PHYSICAL REVIEW B **72**, 115438 (2005)

Electronic transport properties of Pd-H junctions between two PdH$_x$ ($x=0,0.25,0.5,0.75,1$) electrodes: A nonequilibrium Green's function study

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(Received 28 March 2005; revised manuscript received 17 June 2005; published 28 September 2005)

Using a fully self-consistent nonequilibrium Green's function method combined with the density functional theory, the transport properties of Pd-H junctions between two PdH$_x$ ($x=0,0.25,0.5,0.75,1$) electrodes are investigated systematically. Three different hydrogen bridges are considered, including a single hydrogen atom configuration, a hydrogen molecule configuration with the H—H bond axis parallel to the transport direction and a complex Pd$_2$H$_2$ configuration where the H$_2$ molecule dissociates. For the pure Pd nanojunction, the transmission spectrum drops sharply near the Fermi level and gives an average conductance of about $1.8G_0$. Four channels are found to have significant contributions to the conductance. The electronic structures of the electrodes are modified by the doping of H in the bulk. The presence of hydrogen between and in two electrodes changes the transmission spectra obviously, while the number of the eigenchannels of the junction is only determined by the electronic structure of the neck region. For the pure Pd electrodes, the calculated conductances of three kinds of hydrogen bridges are about 1.1, 0.5, and 0.9 G_0, respectively. For the heavy doping of H in the Pd electrodes, the conductances of hydrogen bridges with a hydrogen molecule or complex Pd$_2$H$_2$ configurations range from 0.3 to 0.7 G_0. The calculated results agree very well with the experimental values.

DOI: 10.1103/PhysRevB.72.115438 PACS number(s): 73.40.Jn, 73.63.Rt, 71.20.Be

I. INTRODUCTION

In recent years, molecular electronics has attracted much research attention with the development of experimental techniques, such as the scanning tunnelling microscopy (STM) and mechanically controllable break junction (MCBJ).[1,2] Previous experiments and theories have shown that the conductance of a single molecule is sensitive to the contact region between the molecule and electrodes, which induces many discrepancies between the theoretical and experimental results.[3]

To understand the fundamental transport properties of molecular electronics, it is interesting to build a stable junction with the simplest molecule. Smit *et al.* used the MCBJ to produce a hydrogen molecule bridge between two platinum electrodes.[4] The conductance is close to one quantum unit ($G_0=2e^2/h$), carried by a single channel. The experimental phonon spectrum indicates that the hydrogen molecule forms a bridge configuration with the H$_2$ bond axis parallel to the transport direction. The theoretical studies have been performed by several groups.[5–7] García *et al.* studied two kinds of arrangements of hydrogen between two Pt electrodes, where the H-H bond axis is parallel or perpendicular to the transport direction, and found that a complex Pt$_2$H$_2$ is responsible for the experimental histogram peak near $1G_0$.[6] Thygesen *et al.* found that the electronic transport is the result of a strong hybridization between the H$_2$ antibonding state and a combination of the *d*- and *s*-like orbitals of the Pt atoms.[7]

Recently, Csonka *et al.* measured the conductance of hydrogen molecule between two Pd electrodes.[8] When the amount of hydrogen is small, two stable configurations of hydrogen bridges are found, which have conductances of order 0.5 and 1.0 G_0, respectively. The conductance fluctuation measurements show that the configuration with $G=1.0G_0$ has more than one channel. If the amount of the hydrogen is increased, the conductance histogram peak at $1.0G_0$ disappears and there is a broader peak ranging from 0.3 to 0.6 G_0. The conductance behavior of Pd-H system is more complex than that of the Pt-H system. In the former, hydrogen molecules will dissociate and enter into the Pd bulk, which has been confirmed by the point contact spectrum. Very recently, Garcia-Suarez *et al.* studied the hydrogen bridge between two pure Pd electrodes theoretically and found that the conductance is about $0.6G_0$.[9] In their simulations, the pure Pd electrodes were used.

