Applied Surface Science 279 (2013) 479

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Erratum

Erratum to “Growth of carbon structured over Pd, Pt and Ni: A comparative DFT study” [Appl. Surf. Sci. 268 (2013) 11–15]

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ARTICLE INFO

Article history:
Received 26 March 2013
Accepted 27 March 2013
Available online 9 May 2013

Unfortunately, I have committed a mistake and one of the authors was omitted in the original submission and I have lost the opportunity to amend this in the gallery proof. Prof. Gabriela Cabeza was my PhD advisor and the authorship of this original research was performed in the framework of my doctoral thesis.

The authorship of the manuscript must be written as:

Matías Abel Quiroga, Gabriela Fernanda Cabeza

DOI of original article: http://dx.doi.org/10.1016/j.apsusc.2012.11.081.

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http://dx.doi.org/10.1016/j.apsusc.2013.03.169

Applied Surface Science 268 (2013) 11–15

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Growth of carbon structured over Pd, Pt and Ni: A comparative DFT study

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ARTICLE INFO

Article history:
Received 1 October 2012
Received in revised form
12 November 2012
Accepted 15 November 2012
Available online 28 November 2012

Keywords:
Graphene
DFT
Pd
Ni
Pt

ABSTRACT

To elucidate the graphene-like structures mechanisms growth over the M(1 1 1) surface (M = Pd, Pt and Ni) we performed ab initio calculus in the frame of density functional theory with the exchange-correlation functional treated according to the Generalized Gradient Approximation (GGA). In order to avoid the problem that represent the complex interaction between the well formed graphene layer and the metallic surface, we recreate the carbon rings formation initial steps, by adding one by one carbon atoms over M(1 1 1) surface. With this strategy, the chemical bonding is always present until the graphene layer is well formed, in which case the GGA neglects van der Waals dispersive forces. We investigate the electronic properties by studying the band structure and the density of states.

1. Introduction

Discovered in 2004 [1], graphene is a perfect 2D hexagonal carbon layer with exceptional electronic and mechanic properties. Many metal surfaces are promising intermediaries for carbon growing into graphene. Hence, it has become very important to throw light upon the interaction between graphene and metals.

It is not easy to understand the graphene interaction with the metallic surface. Olsen et al. [2] discuss the importance of selecting theoretical frames to study this interaction. Because many exchange-correlations fail to explain this kind of adsorption, the problem must be treated by studying the van der Waals dispersion forces present in this interaction. Hamada and Otani [3] studied the graphene adsorption over metallic surface (Ni, Cu, Pd, Ag, Pt and Au) showing the importance of the van der Waals density functional.

From the electronic point of view, there are some metal-graphene systems for which the π-band has an important decrease in energy compared with the free graphene band, so the valence band and the conduction band open a gap around the K point in the Brillouin Zone, conducting the system to a semiconductor state. Meanwhile, for other metal-graphene systems, those characteristic bands do not have significant changes [4,5].

The graphene adsorption over different metal surfaces has been extensively studied. Giovannetti et al. [6] report that graphene adsorption over Pd is a chemisorption, because of the mean distance Z, between the graphene layer and substrate is less than 2.3 Å. Meanwhile, Khomyakov et al. [7] affirm that it is a chemisorption because of the Dirac cone distortion in the electronic structure in the Fermi level. On the other hand, Hu et al. [8] affirm that the graphene is physisorbed over Pd surface, while it is chemisorbed with a single Pd atom. Wintterlin and Bocquet [9] fixed, as a criterion, that if the graphene is separated by an equilibrium distance of 3.35 Å, the adsorption should be considered physisorption. Mittendorfer et al. [10] studied graphene on Ni(1 1 1) reporting the presence of two mean distances, one at 3.3 Å (typical physisorption), and the other at 2.17 Å.

By adding carbon atoms one by one over the metallic surface, we always keep the chemical bonding present, neglecting in this way, the van der Waals interaction. We also perform a band structure and density of states analysis to study the electronic properties of the graphene.

