Hindawi Publishing Corporation
Advances in Condensed Matter Physics
Volume 2013, Article ID 130868, 4 pages
http://dx.doi.org/10.1155/2013/130868

Research Article

Catalytic Mechanism of Pd Adsorption on S-Terminated GaAs(001)-(2 × 6) Surface

Deng-feng Li, Zhi-cheng Guo, Bo-Lin Li, and Ming Luo

Department of Mathematics and Physics, Chongqing University of Posts and Telecommunications, Chongqing 400065, China

Correspondence should be addressed to Deng-feng Li; phyldf@gmail.com

Received 29 May 2013; Accepted 24 July 2013

Academic Editor: Haiyan Xiao

Structural and electronic properties of Pd adsorption on clean and S-terminated GaAs(001)-(2 × 6) surfaces are studied using first-principle simulations. Our calculations show that the Pd atom prefers to occupy the HH3 site. The Pd atom is lower than the S atom with 0.15 Å. The density of states analysis confirms that S–Ga bond plays an important role in Heck reaction. We also find that the Pd catalysis activity for Pd adsorption on clean GaAs(001)-(2 × 6) surface is weak while it is enhanced when the Pd atom is adsorbed on the S-terminated GaAs(001)-(2 × 6) surface, which is in good agreement with the experiments.

1. Introduction

Transition metals such as palladium (Pd) and platinum (Pt) are very important catalysts in the field of synthetic chemistry since they have favorable catalysis properties in Heck reaction [1–3]. Heck reaction plays an important role in drug discovery and pharmaceutical industries. However, the homogeneous Pd catalysis has some disadvantages, such as low reusability, difficulty of separating the catalyst from the products or solvents after reaction.

Recently, heterogeneous catalyst has been extensively investigated in order to reduce the waste of noble metal and develop the high yield of Heck reaction. For Pd adsorption on the sulfur-terminated GaAs(001) surface, experimental results show that the Pd catalyst is reusable [4–8]. Arisawa et al. prepare it with $Pd(PPh_3)_4$ [5]. They find that Pd is adsorbed on the S-terminated GaAs surface by X-ray photoelectron spectroscopy (XPS) and Pd can be reused at least 3 times. Takamiya et al. find that Ga–S bond fixes Pd on S-terminated GaAs(001)-(2 × 6) surface [6, 7], which plays an important role in Heck reaction. It effectively enhances the activity of the Heck reaction more than homogeneous Pd catalyst and could be recycled at least 10 times. In their further study [8], using a new Pd source of $Pd(OAc)_2$ and another technique of heated washing, they obtain a higher catalysis activity and stability for Heck reaction than the sophisticated method of deposition organometallic $Pd(PPh_3)_4$ on S-terminated GaAs(001)-(2 × 6) surface. Recently, Konishi et al. report that S-GaAs(2 × 6) surface structure is preserved after deposition $Pd(CH_3COO)_2$ on its surface using reflection high-energy electron diffraction (RHEED) and scanning tunneling microscopy (STM) [9]. However, the detailed structure and micromechanism are unknown. Earlier theoretical study is focused on the system of Pd adsorption on S-terminated GaAs(001)-(2 × 1) surface [10], which is different from the experiments [7, 9, 11].

In this paper, in order to explain the intrinsic mechanism of Pd catalysis, we investigate the surface structure and electronic property of Pd adsorption on S-GaAs(2×6) surface, based on the density functional theory (DFT). We confirm that the S–Ga band is essential for catalytic reaction.

2. Calculation Method

All the calculations were performed using Vienna ab initio simulation package (VASP) with cutoff energy 500 eV.

The ion-electron interaction was described by the projector augment wave method (PAW). Local density approximation (LDA) approach was used to deal with the energy of exchange correlation. The d electrons are included for Ga atom. Integration over an irreducible Brillouin zone was carried out using the Monkhorst-Pack grid of $5 \times 5 \times 1$. The unit supercell of S adsorption on GaAs(001)-(2 × 6) surface consists of 5 atomic layers and plus a vacuum layer equivalent to 5 atomic layers in thickness. The position of bottom layer As atoms was fixed. Hydrogenlike pseudoatoms with 0.75 charges were used to saturate the surface As dangling bonds at the bottom of slab. The optimized lattice constant was 5.610 Å, consistent with the experimental value of 5.653 Å [12].

