip} is large; NDR.

A lower value of β indicates high tunneling efficiency and long-range transport in Pd-alkanethiolate bilayers. It also gives an idea that the nonresonant tunneling, in this case, is very different from that through the free space since weakly conducting chain states become resonant for small tip bias values. The mechanism of tunneling in the low bias regime is schematically shown in Fig. 4.

A sharp increase in the current with higher bias voltages (>0.6 V, see dotted line intersections in Fig. 2) can be attributed to resonant tunneling.[16,17] This happens when the Fermi level of the electrode approaches the energy of the molecular orbitals resulting in electron tunneling. The bias at which this sudden jump occurs shifts toward higher values for larger bilayer thickness [Fig. 2(d)] due to larger barrier widths. Thus, it suggests that the current derived is not only due to the one-dimensional Pd–S chain but also includes contributions from free space and possibly from the hydrocarbon chains in the two-dimensional bilayer. Asymmetry in the I-V might be arising from the difference in the work functions of gold (AFM tip) and graphite electrodes.

The appearance of NDR peak is quite interesting. Recently, it has been predicted that single alkane dithiolate molecules bridging transition metal nanoelectrodes can exhibit NDR, on the basis of *ab initio* and semiempirical calculations.[23] In our case, however, there is a charge transfer between metal ion and sulfur in the chain itself.[7,24] Due to this, similar to interface states, our system has states with localized character.[25] The decrease of current with increase of bias is due to the tunneling of electrons through such states. Moreover, since the charge transfer is unidirectional, the current flow encounters localized states only in one direction. The nature and characteristics of such charge-transfer state get renormalized and depend strongly on the multiple tunneling pathways between chains, which tailor the critical bias at which these states appear. Interestingly, the very formation of such states with a degree of localization depends strongly on the interchain width as well as sample quality and morphology of the substrate together with the electric field gradient.[26] In fact, the hopping induced competition between delocalization along the charge transfer pathway in the chain and the space limited tunneling between chains together with electric field induced localization quantify NDR behavior in these systems (see Fig. 4).

In conclusion, we have probed the electrical characteristics of lamellar palladium alkanethiolates with varying chain length using C-AFM. The resistance measured from the low bias region varies exponentially with the chain length (simi-lar to alkanethiol monolayers) but β is five times lower suggesting a different nonresonant tunnel mechanism. At higher bias, resonant tunneling occurs through molecular states leading to a sudden jump in the current. Interestingly, a NDR feature is seen at the crossover region due to resonant conduction through localized states arising from unidirectional charge transfer between S and Pd. It would be potentially useful to monitor the NDR behavior with changing electric field gradient especially in presence of magnetic metal ions such as Ni.[24]

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