2. Computational details

Density Functional calculations were performed with the *Vienna Ab Initio Simulation Package* (VASP) [11–13]. The Kohn-Sham one-electron wave functions were expanded on a basis of plane waves with a cutoff value of 500 eV for the kinetic energy. The exchange-correlation functional was treated according to the Generalized Gradient Approximation (GGA) in the parameterization of Perdew–Wang (PW91) [14]. Previous studies [15] and present tests do not reveal any noticeable spin polarization effects for neither the substrate Pd models nor the adsorption atoms on them. Thus, all calculations (except for the free carbon atom and Ni) were spin-restricted.

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http://dx.doi.org/10.1016/j.apsusc.2012.11.081

The interaction between atomic cores and valence electrons was described by the projector augmented wave (PAW) method [16,17]. The blocked Davidson approach was applied as the electronic minimization algorithm. We used Monkhorst-Pack k-point mesh [18] and the Methfessel-Paxton technique [19] with a smearing factor of 0.2 for the electronic levels. The convergency of the k-point mesh was checked by increasing the k-point mesh until the energy had converged with a precision better than 1 meV/atom. In this way the size of the k-point mesh considered was 5 × 5 × 1.

Structures were optimized until the maximum forces acting on each atom became less than 10 meV/Å. The electronic structure for C adsorbed was analyzed in terms of Density of States (DOS).

3. Slab models

An FCC stacking layered structure was assumed for the calculations. The reference M(1 1 1) (M = Pd, Pt and Ni) surface was represented by four-layer slabs. Preliminary tests with slab models containing up to five atomic layers have shown that a slab with four layers provides converged results; the difference in the surface energy between four and five layer-slabs was about 0.005 eV. The repeated atom slabs were separated in *z* direction by a vacuum region equivalent to five interlayer spaces optimized to avoid the interaction between them. Atom positions in the bottom three layers were kept frozen as optimized for M bulk, whereas the other layer (closer to adsorbate) was allowed to relax completely within a maximum force criterion of 0.01 eV/Å, providing an interatomic distance relaxation never greater than 1.5%. The cell parameter was calculated to be 2.79 Å for Pd, 2.82 Å for Pt and 2.50 Å for Ni. As it could be expected, calculated GGA bond distances are longer than the respective experimental value (2.75 Å (Pd), 2.72 Å (Pt) and 2.49 Å (Ni) [20]).

4. Results and discussion

The current section is divided into two parts. In Section 4.1, in order to study the graphene structure mechanism's growth, we present the relaxed geometries of successive C incorporation in different M(1 1 1) surfaces with corresponded energies. In Section 4.2 we present Density of State and Band Structure analysis for the different systems.

4.1. Successive C incorporation and ring formation

In order to simulate the carbon structures growth dynamic, we proposed a tentative one by one C addition over Pd, Pt and Ni. The implemented metal surfaces were: ($\sqrt{3} \times \sqrt{3}$)R.30° supercell for Pd and Pt; and a (2 × 2) supercell for Ni. These supercells allow the match between the graphene and the metal surface [7].

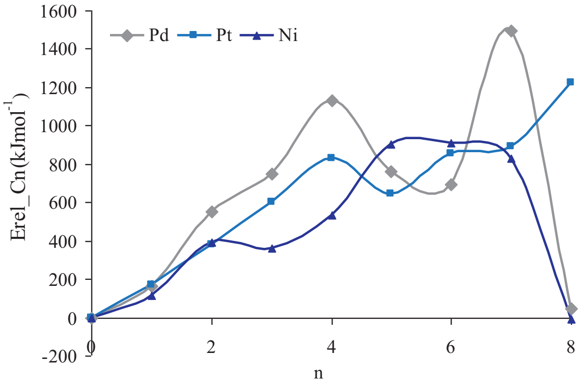

Fig. 1. *Formation energy related to graphene* vs. number of incorporated C atoms over Pd, Pt and Ni.