In this paper, we study the electronic transport properties of the Pd-H junctions between two PdH$_x$ ($x=0,0.25,0.5,0.75,1$) electrodes with the first principles method. Three different hydrogen bridges are considered, including a single hydrogen atom configuration, a hydrogen molecule configuration with the H-H bond axis parallel to the transport direction and a complex Pd$_2$H$_2$ configuration where the H$_2$ molecule dissociates. The existences of the H atoms both in the tips and electrodes are also considered.

II. METHOD

The electronic structures of all systems are calculated with the density functional theory (DFT) implemented in SIESTA code,[10] which solves the standard Kohn-Sham equations using numerical atomic orbitals as basis sets, and the

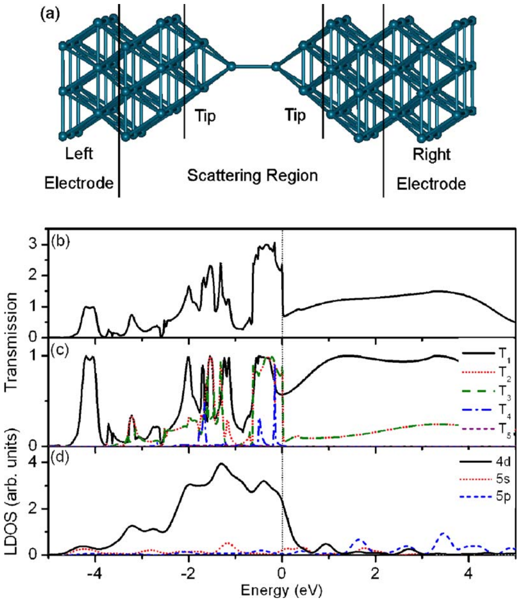

FIG. 1. (Color online) (a) The schematic picture of the pure Pd junction. (b) and (c) The total transmission and the main contributed eigenchannels for the pure Pd junctions. (d) The LDOS projected on the central two Pd atoms in the neck region.

electronic transport properties are explored with the fully self-consistent nonequilibrium Green's function (NEGF) method implemented in TranSIESTA code,[11] which has been applied in many systems.[12] Ceperley-Alder local density approximation is used and core electrons are modelled with Troullier-Matrins nonlocal pseudopotential,[13] while the valence electrons are expanded in a SIESTA localized basis set. To save our computational effort, single zeta plus polarization (SZP) basis for Pd atoms, and double zeta plus polarization (DZP) basis for H atoms are used. Test calculation gives the similar results by using DZP basis sets for all atoms. A cutoff of 100 Ry for the grid integration is used to present the charge density.

With these parameters, we calculated the electronic structure of the pure Pd bulk and the bond length and binding energy of a H_2 molecule. For the pure Pd bulk, the obtained band structure is similar with the previous result.[14] The calculated bond length and binding energy of the H_2 molecule are 0.79 Å and 4.84 eV, respectively, in good agreement with the experimental results of 0.74 Å and 4.48 eV.[15]

III. RESULTS AND DISCUSSION

First, we consider the conductance of a pure palladium junction without H_2. Contrasted to Au and Pt, which spontaneously form chains of atoms before the break in the STM or MCBJ experiments, Pd breaks essentially at the level of a single atom and can be viewed as a chain of two Pd atoms with atomic tips touching.[16] Here, the junction is modelled with two contacted Pd tips sandwiched between two Pd(001) surfaces, as shown in Fig. 1(a). Each tip contains five Pd atoms forming a pyramid configuration. The Pd(001) surface is represented by a (3×3) cell with the periodic boundary condition. The nearest Pd-Pd distance is 1.95 Å. The whole system is divided into three parts, the left electrode, the scattering region, and the right electrode. The scattering region includes two Pd tips and two surface layers of the left and right electrodes, where all the screening effects are included into the contact region and the charge distribution in the electrodes can be looked at as the same as that of the bulk phase. The charge density matrix of the scattering region is solved self-consistently with the NEGF method.