3. Results and Discussions

3.1. Structural Parameters. To understand the important role of S atom in Pd catalyst on S-terminated GaAs(001)-(2 × 6) surface, we have investigated the atomic and electronic structures of Pd adsorption on pure GaAs(001)-(2 × 6) and S-terminated GaAs(001)-(2 × 6) surfaces. Nine possible adsorption sites, such as HH, HH2, HH3, B1, B2, B3, H1, H2, and H3, are considered, as shown in Figure 1. We obtain the most stable structure by the calculated adsorption energy. The adsorption energy is defined as $E_1 = E_{\text{Pd/GaAs(001)}} - E_{\text{GaAs(001)}} - E_{\text{Pd}}$ and $E_2 = E_{\text{Pd/S-GaAs(001)}} - E_{\text{S-GaAs(001)}} - E_{\text{Pd}}$ for Pd deposition on GaAs(001) and S-terminated GaAs(001) surfaces, respectively. $E_{\text{Pd/GaAs(001)}}/E_{\text{Pd/S-GaAs(001)}}$, $E_{\text{GaAs(001)}}$, $E_{\text{S-GaAs(001)}}$, and E_{Pd} denote the total energies of adsorbed system, the clean GaAs(001) surface, the S-terminated GaAs(001) and a free of Pd atom, respectively. The results show that Pd prefers to occupy the HH3 site both on clean and S-terminated GaAs(001)-(2 × 6) surfaces.

The detailed structures of Pd adsorption on GaAs(001)-(2 × 6) and S-terminated GaAs(001)-(2 × 6) surfaces are presented. We find that the position of Pd is lower than the surface As or S atom for both model cases, which is similar to the result of Pd adsorption on S-terminated GaAs(001)-(2 × 1) surface [10]. The height between Pd and underlying S layer is 0.15 Å and Pd–S bond length is 2.53 Å on S-terminated GaAs surface. Pd–As bond length is calculated to be 2.51 Å on clean GaAs surface, which is similar to the Au–As bond length of 2.50 Å for Au adsorption on GaAs(001) surface [13]. For Pd adsorption on S-terminated GaAs (001)-(2 × 6) surface, the S-S dimer remains on the substrate and the bond length is calculated to be 3.568 Å, which is consistent with the experimental findings that (2 × 6) reconstruction is preserved when Pd immobilized on the S-terminated GaAs from the RHEED and STM investigations [9].

3.2. Electronic Properties. Figure 2 shows the total density of states (TDOS) and local density of states (LDOS) of Pd adsorption on clean GaAs(001)-(2 × 6) surface at HH3 position. The calculated band gap is only 0.3 eV, which is remarkably smaller than that for clean GaAs surface (1.43 eV). The significant reduction of band gap induced by the adsorption of metal is also found in other systems, such as Pd adsorption on TiO_2 and Au adsorption on MgO [14–16]. It is derived from the fact of charge polarization by metal adsorption and an increase of the potential in the adsorption layer. For Pd adsorption on the clean GaAs(001)-(2 × 6) surface, the catalyst activity of Pd is weak due to a few electronic states at the Fermi energy.

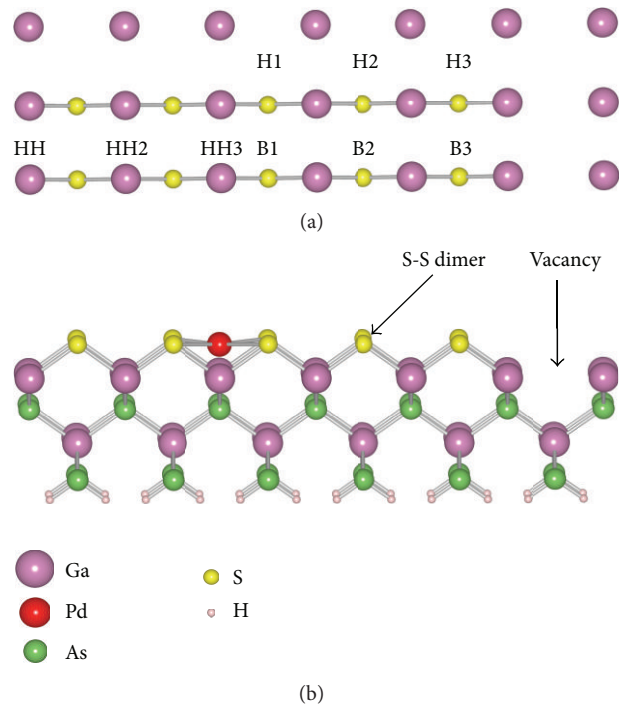

Figure 1: Top (a) and side views (b) structure of Pd adsorption on S-terminated GaAs(001)-(2 × 6) surface.