In order to study each step of the C incorporation, we defined the *formation energy related to graphene* ($E_{\text{rel\_Cn}}$) with the follow expression:

$$E_{\text{rel\_Cn}} = (E_{\text{Cn\_M}} - E_{\text{M}} - nE_{\text{C\_graph}})/n$$

where $E_{\text{Cn\_M}}$ is the total energy of the M(1 1 1) surface with n C atoms adsorbed; E_{M} is the total energy of the clean surface; $E_{\text{C\_graph}}$ is the total energy of a single C atom in a graphene monolayer. This $E_{\text{rel-Cn}}$ compares the single C atom specific energies: in the simulated structure versus in a graphene monolayer. If the $E_{\text{rel-Cn}}$ is a positive value, this means that each C atom prefers, energetically, to be bonded in its perfect graphene structure than to be in its structure over M surface.

In Fig. 1 we present the curve $E_{\text{rel-Cn}}$ versus n (the number of C atoms adsorbed). The clean surface energy is fixed to cero.

In Figs. 2–4 we present the successive C added geometries over M(1 1 1); while in Fig. 5, we present the final lateral perspective geometries.

The $E_{\text{rel\_C8}}$ is 46, 1223 and −12 kJ mol^{-1} for Pd, Pt and Ni, respectively. The $E_{\text{rel\_C8}}$ is much higher for Pt than for Pd and Ni, because the obtained final C structure over Pt is completely amorphous, which implies less involved energy respect to a well formed graphene monolayer.

The $E_{\text{rel-Cn}}$ increases linearly for C added on Pt. Meanwhile, for Pd and Ni, the situation is similar until $n = 8$, where the energy decreased close to cero. Just for C–Ni the final energy is a negative

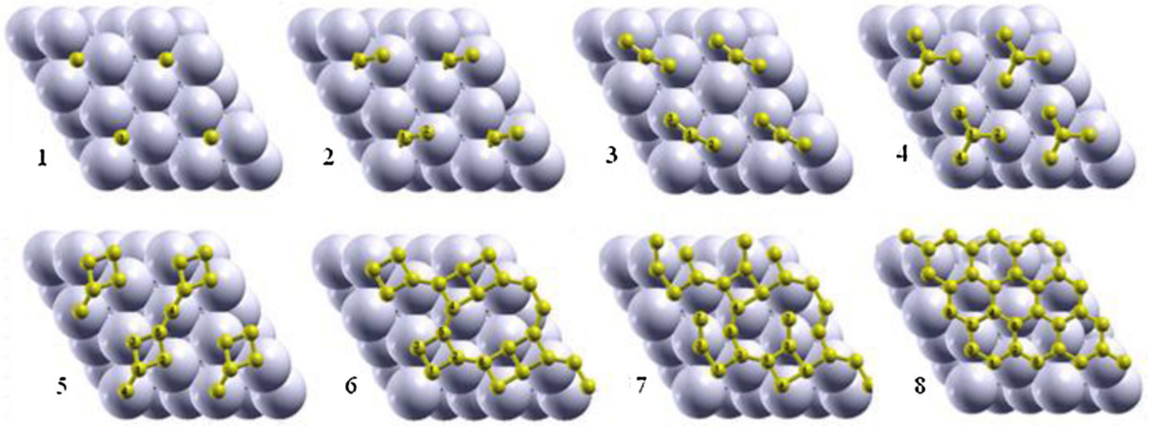

Fig. 2. Successive steps for C atoms incorporation over Pd surface with n running from 1 to 8. In the step 8, obtained graphene layer can be seen.