The transmission spectrum of the pure Pd junction at zero bias voltage is displayed in Fig. 1(b). The transmission coefficient drops sharply from 2.4 to 0.7 in a narrow energy window $[-0.02,0.02]$ eV around the Fermi level (set as zero), and gives an average conductance of $1.8G_0$. This value agrees well with the experimental result.[8] Figures 1(c) and 1(d) show the local density of states (LDOS) projected on the central two Pd atoms in the neck region and the transmission eigenchannels. It is clear that the transmission is contributed by the Pd's d orbitals. The Fermi level locates at the edge of the d band, which results in the sharp drop of the total transmission at the Fermi level. Four eigenchannels contribute to the total transmission. The dominant channel T_1 is contributed by a combination of the Pd's s and d_{z^2} orbitals, the degenerate T_2 and T_3 channels origin from the Pd's d_{xz} and d_{yz} orbitals, and T_4 channel mainly comes from the Pd's d_{xy} orbitals. This result is similar to that of the previous studies.[5,17,18]

When the Pd junction is set in the H_2 atmosphere, the conductance histograms change obviously, which may originate from both the formation of hydrogen bridges between two Pd tips and the doping of hydrogen in the electrodes.[8] At first, we consider the hydrogen bridges sandwiched between two pure Pd electrodes. Three different kinds of hydrogen bridges have been suggested,[8] including a single hydrogen atom (H configuration), a hydrogen molecule with the H-H bond axis parallel to the transport direction [$H_2(p)$ configuration] or a complex Pd_2H_2 [$H_2(v)$ configuration], as shown in the insert of Fig. 2(a). In our calculation, the lengths of Pd-H bonds are fully relaxed with the Pd atoms fixed at their bulk positions. The optimized distances of the Pd-H bonds are 1.65, 1.73, and 1.78 Å for the H, $H_2(p)$, and $H_2(v)$ configurations, respectively. The distances between two H atoms in the $H_2(p)$ and $H_2(v)$ configurations are 0.97 and 2.26 Å, respectively, and the hydrogen molecule dissociates in the $H_2(v)$ configuration.

The transmission spectra for these three configurations are shown in Fig. 2(a). It is clear that the transmission coefficients and the numbers of eigenchannels change remarkably. For the $H_2(p)$ configuration, the total transmission coefficient is about 0.5 at the Fermi level carried by a single channel. For the H and $H_2(v)$ configurations, the total transmission coefficients are about 1.1. The conductance of the H configuration is dominated by a single channel, while more than one channel contribute to the conductance of the $H_2(v)$ configuration, which results from the direct interaction between two Pd atoms in the neck region. From the LDOS projected on the central neck region [Pd_2H_n $(n=1,2)$], as shown in Fig. 2(b), we find that the bonding and antibonding states of the hydrogen locate far away from the Fermi level and the large

