ISSN 1063-7834, Physics of the Solid State, 2010, Vol. 52, No. 3, pp. 641–648. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © K.M. Tsysar', D.I. Bazhanov, A.M. Saletsky, V.S. Stepanyuk, W. Hergert, 2010, published in Fizika Tverdogo Tela, 2010, Vol. 52, No. 3, pp. 593–599.

LOW-DIMENSIONAL SYSTEMS AND SURFACE PHYSICS

Effect of Hydrogen Impurity Atoms and Molecules on the Atomic Structure of Palladium Nanocontacts

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Received March 24, 2009; in final form July 17, 2009

Abstract—The interaction of hydrogen impurity atoms and molecules with palladium nanocontacts and its effect on the atomic structure and strength of the nanocontacts have been studied using the computer simulation. It has been revealed that the sorption of hydrogen atoms and molecules increases the specific cohesive energy between the palladium atoms nearest to the hydrogen atom in the chain of the nanocontact, which leads to an increase in the strength of the palladium nanocontact. An analysis of the electronic structure of the palladium nanocontact in the presence of the hydrogen molecule has demonstrated that the strong interaction of the molecule with the contact can result in its disassociation due to the hybridization of the *s* and *d* orbitals of palladium and the *s* orbitals of hydrogen atoms upon sorption in the nanocontact chain.

DOI: 10.1134/S1063783410030285

1. INTRODUCTION

Unique physical properties of nanostructures, such as the magnetism, quantum conductance, and high adsorption capacity, have attracted the particular attention of many scientific groups around the world. Investigations of properties of one-dimensional nanostructures, i.e., nanocontacts and nanowires, are of special interest. These structures are spontaneously formed during the operation of a scanning tunneling microscope between the microscope probe and the surface under investigation and also at points of fracture of solid crystals [1–3]. One of the unique properties of one-dimensional nanostructures is the quantum electronic conductance that manifests itself already at room temperature. In these structures, the current can be carried by only one electron [4–8]. Investigations of the electronic properties of one-dimensional nanostructures occupy an important place in modern research [9–13]. The experimental data confirm the theoretically predicted quantum nature of conductance of nanocontacts [3]: the conductance takes on integer values multiple to the conductance quantum $G_0 = 2e^2/h$, where e is the elementary charge and h is the Planck constant. However, there are a number of works in which the authors observed that the conductance deviates from integer values [13, 14]. This phenomenon is explained by the possible interaction with impurity atoms and molecules, which in small numbers can always be present in experiments [15, 16]. In the interaction, these impurities can strongly affect the nanostructures and change their atomic and, correspondingly, electronic structures and, as a result, their physical properties [17–20]. In this case, the presence of impurities can lead to the destruction or stabilization of the structure, i.e., to an increase in its strength [19]. Therefore, the investigation of the influence of impurity atoms and molecules on the properties of nanostructures is the most important problem of physics and chemistry of low-dimensional systems. In recent years, the attention of many scientific groups has been focused on theoretical and experimental investigations into the influence of impurities on palladium, gold, silver, and platinum nanocontacts and nanowires [3, 17–20].

The properties of the atomic and electronic structures of palladium nanocontacts have been investigated beginning with the experimental work by Matsuda and Kizuka [3], who were the first to produce a stable palladium nanocontact at room temperature by using the scanning tunneling microscope. It was also found in [3] that the palladium contacts have a quantum tunneling conductance. Subsequently, in many theoretical works, the authors studied in detail the atomic structure and electronic properties of one-dimensional palladium systems, obtained results on the conductance of palladium nanocontacts [5, 6, 15], and examined their magnetic properties [12, 21–23]. However, in these works, the properties of one-dimensional palladium structures were studied in the absence of impurities. At the same time, it has been