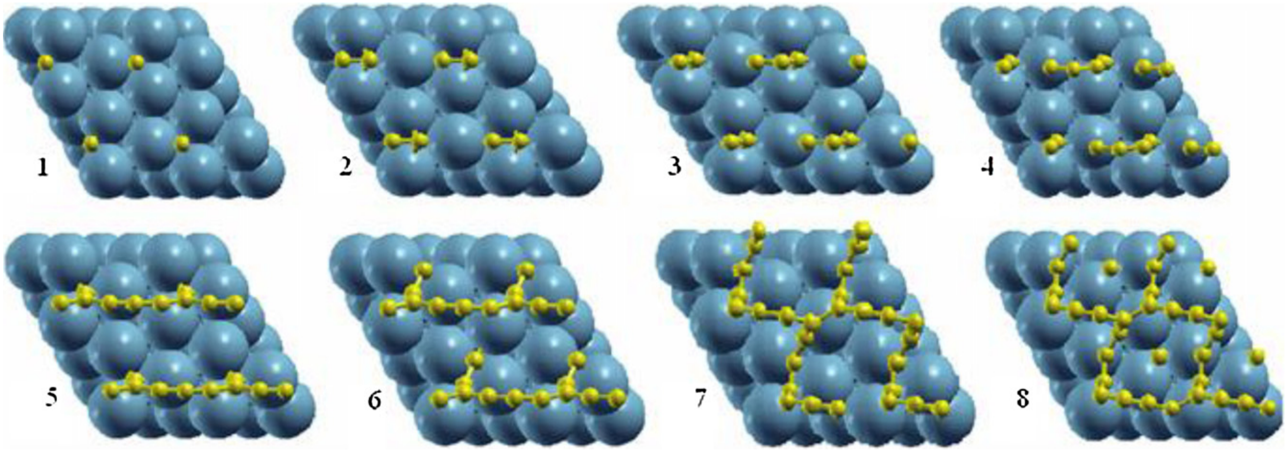

Fig. 3. Successive steps for C atoms incorporation over Pt surface. In the step 8, an amorphous carbon structured can be seen.

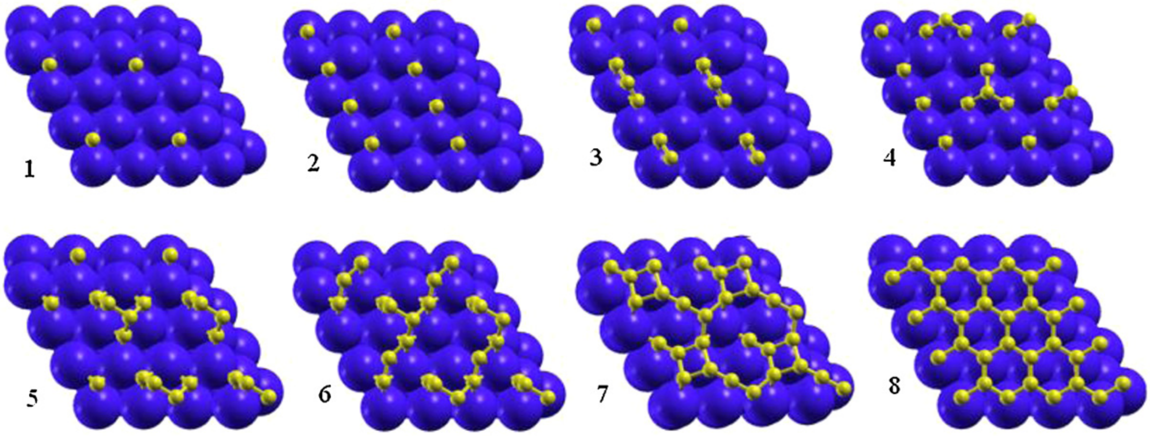

Fig. 4. Successive steps for C atoms incorporation over Ni surface. In the step 8, obtained graphene layer can be seen.

value, this means that the C prefer to stay in its graphene structure over Ni than to stay in its isolated graphene structure.

We found that the graphene layer tends to grow parallel to Pd and Ni surfaces (see Figs. 2, 4 and 5); the difference is that the graphene layer is bound to the Pd surface at 3.3 Å thanks to the weak van der Waals interaction, meanwhile, the graphene is clearly chemically bonded with the Ni surface at 2.1 Å (Fig. 5c) [2,7,10].