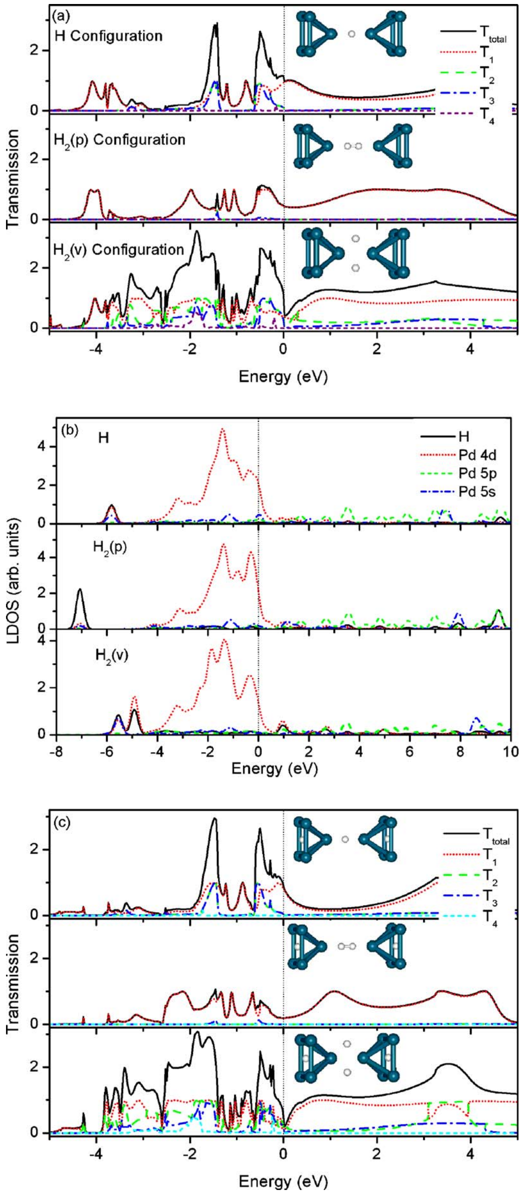

FIG. 2. (Color online) (a) The total transmission spectra of three different hydrogen bridges between two pure Pd electrodes without and with doping of a H atom in the tips. (b) The LDOS projected on the central Pd_2H_n ($n=1,2$) complex for different hydrogen bridges. (c) The transmission eigenchannels of three different hydrogen bridges.

DOS around the Fermi energy mainly comes from the *d* band of Pd. The conductances of these junctions are possibly due to the hybridization of *d* bands of Pd with the states of the hydrogen atom, and the main channels in the H and $H_2(p)$ configurations come from the H's *s* orbital, Pd's *s* and d_{z^2} orbitals.[5]

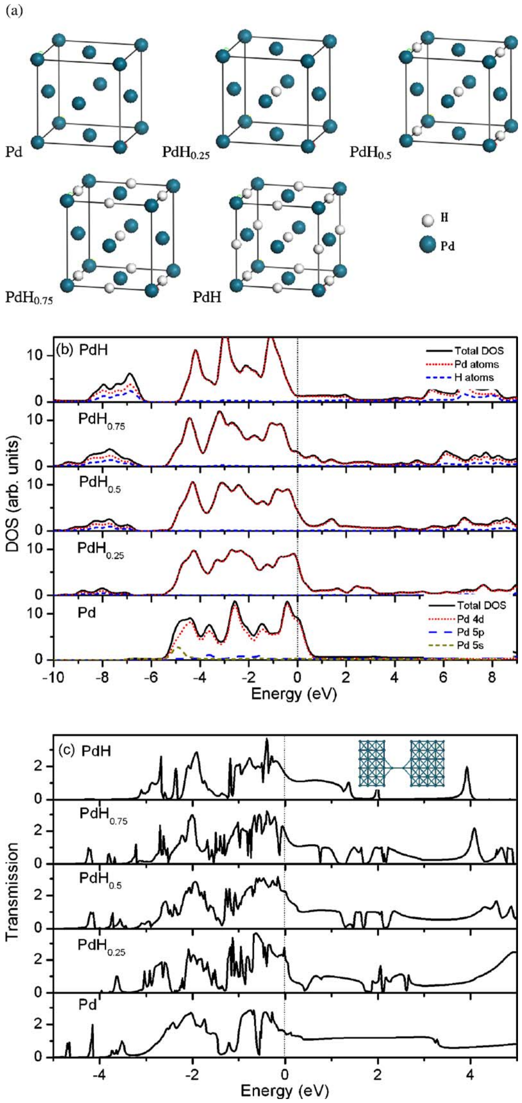

FIG. 3. (Color online) (a) The geometric structures of PdH_x ($x=0,0.25,0.5,0.75,1.0$) hydrides. (b) The DOS and LDOS projected on Pd and H atoms of five kinds of PdH_x hydrides with different doping concentration. (c) Transmission spectra of two-Pd-atom wire connected between PdH_x electrodes.