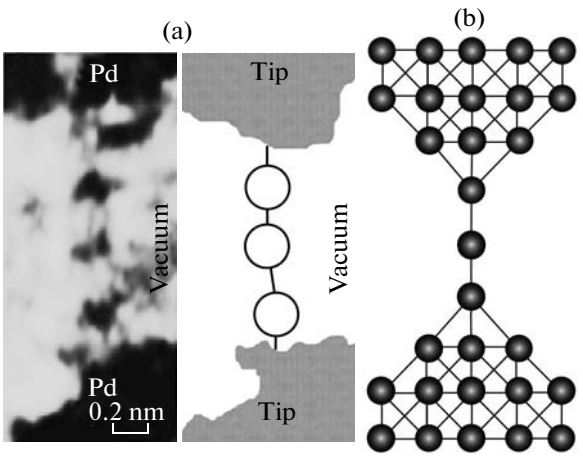

Fig. 1. Model of the palladium nanocontact: (a) palladium nanocontact produced by Matsuda and Kizuka [3] and (b) model of the palladium nanocontact used in the calculations.

experimentally established that the growth and formation of nanostructures always occur in the presence of impurity atoms and molecules of light gases, which can strongly affect the nanostructures under investigation and significantly change their atomic and electronic properties.

In the present work, we study the effect of hydrogen impurity atoms and molecules on the atomic structure and electronic properties of palladium nanocontacts. The hydrogen atoms are chosen as the impurity because palladium has a high hydrogen affinity and hydrogen is presented in many experiments on the formation of nanostructures and studies of their properties. Hydrogen with the highest probability interacts with palladium nanostructures during their formation and growth.

2. THE METHOD

In this paper, the calculations were performed using the ab initio molecular dynamics method implemented in the Vienna Ab-Initio Simulation Package (VASP) [24, 25]. The method is based on the Thomas–Fermi electron density functional theory, in which the system of the Kohn–Sham equations is self-consistently solved in the plane wave basis set [25]. The Thomas–Fermi theory allows one to reduce the solution of a many-body problem to the solution of a single-particle problem in some effective potential with respect to one variable, i.e., the electron density of the system, which is then used to calculate the energy of the system. The exact value of the total energy of the system was determined by integration in the reciprocal space over a special $4 \times 4 \times 1$ mesh of k points constructed according to the scheme proposed by Monkhorst and Pack [26]. In all calculations presented in this paper, the number of plane waves in the basis set was limited by a cutoff energy of 250 eV. The integration over the Brillouin zone was performed by the tetrahedron method with the Blochl correction [27].

The calculations were carried using the generalized gradient approximation [28] for the exchange–correlation potential and the projector augmented wave method [29]. In the present paper, the relaxation of the atomic structure of the system was performed until the forces acting on the atoms became 0.01 eV/Å^2 and changes in the total energy of the systems became 0.001 eV. The relaxation was performed according to the Newton method using the Hellmann–Feynman theorem on the calculation of the forces acting on the atoms in the system.

The structure of nanowires and nanocontacts was simulated by special periodic superlattices constructed as follows: the Born–von Karman boundary conditions were applied along all three basis directions of the unit cell, and, therefore, the atoms of the unit cell interacted with their images filling the surrounding space.

In the study of the properties of palladium nanocontacts, we used the structure of the contact obtained by Matsuda and Kizuka in their experimental work [3]. The nanocontact was simulated as a tetragonal periodic supercell with a three-atom chain of Pd atoms (along the Z axis) located in vacuum between two Pd electrodes [12]. The electrodes were simulated as the Pd(001) face-centered cubic surface (Fig. 1). The size of the cell was chosen so that the atomic chain would not interact with its image upon translation by ~10 Å.

3. RESULTS AND DISCUSSION

First, we studied the effect of hydrogen on the atomic and electronic structures of ideal one-dimensional palladium nanowires, which are a simplified model of the nanocontact that makes it possible to investigate only interatomic interaction within the wire chain.