The Pt surface presents an irregular C ring formation with some bonds with the surface (Figs. 3 and 5b5). A systematic study reveals that the obtained geometries have a small dependence on the incorporation of successive steps. Despite this, the successive $E_{\text{rel\_Cn}}$ never changed in a factor bigger than a 4%. So, we only reported the most significant cases.

We suspect that the high Pt atoms mobility on the surface, always keeps the chemical bonded with the C and breaks the symmetry needed for the graphene growth.

This hypothesis is supported by part of the literature [21,22]. In the successive C incorporation steps, the first Pt layers suffer relaxations between the 2 and the 9%, meanwhile, for Pd and Ni the relaxation was never greater than 1%. This means that the Pt—Pt bonds are weaker than the Pd—Pd or Ni—Ni bonds. Hence the Pt–C interaction is more important.

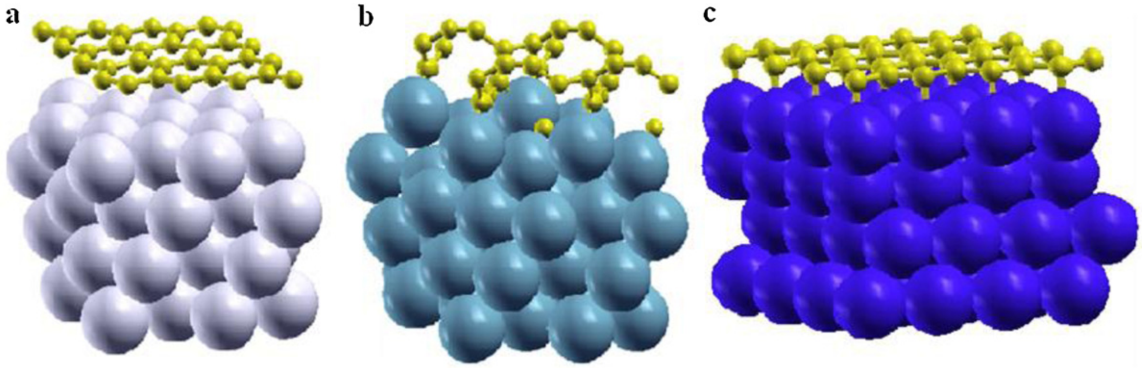

Fig. 5. Lateral perspective for all the obtained geometries thanks to successive C incorporation (a) over Pd; (b) over Pt; (c) over Ni.