Since hydrogen molecules may dissociate and migrate into the Pd bulk, it is possible that hydrogen atoms exist in both the tips and electrodes when the amount of hydrogen is increased. Figure 2(c) shows the calculated transmission spectra for three hydrogen configurations between two pure Pd electrodes with a hydrogen atom doped in each tip. The hydrogen atom is placed at the central site of the layer containing four Pd atoms. Compared with the above junctions which have no hydrogen doped in both tips, the doping of H atom in the tips does not change the main features of the transmission spectra, while the magnitudes of the total transmission coefficients reduce.

Then, we consider the doping of H atoms in the electrodes. Previous work showed that H atoms may migrate into the octahedral sites of the Pd bulks.[19,20] Here, four kinds of PdH_x hydrides ($x=0.25$, 0.5, 0.75, and 1.0) are considered with the hydrogen atoms doped in the octahedral sites of the Pd bulks, as shown in Fig. 3(a). In our calculations, the lattice constants of the PdH_x ($x=0.25$, 0.5, 0.75, and 1.0) are expanded by 1.98%, 3.01%, 4.01%, and 5.99% with respect to the pure Pd's value of 3.89 Å, respectively. These values agree well with the previous work.[19] The DOS of the bulk and LDOS projected on the Pd and H atoms are plotted in Fig. 3(b). Due to the formation of PdH_x hydrides, the width

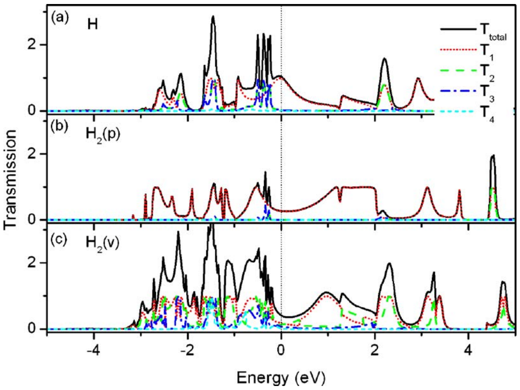

FIG. 4. (Color online) Transmission spectra of Pd—H junctions between two PdH electrodes with (a) H, (b) $H_2(p)$, and (c) $H_2(v)$ hydrogen bridges.

of the Pd's *d* band becomes narrow, which indicates that some states belonging to the Pd's *d* band deplete. A new band is formed far below the bottom of the *d* band corresponding to the bonding state between the Pd and H atoms. Especially, the Fermi energy level shifts upward relative to the Pd's *d* band and reduces the DOS at the Fermi level.

To illustrate the modification on the electronic transport properties of the Pd-H junctions due to the presence of H atoms in the electrodes, we build a simple model of a two-Pd-atom nanowire suspended between two PdH_x electrodes, as shown in the inset of Fig. 3(c). For the pure Pd electrodes, the nanowire is anchored at the hollow site of Pd(001) surface. Differently, it is more complex for the PdH_x hydrides electrodes, where the hollow site may contain a doping H atom. Especially, there are two different surface structures along the (001) direction for the $PdH_{0.25}$ and $PdH_{0.75}$ electrodes. We consider different anchoring sites and find that the profiles of transmission spectra do not change much. The transmission spectra for different doping concentrations are displayed in Fig. 3(c). It is clear that the transmission spectra are similar near the Fermi level and the total transmission coefficients range from 1.5 to 2.3. Moreover, some transmission peaks above the Fermi level disappear and the widths of the transmission peaks below the Fermi level become narrow with the increase of the doping concentration. These reflect the changes of the electronic structures of the electrodes with the doping of H, where some states in the Pd's *d* band deplete due to the interaction between the Pd and H atoms.