In our calculations, the palladium nanowire was simulated by the periodic supercell with five-atom palladium chain located along the Z axis (Fig. 2a). The sizes of the cell in the OY and OX directions were chosen to be sufficiently large (~10 Å) so that the atomic chain would not interact with its image upon translation. We considered three possible positions of the sorbed hydrogen atom near the nanowire (Fig. 2): the hydrogen atom is located at the side of the palladium atom (the "linear" configuration, Fig. 2b), the hydrogen atom is located in the vicinity of the nanowire chain (the "triangular" configuration, Fig. 2c), and

the hydrogen atom is located within the nanowire chain (Fig. 2d). The calculations showed that the sorption of the hydrogen atom near the chain (the triangular configuration) is energetically most favorable, and the gain in the total energy is ~0.3 eV with respect to the other two configurations. Taking into account that palladium has a high hydrogen affinity and can form the hydride PdH, we additionally considered one more configuration in which the nanowire interacts with a large number of hydrogen atoms. Since it was established that the position of the hydrogen atom between the palladium atoms at the side of the wire chain is energetically favorable, we considered the structure containing one hydrogen atom per palladium atom using a "zigzag" configuration (Fig. 2e) as an example.

Then, in this work, we studied the stability of the palladium nanowires in the presence of hydrogen impurity atoms. For this purpose, we theoretically calculated the cohesive energies between the palladium atoms in the nanowires both with and without hydrogen impurities. The cohesive energy between the Pd atoms in an ideal nanowire without impurities was calculated from the formula

$$E_{coh}^{pure} = (E_{tot}^{pure} - N_{Pd}E_{isol}^{Pd})/N_{Pd}, \quad (1)$$

where N_{Pd} is the number of Pd atoms in the system ($N_{Pd} = 5$ in our case), E_{isol}^{Pd} is the energy of the isolated Pd atom, and E_{tot}^{pure} is the total energy of the system.

Since our calculations revealed that the sorbed hydrogen atom is located at the side of the chain, we calculated the cohesive energy only for the triangular configuration in the case of sorption of one hydrogen atom and the zigzag configuration. The analysis of the electronic structure in the triangular configuration showed that the electronic structures of the hydrogen atom and the nearest palladium atoms (Pd1, Pd2) (Fig. 2c) are changed because of the strong interaction between them. As a result, apart from the s–d_{z^2} band hybridization between the palladium atoms in the wire [10, 12], there arises a new hybrid band, which consists of the d_{z^2} and $(d_{x^2} + d_{xy})$ states of the palladium atoms Pd1 and Pd2 and the s state of the hydrogen atom. As a consequence, the symmetry of the bonds between the palladium atoms in the nanowire is broken. Therefore, in order to calculate the specific cohesive energy E_{coh}^{Pd-Pd} between the atoms Pd1 and Pd2 nearest to the hydrogen atom, we use the expression

$$E_{coh}^{Pd-Pd} = \left(E_{coh}^{pure} + \frac{\Delta E_{coh}^{Pd-H}}{2}\right), \quad (2)$$

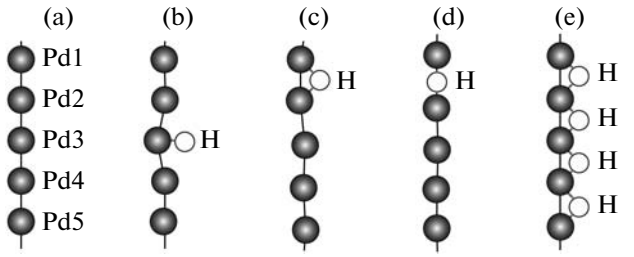

Fig. 2. Possible configurations of the palladium nanowire in a hydrogen atmosphere: (a) pure Pd nanowire, (b) "linear" configuration, (c) "triangular" configuration, (d) configuration "inside the chain", and (e) "zigzag" configuration. Dark spheres are Pd atoms, and white circles are H atoms.

where ΔE_{coh}^{Pd-H} is the cohesive energy between the Pd and H atoms,

$$\Delta E_{coh}^{Pd-H} = (E_{tot} - E_{tot}^{pure} - E_{isol}^{H})/2, \quad (3)$$

E_{isol}^{H} is the energy of the isolated hydrogen atom, and E_{tot} is the total energy of the nanowire with the hydrogen impurity atom.