In Figure 3, the TDOS and LDOS of Pd adsorption on S-terminated GaAs(001)-(2 × 6) surface at HH3 site are presented. Compared with the TDOS of S-terminated GaAs(001)-(2 × 6) surface, we find that the Pd adsorption makes the DOS shift to lower energy, and the Fermi level exists above the conduction band, which is attributed to the strong interaction between Pd adatom and substrate. In addition, the band gap for Pd adsorption on S-terminated GaAs(001) surface is almost disappeared. It is because that the metal induced gap states (MIGS) are found in the energy gap, which is composed of Ga 4p and S 3p states. MIGS can lead to increasing the activity of chemical reaction due to the increase of the probability of getting electrons. It is consistent with the experimental result of important role for S–Ga bond in Heck reaction [7, 9]. On the other hand, comparing the DOS of Pd adsorption on clean GaAs(001) surface, we can see that the electronic state at the Fermi level is remarkably increased for Pd adsorption on S-terminated GaAs(001) surface. It indicates that the Pd catalysis activity is enhanced. Meanwhile, DOS at the Fermi level is mainly arisen from the contribution of Pd 4d and S 3p states, and the hybridization between Pd 4d and S 3p states both in valence band and conduction band is also found. Therefore, a strong Pd–S bond is formed on the surface.

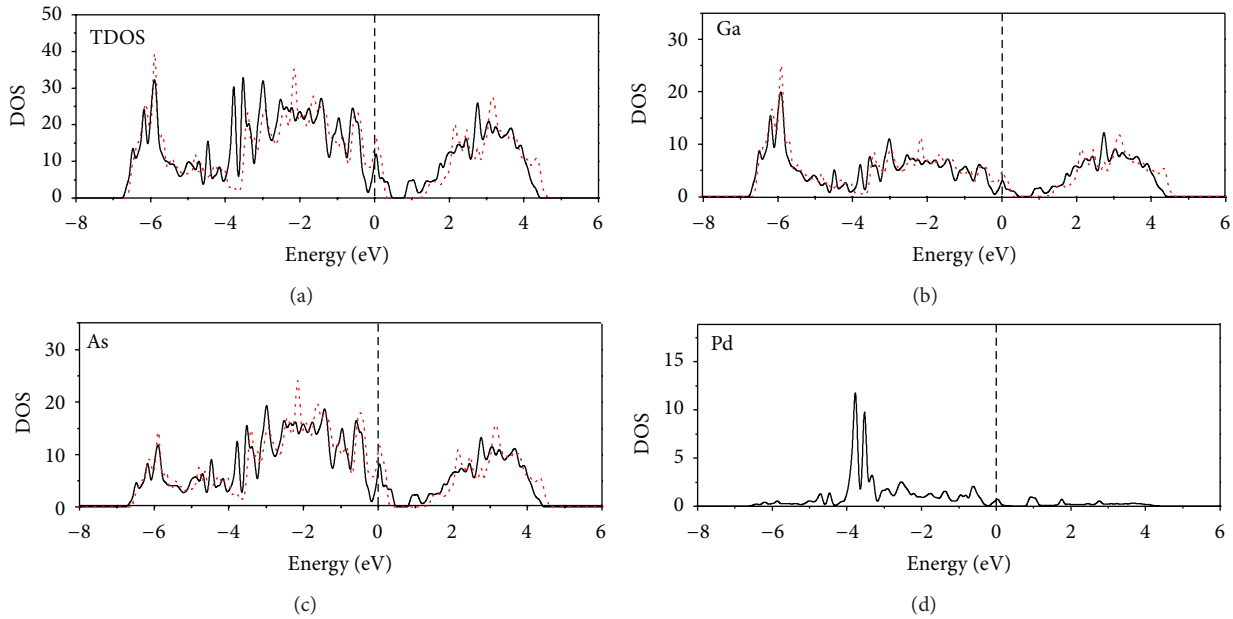

Figure 2: The total and local density of states (DOS) of Pd adsorption on clean GaAs(001)-(2×6) surface at HH3 site. The dashed line denotes DOS for the clean GaAs(001)-(2 × 6) surface without Pd adsorption. The dashed vertical line at zero represents the Fermi level.

