

Migration of the subsurface C impurity in Pd(111)L. Gracia,^{1,2} M. Calatayud,² J. Andrés,¹ C. Minot,^{2,*} and M. Salmeron³¹*Departament de Ciències Experimentals, Universitat Jaume I, Box 224, 12080 Castelló, Spain*²*Laboratoire de Chimie Théorique, Université P. et M. Curie, 4, Place Jussieu case 137, 75252 Paris Cedex 05, France*³*Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

(Received 6 July 2004; revised manuscript received 5 October 2004; published 25 January 2005)

The diffusion of subsurface impurities such as C in palladium surfaces of (111) orientation has been studied under the generalized gradient approximation combining a pseudopotential plane wave scheme as implemented in the VASP code with the aim of providing a better understanding between theoretical and experimental behavior. We analyze the stability of different subsurface sites, the energy barriers separating them from neighboring sites and the corresponding energy profiles. It is found that the most stable sites are located between the first and second surface layers, in good agreement with the experiments.

DOI: 10.1103/PhysRevB.71.033407

PACS number(s): 68.35.Fx, 71.55.Ak, 66.30.Jt, 82.37.Gk

I. INTRODUCTION

The presence of small quantities of impurities can alter the structure and reactivity of materials such as optical, mechanical, and electronic properties of crystalline solids or surfaces. This change in electronic structure can affect the local reactivity of the substrate by enhancing or decreasing the ability of the surface to bind adsorbates and catalyze reactions. Cleaning by sputtering and exposure to reactive gases under ultrahigh vacuum conditions is usually sufficient to temporarily remove impurities bound externally to the surface or situated in the few outermost layers of the crystal. In some cases impurities in such sites can be quite stable, with significant energy barriers either to segregate onto the surface or migrate deeper into the bulk. Despite the interest generated, little is known about the diffusion processes of these subsurface impurity atoms.

Recent STM experiments^{1,2} report the presence of three types of impurity in the (111) Pd surface trapped between the first and second surface layers in interstitial sites. O and C have been proposed as the most likely candidates for the so called α and β impurities, respectively, while the presence of S is confirmed by Auger spectroscopy. The α and β impurities occupy octahedral sites. Third impurity, sulfur is located in substitutional sites in the first layer. The diffusion of these species is remarkable in that it appears to be confined to the plane parallel to the surface, and could be measured directly from the STM images at low temperatures. The values obtained for the diffusion activation energies were 0.65 and 0.72 eV for α and β impurities, respectively.

In this paper, we analyze the diffusion of a carbon impurity that can be present under the surface of Pd(111) by means of periodic calculations. We discuss the stability of the impurity atoms in octahedral and tetrahedral interstitial sites, and their barriers for interstitial diffusion. Diffusion toward the bulk and to the surface is found to be less favorable than the horizontal *in plane* motion: the impurity atom is then trapped in the subsurface in agreement with the experimental results. Energy profiles are calculated and the transition states associated to diffusion are characterized.

II. METHODOLOGY

All geometry optimizations and minimization of the total energy have been performed using the VASP program.^{3,4} The Kohn-Sham equations of the DFT have been solved with the generalized gradient approximation (GGA) proposed by Perdew and Wang,^{5,6} and the electron-ion interaction described by ultrasoft pseudopotentials,^{7,8} so that plane-wave expansion can be truncated at a cutoff energy of 290 eV. For the Brillouin-zone integration a $3 \times 3 \times 1$ Monkhorst-Pack special k -points grid has been used for the $(2\sqrt{3} \times 2\sqrt{3}) R30^\circ$ unit cell. Finally, a spin-restricted approach has been employed since spin polarization effects have been found to be negligible. Despite the intrinsic error of the GGA in vacancy formation in metals,⁹ this approach has been successfully used to investigate Pd surface phenomena with accurate results.^{10–13} In these references, a cutoff energy of 250 eV is used together with a $8 \times 8 \times 1$ k -points grid for a 1×1 surface cell. We have carried out convergence checks regarding the cutoff energy for the plane waves as well as the k -point grid for our systems, the difference in energy being in the order of 0.002 eV.