The specific cohesive energy of palladium atoms (Pd1, Pd2) nearest to the hydrogen atom in the triangular configuration increases by more than 0.5 eV as compared to the configuration without impurity, for which the specific cohesive energy is $E_{coh}^{pure} = 1.3$ eV in the equilibrium state of the nanowire (Fig. 3a). For the other palladium atoms Pd3, Pd4, and Pd5 distant from the hydrogen atom (Fig. 2c), the cohesive energy is almost the same as the cohesive energy of the Pd atoms in the wire without impurities because of the weak interaction of these atoms with the hydrogen atom.

Thereafter, we studied the electronic structure of the palladium nanowire with several sorbed hydrogen atoms using the zigzag configuration as an example. The calculations showed that the interactions between the palladium atoms in the wire are identical for this configuration. Therefore, the specific cohesive energy per atom for this configuration was calculated from the relationship

$$E_{coh}^{Pd-Pd} = (E_{coh}^{pure} + E_{coh}^{Pd-H}), \quad (4)$$

$$E_{coh}^{Pd-H} = \frac{(E_{tot} - N_{Pd}E_{coh}^{pure} - N_{H}E_{isol}^{H} - N_{Pd}E_{isol}^{Pd})}{2N_{Pd}}, \quad (5)$$

where N_H is the number of hydrogen atoms ($N_H = 5$ in our case).

As a result of our calculations, it was revealed that the specific cohesive energy of the palladium atoms in the zigzag configuration increases by more than 1 eV for each atom in the nanowire. On the other hand, the

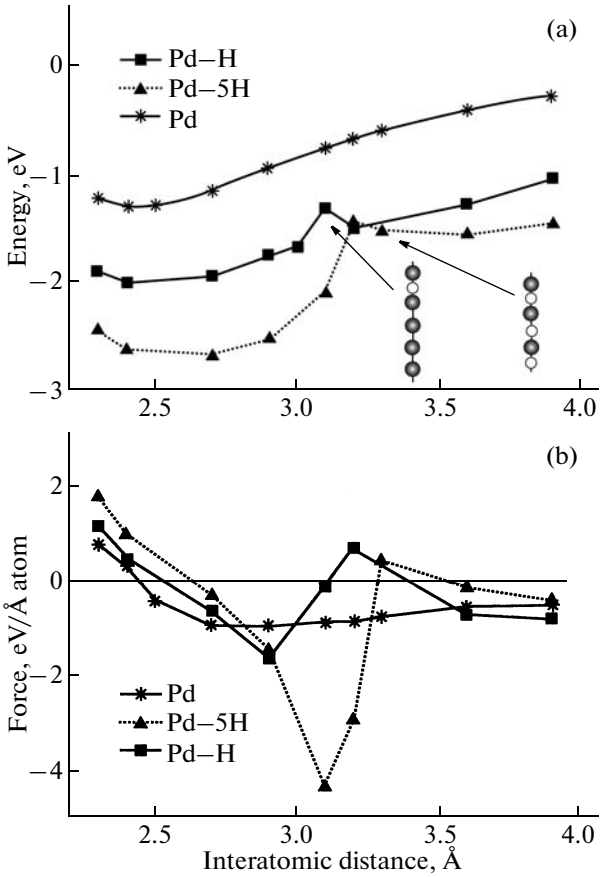

Fig. 3. Dependences of (a) the cohesive energy (per atom) and (b) the projection of the force (per atom) onto the axis parallel to the nanocontact chain on the interatomic distance. Designations: Pd corresponds to the palladium nanowire without impurities, Pd–H corresponds to the palladium nanowire with one hydrogen atom (the triangular configuration), and Pd–5H corresponds to the nanowire with five hydrogen atoms (the zigzag configuration).