Finally, the calculated transmission spectra and eigenchannels for hydrogen bridges between two PdH electrodes are presented in Fig. 4. The total transmission coefficients at the Fermi level are 1.0, 0.3, and 0.4 for the H, $H_2(p)$, and $H_2(v)$ configurations, respectively. Meanwhile, the numbers of the eigenchannels are the same as those of the hydrogen bridges between two pure Pd electrodes. This indicates that the number of the eigenchannels is only determined by the electronic structure of the neck region in the nanojunction.[5] In Table I, the average total transmission coefficients in a narrow energy windows $[-0.02, 0.02]$ eV around the Fermi level for three hydrogen configurations between two PdH_x electrodes are summarized. Different surface structures and anchoring sites are considered. For the pure Pd electrodes, the conductances of three hydrogen bridges are about 0.5 and 1.1 G_0, corresponding well to the experimental conductance histogram when a small amount of H_2 is admitted to the Pd junction. The conductances of the $H_2(p)$ and $H_2(v)$ configurations between two PdH_x ($x=0.75, 1.0$) range from 0.3 to 0.7 G_0, which are in good agreement with the experimental result of 0.3–0.6 G_0 when the amount of hydrogen is increased. For the H configuration between two PdH_x electrodes, the conductance is of order $1.0G_0$. We think this configuration is uncommon when the amount of H_2 is large.

IV. CONCLUSIONS

In conclusion, the electronic transport properties of the Pd-H junctions between two PdH_x ($x=0$, 0.25, 0.5, 0.75, and 1.0) electrodes are investigated by using the NEGF+DFT method. The transmission coefficient of the pure Pd junction drops sharply at the Fermi level and provides an average conductance of about $1.8G_0$. Four eigenchannels contribute to the conductance, which come from the Pd's $4d_{z^2}$, $4d_{xz(yz)}$, and $4d_{xy}$ orbitals. When the H_2 is admitted to the junctions, three different kinds of hydrogen bridges between two PdH_x

TABLE I. The average total transmission coefficients in a narrow window $[-0.02, 0.02]$ eV around the Fermi level for three hydrogen bridges between two PdH_x electrodes ($x=0, 0.25, 0.5, 0.75, 1.0$).

	Pd	Pd[a]	$PdH_{0.25}$	$PdH_{0.5}$	$PdH_{0.75}$	PdH
H configuration	1.09	0.90	1.24 0.98[b]	1.18 1.11[b]	1.03 0.88[b] 1.01[b]	1.04
$H_2(p)$ configuration	0.47	0.19	0.91 0.82[b]	0.41 0.73[b]	0.34 0.66[b] 0.27[b]	0.27
$H_2(v)$ configuration	0.93	0.45	1.26 1.59[b]	0.72 1.00[b]	0.63 0.51[b] 0.41[b]	0.41

[a] A hydrogen atom is doped in each tip.

[b] Different interface structures are considered due to the unequal surface structures and anchoring sites.

electrodes, including the H, $H_2(p)$, and $H_2(v)$ configurations, are considered. The transmission spectra vary due to the existence of H between and in two electrodes, while the numbers of the eigenchannels do not change with the doping concentration. For the hydrogen bridges between two pure Pd electrodes, the conductance of the $H_2(p)$ configuration is about $0.5G_0$, carried by a single channel. For the H and $H_2(v)$ configurations, the conductances are of order $1.1G_0$, where the latter is contributed by more than one channel. When the amount of the hydrogen is increased, the conductances of the $H_2(p)$ and $H_2(v)$ configurations between two PdH electrodes range from 0.3 to 0.7 G_0. The theoretical simulations reproduce the experimental results.

ACKNOWLEDGMENTS

This work was partially supported by the National Project for the Development of Key Fundamental Sciences in China (Grant No. G1999075305), by the National Natural Science Foundation of China (Grants Nos. 20303015, 50121202, 10474087), by the USTC-HP HPC project, by the SCCAS, and by the EDF of USTC-SIAS.

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