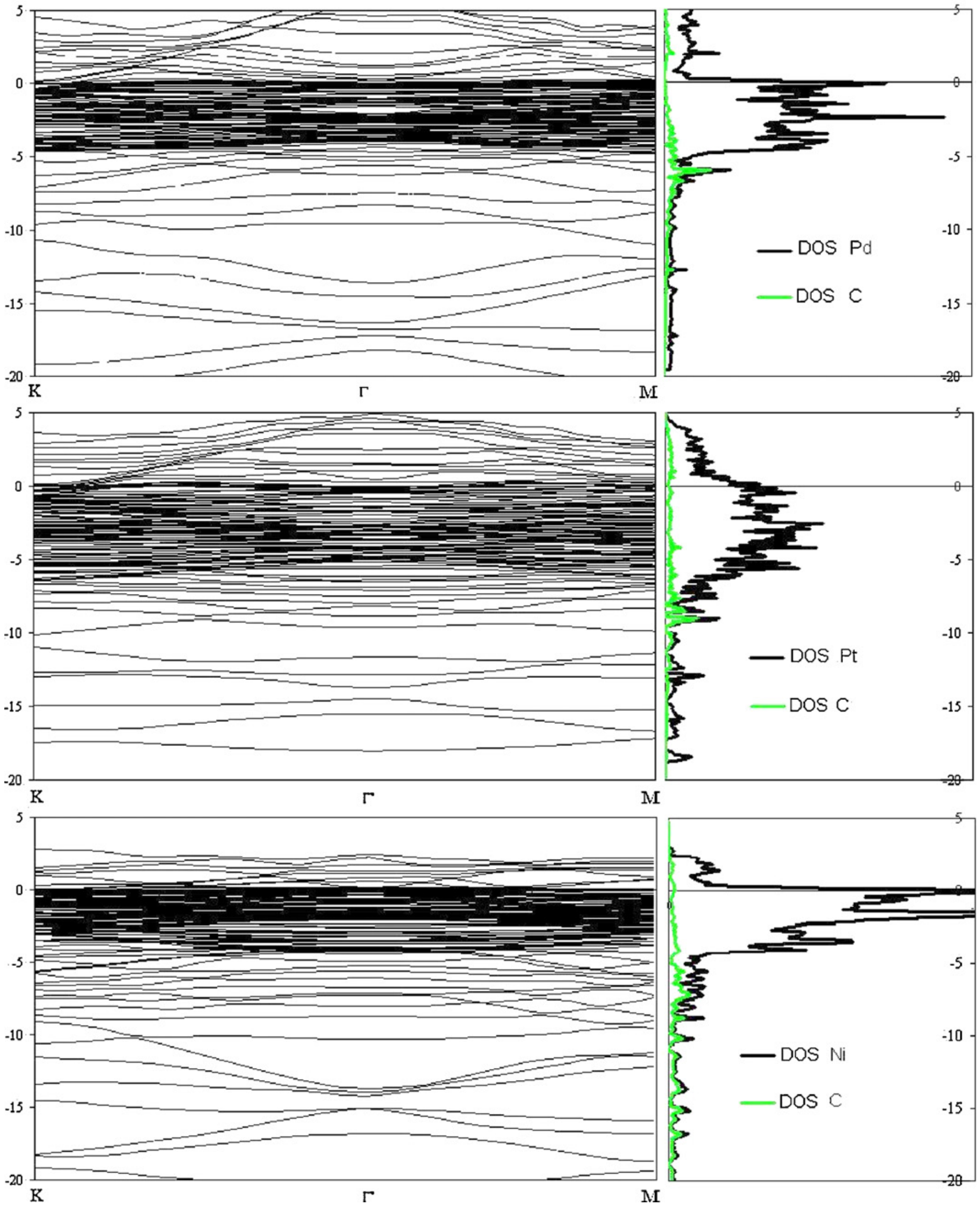

Fig. 6. Band Structures and Density of States for the systems G-Pd, G-Pt and G-Ni.

4.2. Electronic properties

To study the amazing electronic graphene properties [23] the Density of States and the Band structures were performed (Fig. 6). The selected systems were studied from the optimized structures obtained in Fig. 5. The k-point mesh was 15 × 15 × 1, and explicitly including the K, Γ and M high-symmetry points.

We can appreciate a clear metallic electronic structure for all systems. The overlap between the metallic bands and the graphene bands close to Fermi level, does not allow us to see the surface interaction effects in the graphene characteristic conical points at K. In the DOS we can see hybridization effects between the C orbital and each metal, specially, down the −5 eV for Pd and Ni; meanwhile, for Pt the hybridization became important down the −8 eV.

5. Conclusions

The study of the electronic structure has shown the existence of high hybridization effects between the graphene and the metallic substrates.

Because of the amorphous structures for C–Pt we can separate this system from the other two. Also between the systems C–Pd and C–Ni we can distinguish the importance of the attraction and the involved energies. This may mean that Pd layers could be used as support for the growth of a graphene monolayer. The advantage, respect to a Pt support, is that the graphene layer can grow parallel to the surface with a good Moiré pattern; and the advantage respect to a Ni support, is that the graphene monolayer could be easy to extract once it is grown. This may suggest an experiment like graphite deposition over Pd, like Novoselov [1] has done with Si.

Acknowledgments

The author is indebted to the Departamento de Fisica of UNS, IFISUR-CONICET for their financial support and to Mr. and Mrs. Owen for checking the English spelling and grammar.

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