calculations demonstrated that the presence of hydrogen impurities also increases the equilibrium distance between the palladium atoms in the nanowire as compared to the palladium nanowire without impurities. For example, the equilibrium distance between the palladium atoms increases to 2.5 Å for the triangular configuration and to 2.7 Å for the zigzag configuration, whereas, in our earlier work [12], we obtain a value of 2.43 Å for an ideal one-dimensional palladium wire. Therefore, the presence of the hydrogen atom stabilizes the nanowire with larger distances between the palladium atoms. Figure 3b shows the dependences of the projection of the force acting on the individual palladium atom onto the axis parallel to the nanowire chain on the interatomic distance. The maximum in the graph corresponds to the beginning of a decrease in the interatomic interaction energy in the palladium nanowire. It can be seen from the graph that, when number of hydrogen impurity atoms H increases (for the zigzag configuration), the maximum shifts to the right toward larger interatomic distances (Fig. 3b).

The calculations showed that, when the hydrogen atom is sorbed inside the chain of the palladium nanowire, its linear geometry is distorted (Figs. 2b, 2c). However, when the nanowire is elongated to interatomic distances larger than 2.8 Å, the hydrogen atom is embedded inside the wire and, as a result, the palladium nanowire again takes the ideal linear geometry. Our calculations for the triangular and zigzag configurations demonstrated that this transition leads to a change in the specific cohesive energy and forces in the system, which can be explained by the accompanying change in the electronic configuration. Figure 3a shows that, for both configurations under consideration, the dependence of the specific cohesive energy on the interatomic distance in the palladium wire with the hydrogen impurity atoms is changed for distances between Pd atoms larger than 2.8 Å. This change is reflected in the dependence of the forces acting on the atoms in the system (Fig. 3b). The jump is observed in the graph for the force when hydrogen is embedded in the nanowire structure (Fig. 3b). Therefore, the structural transition is observed in the system of the nanowire with the hydrogen impurity, which is related to the change in the location of sorbed hydrogen atom in the palladium nanowire and, consequently, with the change in the interaction between the atoms.

The next step was the study of the influence of hydrogen on the atomic structure of the palladium nanocontacts. As in the case of the one-dimensional palladium nanowire, we studied the effect of impurity atoms on the structure of the nanocontact by analyzing several possible positions of the hydrogen atom with respect to the nanocontact chain: (a) the hydrogen atom is located within the chain of the palladium nanocontact (Fig. 4a), (b) the hydrogen atom is located between the palladium atoms at the side of the nanocontact chain (zigzag configuration, Fig. 4b), and (c) the hydrogen atom is located near the chain of the palladium nanocontact (linear configuration, Fig. 4c).

The calculations demonstrated that the position of the hydrogen atom near the chain (zigzag configuration) is energetically favorable. The difference in the mean cohesive energy per atom is approximately equal to 0.2 eV with respect to all the other configurations under consideration. The sorption of the hydrogen atom strongly affects the structure of the nanocontact, and its chain becomes nonlinear. The central atom of the nanocontact chains is displaced by 0.65 Å with respect to its initial position in the chain. The distance between the Pd and H atoms in the linear configura-