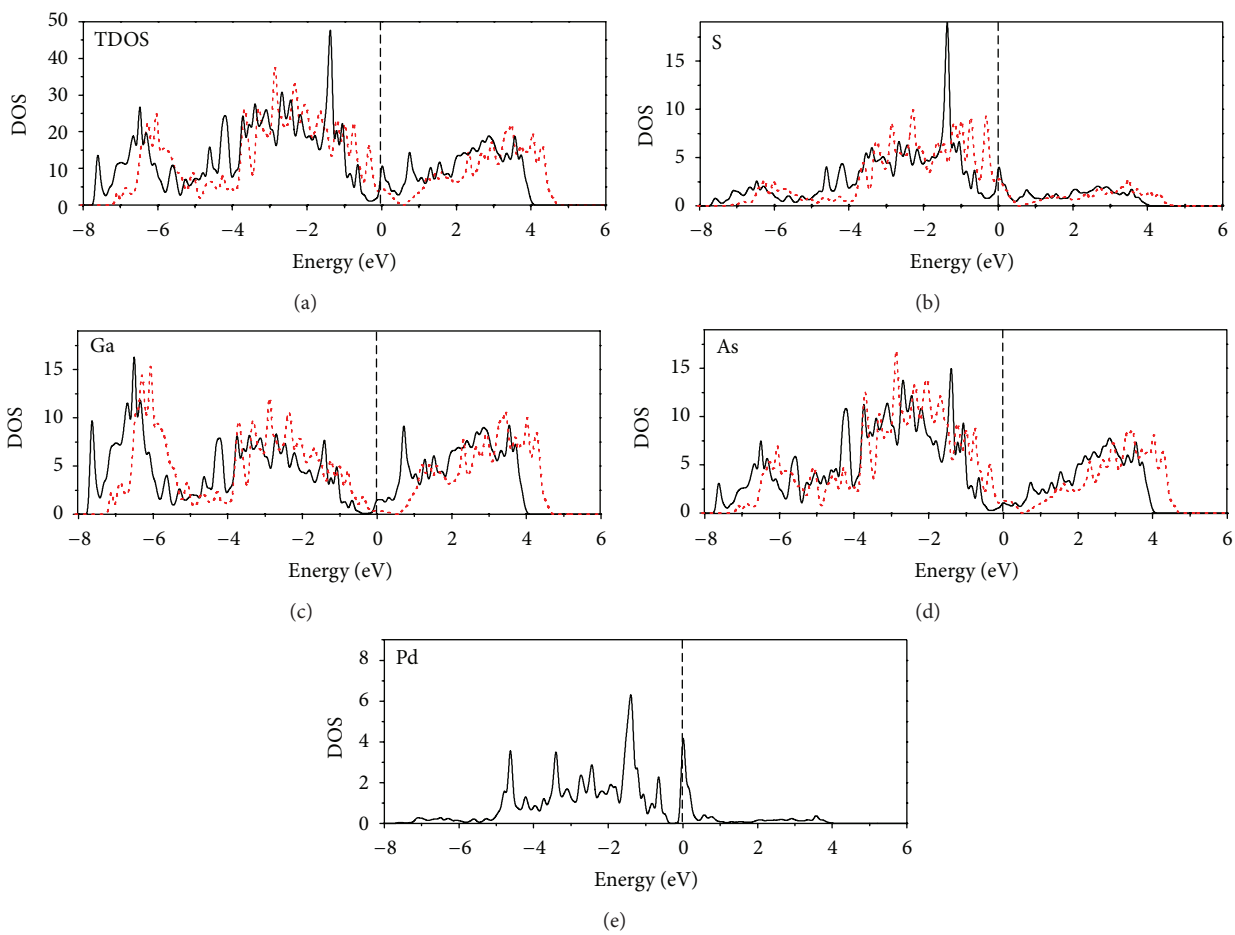

Figure 3: The total and local DOS of Pd adsorption on S-terminated GaAs(001)-(2 × 6) surface at HH3 site. The dashed line denotes DOS of S-terminated GaAs(001)-(2 × 6) surface without Pd adsorption.

4. Conclusion

We have investigated the structural and electronic properties of Pd adsorption on clean and S-terminated GaAs(001)-(2 × 6) surfaces using first-principle simulations. The calculated adsorption energy shows that Pd atom prefers to occupy the HH3 site. The detailed structure is presented and the Pd atom is lower than the S atom with 0.15 Å. The density of states demonstrates that S–Ga bond plays an important role in Heck reaction. We also find that the Pd catalysis activity for Pd adsorption on clean GaAs(001)-(2 × 6) surface is weak while it is enhanced when Pd atom is adsorbed on the S-terminated GaAs(001)-(2 × 6) surface, which is in good agreement with the experiments.

Acknowledgment

The authors acknowledge financial support from the Key Program of the Natural Science Foundation of Chongqing (cstc2012jjB50010).

References

[1] M. Smiljanic, I. Srejic, B. Grgur, Z. Rakocevic, and S. Strbac, "Catalysis of hydrogen evolution on Au(111) modified by spontaneously deposited Pd nanoislands," *Electrocatal*, vol. 3, no. 3-4, pp. 369–375, 2012.

