Computational Materials Science 51 (2012) 165–171

Contents lists available at SciVerse ScienceDirect

Computational Materials Science

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

Site dependent metal adsorption on (3×3) h-BN monolayer: Stability, magnetic and optical properties

D. Sen [a], R. Thapa [a], K. Bhattacharjee [b], K.K. Chattopadhyay [a,b,*]

[a] Thin Film and NanoScience Laboratory, Department of Physics, Jadavpur University, Kolkata 700 032, India
[b] School of Materials Science & Nanotechnology, Jadavpur University, Kolkata 700 032, India

ARTICLE INFO

Article history:
Received 29 April 2011
Received in revised form 18 July 2011
Accepted 22 July 2011
Available online 28 August 2011

Keywords:
DFT
Site preference
Boron nitride
Adsorption
Magnetic properties
Optical properties

ABSTRACT

Cu, Pd and Au metal adatom adsorption on different adsorption sites of graphene analog h-BN monolayer is presented. The results demonstrate that the atop N (A_N) being the most favorable site for Cu while atop B (A_B) for Pd/Au; as well as occurrence of chemisorption is also found in these sites. A general model has been proposed which essentially indicate electronegativity (χ) to be the governing reason regarding the choice of adsorption sites on h-BN sheet in a way such that the adatoms with $\chi < 2.04$ are the most stable on A_N site while adatoms with χ lying in the range 2.04–3.04 are the most stable on A_B site. A detail study regarding magnetic properties reveal 100% spin polarization at Fermi level i.e. half metallic characteristics and $1\mu_B$/supercell magnetic moment in case of Cu and Au adatom adsorption at the most favorable sites. For Cu adsorbed h-BN system, the half metallic characteristics and strong chemical bonds arise from good hybridization at 0 eV between the outermost 2p orbital of nitrogen and the outermost 4s orbital of copper and at −1.49 eV between Cu 3d and 4s orbital with N 2p orbital. A thorough optical study on the above mentioned systems exhibits evolution/disappearance of different hump/shoulder peaks in the calculated absorption coefficient vs. energy plot which may be useful for experimental identification of the adsorbed systems.

1. Introduction

Two dimensional crystalline systems, due to its speculated novel properties, have drawn the attention of the theoreticians for more than half a century [1]. Successful separation of monolayer graphene as freestanding 2D crystallite in 2004 [2] spurred a phenomenal interest and is still being followed by multitudes of works in both theoretical [3–6] and experimental [7–9] communities. Hexagonal boron nitride (h-BN) sheet is a 2D nanoscale material analogous [10] to graphene in structure but varying widely in terms of other properties [11,12]. Among the pioneering works in this field, Corso et al. [13] in 2004 have been successful to produce h-BN nanomesh on Rh(1 1 1) single crystalline surface by self assembly and in the following year Novoselov et al. [14] reported production of free standing h-BN crystallites using mechanical cleavage [2].

In a very recent work Song et al. [15] reported large scale growth and characterization of atomic h-BN monolayers. Boron nitride sheets have the advantage over graphene in being more resistant to oxidation than carbon and hence they are more suitable for high-temperature applications in which carbon nanostructures are expected to burn [16,17]. With the production of pristine h-BN sheet becoming feasible, focus of the researchers in the recent times has been shifted to explore the properties of defect boron sheets [18,19] and towards more application oriented works like hydrogen storage on pristine [20] or doped [21] h-BN sheet. In a recent work Zhou et al. [17] presented a detail report on spin and bandgap engineering in Cu doped BN sheet from *ab initio* calculations. They predicted Cu adsorption on BN sheet can reduce the bandgap of BN sheet due to the emergence of certain impurity states rising from Cu atom and the value of bandgap depends on the adsorption configuration. However as per their calculations, no half metallic characteristics were found in case of Cu adatom adsorption, which can be accounted to their using PW91 functional. It is well documented that PBE and PW91 while both implement GGA, are not equivalent and PBE is expected to produce better result for surface [22]. In another recent work, Ataca and Ciraci [23] reported the stability and magnetic properties of functionalized (2×2) and (4×4) h-BN supercells using projector-augmented-wave potentials. Their results for adatoms are somehow different from ours and other results calculated using plane wave potentials. To the best of our knowledge, there exist no other published reports on the optical and magnetic properties of these metals adsorbed h-BN systems.

* Corresponding author at: Thin Film and NanoScience Laboratory, Department of Physics, Jadavpur University, Kolkata 700 032, India. Tel.: +91 33 2413 8917; fax: +91 33 2414 6584/6007.
E-mail address: kalyan_chattopadhyay@yahoo.com (K.K. Chattopadhyay).