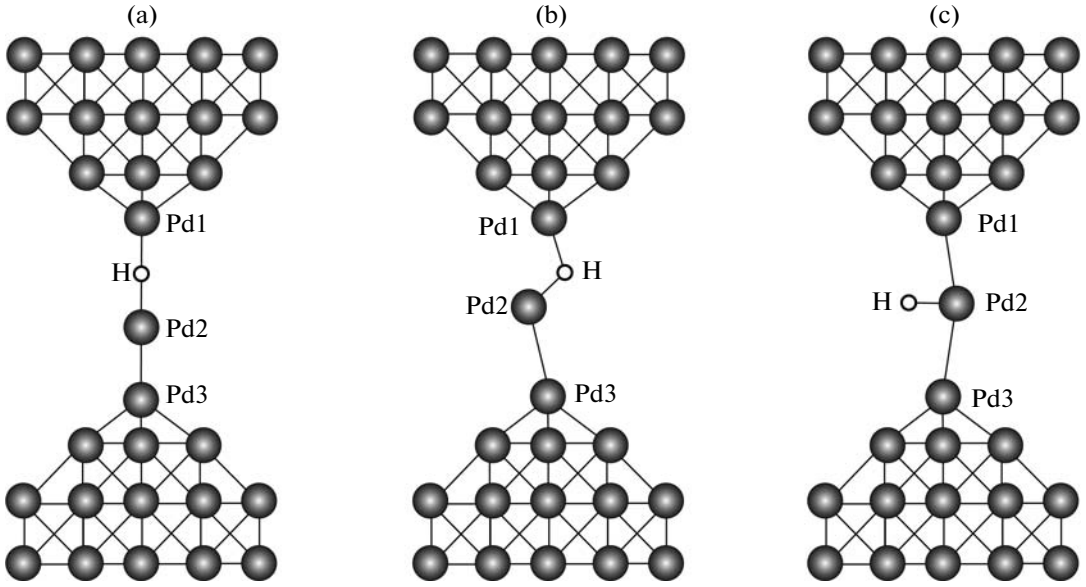

Fig. 4. Possible positions of the hydrogen atom in the chain of the palladium nanocontact: (a) "in the chain", (b) zigzag, and (c) linear configuration. Dark spheres are Pd atoms, and white circles are H atoms.

tion is 1.55 Å. It is interesting to note that the same value was obtained in the calculation of the equilibrium interatomic distance in a free dimer formed by the palladium and hydrogen atoms. The corresponding changes in the interatomic distances for the zigzag configuration (Fig. 4b) and for the case when the hydrogen atom is located inside the chain of the nanocontact (Fig. 4a) are presented in Table 1.

Then, we performed a series of calculations in the study of the influence of the sorbed hydrogen atoms on the properties of the palladium nanocontact for different distances between the electrodes. The distance between the electrodes was varied from 8 to 10 Å. These values correspond to the boundaries of the existence of the palladium nanocontact according to the data obtained by Matsuda and Kizuka [3] and in our previous work [12]. It was revealed that, in the zigzag configuration (Fig. 4b), the distances between the hydrogen atom and the nearest palladium atoms (Pd1, Pd2) (Table 1) do not change with a change in the distance between the electrodes. Only the distance between the central and terminal palladium atoms Pd2 and Pd3 (Fig. 4b) varies. Therefore, it can be expected that, with a further stretching of the palladium nanocontact with the hydrogen impurity, the probability of its breaking at the Pd–H bond is very low. The breaking can take place only at Pd–Pd bonds, i.e., between the palladium atoms.

We calculated the mean cohesive energy in the chain of the palladium nanocontact with one hydrogen impurity atom from the expression

$$E_{\text{coh}}^{NC} = (E_{\text{tot}} - E_{\text{electr}} - E_{\text{isol}}^{\text{H}} - N_{\text{Pd}}E_{\text{isol}}^{\text{Pd}})/N, \qquad (6)$$

where E_{electr} is the energy of the electrodes, N_{Pd} is the number of palladium atoms in the nanocontact chain ($N_{\text{Pd}} = 3$ in our case), and $N = N_{\text{Pd}} + N_{\text{H}} = 4$. The calculations of the mean cohesive energy showed that hydrogen stabilizes the nanocontact structure in the

Table 1. Characteristic interatomic distances in the palladium nanocontacts in the presence of hydrogen atoms

Distance between electrodes, Å	Pd2–H interatomic distance, Å		Pd1–H interatomic distance, Å	
	configuration		configuration	
	"zigzag"	H atom inside the nanocontact chain	"zigzag"	H atom inside the nanocontact chain
8.43	1.63	1.60	1.80	1.60
8.93	1.65	1.64	1.79	1.65
9.43	1.68	1.69	1.77	1.70
9.70	1.64	1.70	1.79	1.73