The surfaces were represented by periodic slabs using a vacuum of at least 10 Å between them. Two slab models are used, a three-layer slab containing 36 Pd atoms (Fig. 1) and a four-slab model containing 48 Pd atoms. The latter is used for studying the diffusion to the bulk (Sec. III C). Tests regarding the slab thickness show that the difference in surface energy between a bare three- and four-layer slab is 0.008 J m⁻² which is rather small. Our models represent a good compromise between accuracy and computational limitations. The dimensions of the $(2\sqrt{3} \times 2\sqrt{3}) R30^\circ$ unit cell used in our calculations are 9.526×9.526 Å and is 12 times bigger than the 1×1 unit cell. The topmost layer was relaxed in all calculations, whereas the bottom one was kept fixed to the relaxed slab positions of the clean Pd(111) surface. The intermediate layers are selectively relaxed depending on the system, the first neighbors of the impurity being always relaxed in their x, y, z positions. Relaxation of the second neighbors around the impurity results in a gain in energy of at most 0.05 eV. However, for some systems relaxation of

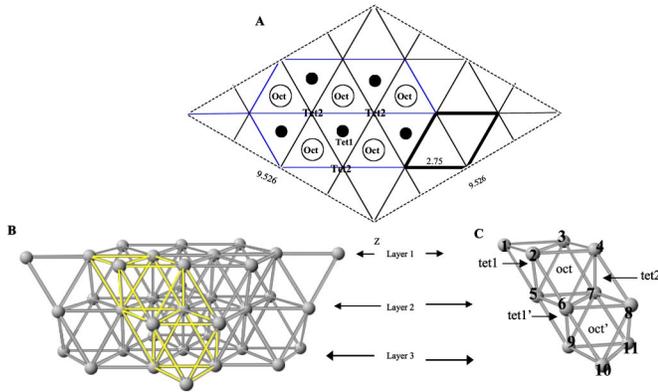


FIG. 1. Slab model for Pd (111). (A) Top view, the 1×1 and $(2\sqrt{3} \times 2\sqrt{3}) R30^\circ$ unit cells are shown in bold and dashed lines, respectively (distances in Å). The octahedral and tetrahedral sites are displayed. (B) Side view of the $(2\sqrt{3} \times 2\sqrt{3}) R30^\circ$ unit cell involving 36 Pd atoms (three layers of Pd, each layer contains 12 Pd atoms). (C) Detail of the sites present in the slab, octahedral (oct and oct') and tetrahedral (tet1, tet2 and tet1').

the second neighbors resulted in severe energy convergence problems and only first neighbors were relaxed for all systems. Thus, 0.05 eV can be considered as a measure of the degree of uncertainties due to the method and model used and shows the reliability of the approach chosen.

The energy profiles for the different diffusion processes have been calculated. The position of the projection of the impurity atom on the surface plane is taken as the reaction coordinate, the z coordinate of the impurity is optimized together with the nearest atoms of Pd. The transition states associated to such processes are calculated, the atom being initially placed in a triangle of Pd atoms at the border between two interstitial sites. The validity of the transition state obtained in this way was checked by a full vibrational frequency calculation achieved by calculation of the Hessian matrix followed by a diagonalization procedure to obtain the eigenmodes. The corresponding transition states only present one negative force constant. We then checked that the eigenvector associated with the negative force constant was related to the considered reaction pathway. This procedure allows one to obtain accurate transition states and activation barriers. The details of the geometry, energetics, and vibrational frequencies of these transition states are reported in the following section.

III. RESULTS AND DISCUSSION

We have considered the presence of a C atom in a Pd (111) slab. As a first step, the stability of the impurity is analyzed at both octahedral and tetrahedral subsurface sites. Then, the pathways for migration of such impurity trapped between the first and second Pd surface layers are calculated and the associated transition states are characterized. Finally the possibility of a migration process toward the bulk and to the external surface are also considered.

TABLE I. Relative energy in eV for the different sites in the Pd slab. TS indicates the energetic barriers of the transition states. The imaginary frequency associated to the transition vector is also shown in cm^{-1} . Three diffusion paths of the C atom have been explored, horizontal diffusion, vertical diffusion toward the bulk, and vertical diffusion toward the surface. The fourth column indicates the Pd atoms close to the studied site as labelled in Fig. 1(c).

	ΔE	Imaginary frequency	Neighbors [Fig. 1(c)]
Horizontal diffusion			
tet1	0.41		1,2,3,5
ts1	0.74	131.1	2,3,5
oct	0.00		2,3,4,5,6,7
ts2	0.86	347.3	4,6,7
tet2	0.52		4,6,7,8
Vertical diffusion toward the bulk			
oct (layer 1)	0.00		2,3,4,5,6,7
ts1'	1.93	312.3	5,6,7
tet1' (layer 2)	1.14		5,6,7,9
tet2 (layer 1)	0.63		4,6,7,8
ts2'	1.80	397.9	6,7,8
oct' (layer 2)	0.27		6,7,8,9,10,11
Vertical diffusion toward the surface			
oct	0.00		2,3,4,5,6,7
ts''	1.21	219.7	2,3,4
s''	0.66		2,3,4
tet1	0.41		1,2,3,5
ts1''	1.03	126.7	1,2,3
s1''	0.72		1,2,3

A. Stability of the carbon impurity in interstitial sites

Atomic carbon has been proposed to be the β impurity in STM experiments.¹ We have then explored the stability of such species at different sites in the surface. The highest symmetry sites are octahedral (oct) and tetrahedral with up and down orientation (tet1 and tet2) as in Fig. 1(c). We have explored the first interstitial region (between Pd layers 1 and 2) and the second interstitial region (between Pd layers 2 and 3).