[2] S. E. Bae, D. Gokcen, P. Liu, P. Mohammadi, and S. R. Brankovic, "Size effects in monolayer catalysis-model study: Pt submonolayers on Au(111)," *Electrocatal*, vol. 3, no. 3-4, pp. 203–210, 2012.

[3] H. Y. Xu, Y. N. Guo, Z. M. Liao et al., "Catalyst size dependent growth of Pd-catalyzed one-dimensional InAs nanostructures," *Applied Physics Letters*, vol. 103, no. 20, Article ID 203108, 2013.

[4] N. Nishiwaki, T. Konishi, S. Hirao, Y. Yamashita, H. Yoshikawa, and M. Shimoda, "Hydroxylated surface of GaAs as a scaffold for a heterogeneous Pd catalyst," *Physical Chemistry Chemical Physics*, vol. 14, no. 4, pp. 1424–1430, 2012.

[5] M. Arisawa, S. Tsukamoto, M. Shimoda, M. Pristovsek, and A. Nishida, "Novel organopalladium material formed on a sulfur-terminated GaAs(001) surface," *Japanese Journal of Applied Physics, Part 2*, vol. 41, no. 11, pp. L1197–L1199, 2002.

[6] I. Takamiya, S. Tsukamoto, M. Shimoda et al., "Novel palladium catalyst supported on GaAs(001) passivated by ammonium sulfide," *Chemistry Letters*, vol. 33, no. 9, pp. 1208–1209, 2004.

[7] I. Takamiya, S. Tsukamoto, M. Shimoda, M. Arisawa, A. Nishida, and Y. Arakawa, "Highly reactive organopalladium catalyst formed on sulfur-terminated GaAs(001)-(2 × 6) surface," *Japanese Journal of Applied Physics, Part 2*, vol. 45, no. 17–19, pp. L475–L477, 2006.

[8] M. Arisawa, M. Hamada, I. Takamiya et al., "Development of a method for preparing a highly reactive and stable, recyclable and environmentally benign organopalladium catalyst supported on sulfur-terminated gallium arsenide(001): a three-component catalyst, Pd-S-GaAs(001), and its properties," *Advanced Synthesis and Catalysis*, vol. 348, no. 9, pp. 1063–1070, 2006.

[9] T. Konishi, T. Toujyou, T. Ishikawa, G. R. Bell, and S. Tsukamoto, "Organopalladium catalyst on S-terminated GaAs (001)-(2×6) surface," *Journal of Vacuum Science and Technology B*, vol. 27, no. 5, pp. 2206–2208, 2009.

[10] A. Ishii, H. Asano, M. Yokoyama, S. Tsukamoto, S. Shuto, and M. Arisawa, "Structure determination of Pd-catalyst supported on S-terminated GaAs(001) using DFT calculation," *Physica Status Solidi (C) Current Topics in Solid State Physics*, vol. 7, no. 2, pp. 359–361, 2010.

[11] S. Tsukamoto, T. Ohno, and N. Koguchi, "Scanning tunneling spectroscopy and first-principles investigation on GaAs(001)(2×6)-S surface formed by molecular beam epitaxy," *Journal of Crystal Growth*, vol. 175-176, no. 2, pp. 1303–1308, 1997.

[12] V. Milman, B. Winkler, J. A. White et al., "Electronic structure, properties, and phase stability of inorganic crystals: a pseudopotential Plane-Wave Study," *International Journal of Quantum Chemistry*, vol. 77, no. 5, pp. 895–910, 2000.

[13] S. Yang, L. Zhang, H. Chen, E. Wang, and Z. Zhang, "Generic guiding principle for the prediction of metal-induced reconstructions of compound semiconductor surfaces," *Physical Review B*, vol. 78, no. 7, Article ID 075305, 2008.

[14] Z. Yang, R. Wu, and D. W. Goodman, "Structural and electronic properties of Au on TiO_2(110)," *Physical Review B*, vol. 61, no. 20, pp. 14066–14071, 2000.

[15] J. F. Sanz and A. Márquez, "Adsorption of Pd atoms and dimers on the TiO_2 (110) surface: a first principles study," *Journal of Physical Chemistry C*, vol. 111, no. 10, pp. 3949–3955, 2007.

[16] M. Amft and N. V. Skorodumova, "Catalytic activity of small MgO-supported Au clusters towards CO oxidation: a density functional study," *Physical Review B*, vol. 81, no. 19, Article ID 195443, 2010.