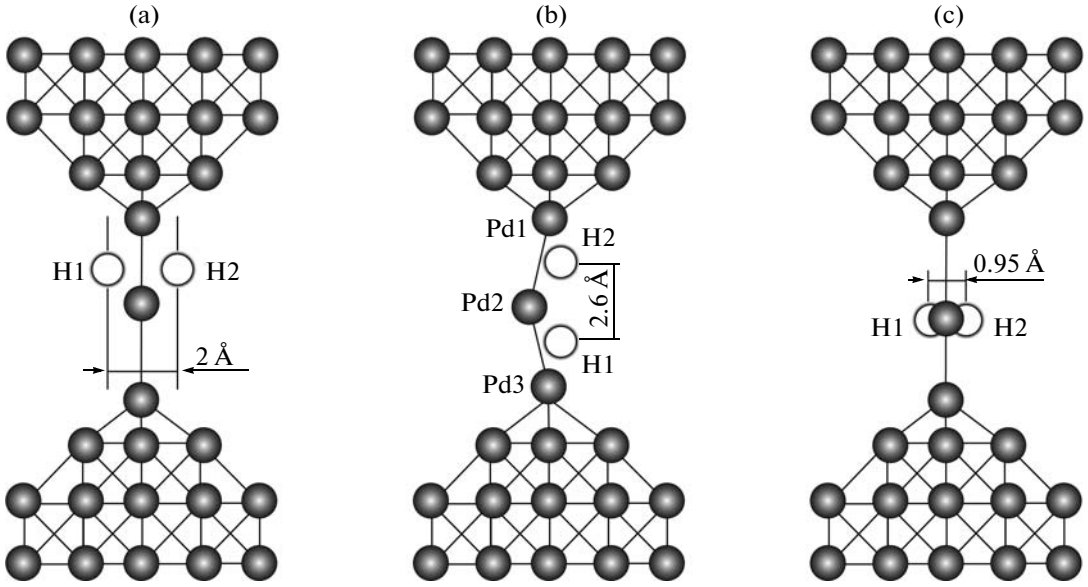

Fig. 5. Possible positions of the hydrogen molecule with respect to the chain of the palladium nanocontact: (a, b) H_2 molecule in the same plane with the nanocontact chain and (c) H_2 molecule in the plane parallel to the nanocontact chain. White circles are H atoms, and dark spheres are Pd atoms.

same way as in the case of the one-dimensional palladium nanowire. The mean cohesive energy per atom increases by $\Delta E_{\text{coh}}^{NC} \sim 0.1$ eV as compared to the mean cohesive energy per atom in the pure palladium nanocontact ($E_{\text{pure}}^{NC} = 2.78$ eV), which was calculated from the formula

$$E_{\text{pure}}^{NC} = (E_{\text{tot}} - E_{\text{electr}} - N_{\text{Pd}} E_{\text{isol}}^{\text{Pd}})/N. \quad (7)$$

Since not only hydrogen impurity atoms H but also hydrogen molecules H_2 were always presented in the experiments associated with the formation of nanocontacts, we also studied the interaction of the palladium nanocontact with the hydrogen molecule. In these investigations, we used the model of the nanocontact with a distance of 9.7 Å between the palladium electrodes, which corresponds to the initial instant of the breaking of the contact [3]. Therefore, this distance was chosen for demonstrating the influence of hydrogen on the strength of the palladium nanocontact. Our studies of the interaction of the H_2 molecule with the palladium atoms in the nanocontact chain revealed that the H_2 molecule can disassociate near the nanocontact chain due to the strong overlap between the *s* and *d* atomic orbitals of the palladium atoms and the *s* orbitals of the hydrogen atoms. The calculations showed that the disassociation of the hydrogen molecule occurs only in certain positions of the sorbed molecule with respect to the nanocontact chain. The hydrogen molecule disassociates if it is embedded inside the contact chain in the perpendicular direction or is located along the nanocontact chain in the same plane (Figs. 5a, 5b). If the H_2 molecule disassociates, the configuration under investigation is reduced to the aforementioned case of the interaction of the palladium nanocontact with two individual hydrogen atoms. The calculations of the mean cohesive energy E_1^{NC} between the palladium atoms in the nanocontact chain in the presence of the hydrogen molecule were performed for the case of its disassociation according to the formula