The insertion of a C atom in a Pd slab is exothermic (positive value) calculated by the formula

$$E_{\text{ins}} = (E_{\text{C}} + E_{\text{slab}} - E_{\text{C+slab}})$$

the most stable site being the octahedral site (7.15 eV) in the first interstitial region in agreement with the STM experiments. Table I shows the relative energy for the different sites. Diffusion paths are discussed below. The imaginary frequency values associated to the transition states are also shown in Table I.

B. Horizontal diffusion

Figure 2 shows the schematic reaction path for the two possible interstitial diffusion pathways of C confined between the first and second layer.

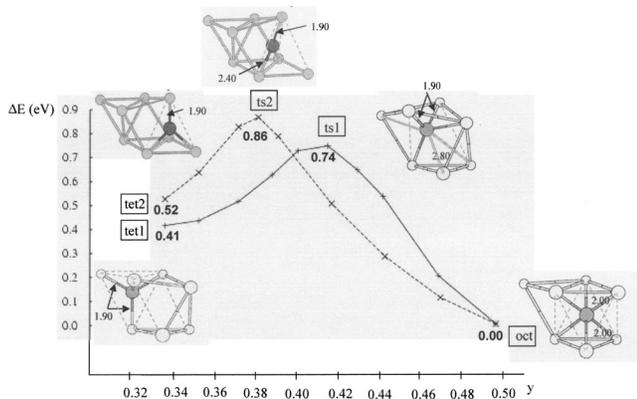


FIG. 2. Energy profiles for the diffusion of interstitial C impurities from octahedral to tetrahedral sites through two transition states. Relative energy in eV, selected distances in Å.

Tet1 → Oct: A straight path from the tetrahedral site tet1 to the octahedral position goes through the triangle formed by two atoms from the top Pd layer and one from the second Pd layer [number 2,3,5 in Fig. 1(c)]. A transition state ts1 has been characterized close to this geometry. The barrier energy is found to be 0.74 eV, which is close to the experimental value of 0.67 eV (Ref. 1) for C. An imaginary frequency associated to the reaction coordinate Table I confirms the nature of the transition state.

Tet2 → Oct: A straight path from the tetrahedral site tet2 to the octahedral position through the triangle formed by two atoms Pd in the second layer and one Pd atom in the top layer [atoms 4,6,7 in Fig. 1(c)]. A transition state ts2 is obtained for this geometry. The activation barrier (0.86 eV) is higher than for ts1, so the latter would be preferred.

C. Migration of the C impurity toward a bulk position

We have also investigated the stability of the octahedral and tetrahedral sites in the second interstitial spacing (between layers 2 and 3). Again, the octahedral site represents the most stable position of the three different high symmetry sites, as shown in Table I. However, this site is less stable than the oct site in the first interstitial region by 0.27 eV. In

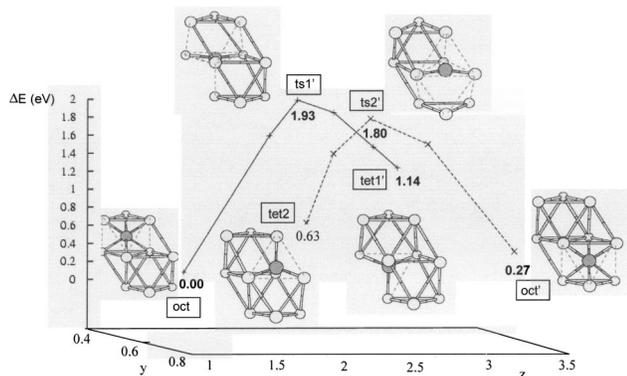


FIG. 3. Energy profile for the vertical displacement of C atoms during the diffusion toward a bulk position. Relative energy in eV, selected distances in Å.

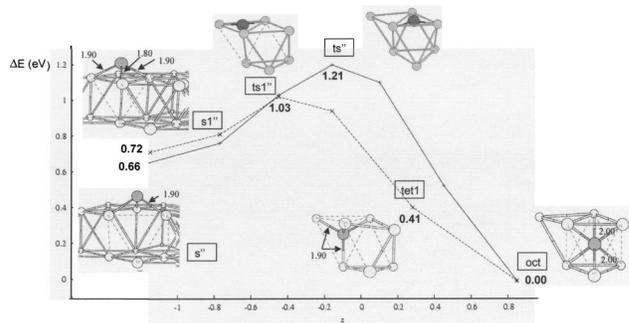


FIG. 4. Energy profile for the vertical motion of C atoms during diffusion toward the surface. Relative energy in eV, selected distances in Å.

this case we have used a four-layer slab. There are two possible pathways for the migration of C from an octahedral position in the first interstitial spacing to an oct position in the second one: (1) a vertical motion to a position tet1' between layers two and three (three atoms belong to the second layer, one to the third layer) followed by a horizontal migration to the oct' position; or (2) a horizontal migration in the first interstitial spacing to the tet2 position followed by a vertical motion to oct'. We have studied the vertical motions (oct → tet1') and (tet2 → oct') and drawn the energetic profile (Figs. 3 and 4). Our results show that vertical migrations toward the bulk are expensive in energy: the barriers for the vertical motions are 1.93 (ts1') and 1.80 eV (ts2') when two of the four layers are allowed to relax. These values are close, high and higher than those for the in-plane displacements. The reason is that there is no possibility for an in-plane relaxation when passing through a horizontal triangle (at least the horizontal cell vectors are fixed); on the contrary when the three atoms of the triangle do not belong to the same layer, there is a possibility for a z relaxation.

D. Migration of the C impurity to the surface

Finally, we have considered two pathways leading to the segregation of C from the subsurface to the surface. First, a vertical motion from an octahedral site to the surface site s'' through a transition state ts''. The barrier for this process is 1.21 eV. The second involves a horizontal migration consisting of a jump from oct to tet1 and then to the surface site s1'', through the transition state ts1''. The barrier is then 1.03 eV. We conclude then that even if expulsion from tet1 is easier, it is still energetically better for the carbon atom to remain confined in the subsurface region between the first and second Pd layers. The vibrational frequency analysis confirms the nature of the transition states.

IV. CONCLUSIONS

DFT calculations using periodic slab models have been carried out to study the diffusion of subsurface C impurity in Pd surfaces of (111) orientation. The main conclusions of

this work can be summarized as follows: (i) C insertion into the Pd surface is an energetically favorable process, being the subsurface C preferentially trapped in octahedral sites with a gain in energy of 7.15 eV. (ii) Horizontal migration takes place between octahedral and tetrahedral sites below the first Pd surface layer. The most favorable path involves a barrier of 0.74 eV. (iii) Diffusion to the bulk or segregation to the surface are energetically costly processes and as a consequence, the C atom is trapped in the subsurface interstitial region of the Pd slab in agreement with experimental results.

ACKNOWLEDGMENTS

This work was accomplished in the frame of the French GdR “Dynamique moléculaire quantique appliqué à la catalyse.” Computational facilities provided by IDRIS and CCR are also acknowledged. L.G. thanks the Ministerio de Ciencia y Tecnología, Project No. BQU2000-1425-C03-02 for financial support. M. C. was supported by the European Commission under Contract No. MCIF-1907. M. S. was supported by the Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

*Corresponding author. Email address: minot@lct.jussieu.fr

- ¹M. K. Rose, A. Borg, T. Mitsui, D. F. Ogletree, and M. Salmeron, *J. Chem. Phys.* **115**, 10927 (2001).
- ²M. K. Rose, T. Mitsui, J. Dunphy, A. Borg, D. F. Ogletree, M. Salmeron, and P. Sautet, *Surf. Sci.* **512**, 48 (2002).
- ³G. Kresse and J. Hafner, *Phys. Rev. B* **49**, 14 251 (1994).
- ⁴G. Kresse and J. Furthmuller, *Comput. Mater. Sci.* **6**, 15 (1996).
- ⁵J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1992).
- ⁶J. P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13 244 (1992).
- ⁷G. Kresse and J. Hafner, *J. Phys.: Condens. Matter* **6**, 8245 (1994).
- ⁸D. Vanderbilt, *Phys. Rev. B* **41**, R7892 (1990).
- ⁹T. R. Mattsson and A. E. Mattsson, *Phys. Rev. B* **66**, 214110 (2002).
- ¹⁰S. Surnev, L. Vitali, M. G. Ramsey, F. P. Netzer, G. Kresse, and J. Hafner, *Phys. Rev. B* **61**, 13 945 (2000).
- ¹¹M. Beutl, J. Lesnik, K. D. Rendulic, R. Hirschl, A. Eichler, G. Kresse, and J. Hafner, *Chem. Phys. Lett.* **342**, 473 (2001).
- ¹²R. Hirschl and J. Hafner, *Surf. Sci.* **498**, 21 (2002).
- ¹³R. Hirschl and J. Hafner, *Surf. Sci.* **498**, 37 (2002).