$$E_1^{NC} = (E_{\text{tot}} - E_{\text{electr}} - N_{\text{H}} E_{\text{isol}}^{\text{H}} - N_{\text{Pd}} E_{\text{isol}}^{\text{Pd}})/N, \quad (8)$$

where $N_{\text{Pd}} = 3$ and $N_{\text{H}} = 2$ are the numbers of palladium and hydrogen atoms in the nanocontact chain, respectively, and $N = N_{\text{Pd}} + N_{\text{H}} = 5$. In the case of disassociation of the molecule on the nanocontact, the mean cohesive energy increases by 0.18 eV as compared to the impurity-free configuration E_{pure}^{NC}. Therefore, the interaction between the nanocontact and the hydrogen molecule (even if it disassociates on the nanocontact chain) leads to the stabilization of the nanocontact.

Thereafter, we similarly investigated the behavior of the H_2 molecule located at the side of the Pd atom in the chain of the nanocontact in the plane parallel to the nanocontact plane (Fig. 5c). It was found that, in the case of this arrangement of the molecule with respect to the chain, it does not disassociate on the

Table 2. Characteristic interatomic distances (in Å) in the pure palladium nanocontact and in the palladium nanocontact in the presence of the H_2 molecule

Distance	Position of H_2 molecule			Without impurity
	according to Fig. 5a	according to Fig. 5b	according to Fig. 5c	
	$E_1^{NC} = 2.79$ eV	$E_1^{NC} = 2.78$ eV	$E_2^{NC} = 2.91$ eV	$E_{pure}^{NC} = 2.61$ eV
H–H	2.00	2.6	0.95	–
Pd1–H	1.76	1.77	2.75	–
Pd2–H	1.67	1.67	1.67	–
Pd3–H	–	1.77	2.75	–
Pd1–*OZ*	0	0.02	0	0
Pd2–*OZ*	0	–0.02	0	0
H–*OZ*	0	0.38	0.46	–
Pd1–Pd2	1.00	3.00	2.70	3.30
Pd2–Pd3	1.00	3.00	2.70	3.30
Pd1–electrode surface	2.75	2.72	2.70	1.87

contact. In this case, the mean cohesive energy E_2^{NC} was calculated from the relationship

$$E_2^{NC} = (E_{tot} - E_{electr} - E_{isol}^{H_2} - N_{Pd}E_{isol}^{Pd})/N_{Pd}, \quad (9)$$

where $E_{isol}^{H_2}$ is the energy of the isolated hydrogen molecule. The calculations showed that the presence of the hydrogen molecule in the nanocontact structure leads to an increase in the mean cohesive energy by 0.3 eV with respect to the configuration without impurity (Table 2). Therefore, the presence of the hydrogen molecule near the chain of nanocontact also leads to its stabilization.

4. CONCLUSIONS

Thus, the theoretical calculations presented in this paper demonstrated that hydrogen can be embedded in the structure of palladium nanowires and nanocontacts. The sorption of the hydrogen atom in the palladium nanowire results in an increase in the specific cohesive energy per atom by more than 0.5 eV. If the hydrogen atom is sorbed in the structure of the nanocontact, the mean cohesive energy (per atom in the contact chain) increases by ~0.1 eV. When the hydrogen molecule H_2 is sorbed within the chain of the nanocontact, the mean cohesive energy increases by ~0.3 eV as compared to the configuration without impurities. Therefore, as a result of the investigations performed in this work, we established that the sorption of hydrogen atoms and molecules in one-dimensional palladium nanostructures leads to an increase in their stability. Moreover, it was revealed that the hydrogen molecule can disassociate as a result of the interaction with atoms of the nanocontact chain.

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Translated by G. Tsydynzhapov