0927-0256/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.commatsci.2011.07.042

In this work we have presented a detail study on the stability, electronic, magnetic and optical properties of Cu, Pd and Au metal adatom adsorption on all the possible highly symmetric sites of h-BN system in which strong chemical interaction i.e. chemisorption has been found to occur. A general model has been developed to predict the preferred sites in case of adsorption of a particular adatom on h-BN 2-D sheet. 100% spin polarization at Fermi level i.e. half metallic characteristics is found in case of Cu and Au adatom adsorption at atop N and B sites respectively.

2. Computational details and models

Our first-principles calculations were performed by CASTEP code [24] which implements a supercell approach to density functional theory. Perdew–Burke–Ernzerhof (PBE) functional [25] within the generalized gradient approximation (GGA) was used to deal with exchange and correlation term. Vanderbilt ultrasoft pseudopotential [26] was used to represent the boron, nitrogen and metal atoms and plane waves up to energy cut off 450 eV was used in the calculation. Brillouin zone integrations were performed within the Monkhorst Pack scheme [27] using $5 \times 5 \times 1$ k-point mesh for a 3×3 supercell containing nine boron and nine nitrogen atoms. For geometrical optimization, the system was allowed to fully relax using BFGS (Broyden–Fletcher–Goldfarb–Shanno) scheme [28] until the total energy converged to less than 2×10^{-5} eV/atom, the maximum force converged to lower than 0.05 eV/Å and the maximum displacement was 0.002 Å. All calculations were performed in spin unrestricted manner.

The optimized lattice parameter of h-BN unit cell have been found to be $a = b = 2.511$ Å, which is in well agreement with the experimental results [13]. A vacuum slab of length 15 Å was used along c axis to ward off the spurious interaction with its own periodic image. For adatom adsorptions on h-BN sheet, interactions at three highly symmetric positions, namely A_N site (Atop Nitrogen site), A_B site (Atop Boron site) and M site (Middle site), as shown in Fig. 1a, were studied. Total energy of isolated metal atoms was computed by putting it in a (10 Å × 10 Å × 10 Å) unit cell.

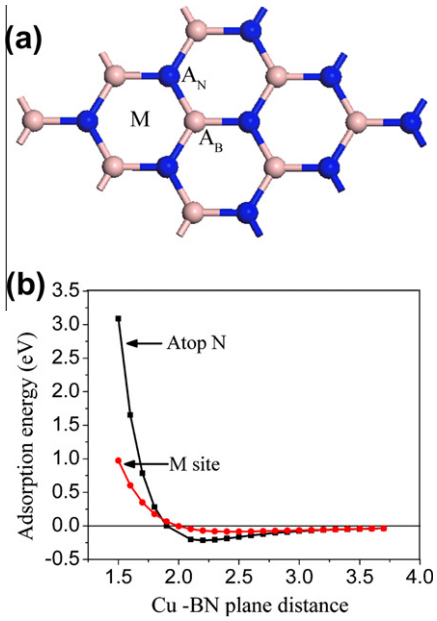

Fig. 1. (a) Schematic representation of the three most symmetric adsorption sites on graphene sheet. (b) Adsorption energy curves for Cu adatom-h-BN sheet interaction as a function of the perpendicular distance between Cu adatom and h-BN sheet.

3. Results and discussion

3.1. Stability

The stability of the metal adatoms on the h-BN surface is determined from first principle analysis. This is done by calculating the adsorption energy of the system where a negative value of the adsorption energy signifies good stability. For our system the adsorption energy can be defined as:

$$E_{\text{adsorption}} = E_{\text{total}} - E_{\text{pure h-BN}} - E_{\text{adatom}} \quad (1)$$

where $E_{\text{adsorption}}$ is the adsorption energy of the adatom adsorbed graphene system, E_{total} is the total energy of the system, $E_{\text{h-BN}}$ is the total energy of h-BN, and E_{adatom} is the total energy of an isolated adatom.

To investigate the adsorption energy of metal adatom on h-BN surface, we manually varied the adatom-h-BN surface distance keeping the system rigid and calculated the adsorption energies in each configuration for each of the highly symmetric sites. The potential energy (PE) curves (adsorption energy, $E_{\text{adsorption}}$ vs. adatom-h-BN sheet distance ($d_{\text{m/hBN}}$)) for the A_N and M sites for Cu adatom adsorption are shown in Fig. 1b. The zero energy in Fig. 1b corresponds to the case when the adatom is far from h-BN sheet. For each symmetry sites, the most stable configurations can be obtained from the global minimum of the total energy curve of each site. From the adsorption energy curve of Cu adatom at A_N site the minimum adsorption energy position is obtained when the Cu adatom is located about 2.2 Å above h-BN surface. Subsequent to the aforementioned calculations, geometrical optimizations have been carried out by placing metal adatoms at different adsorption sites at different distances as indicated by the total energy curves and the whole system was allowed to be fully relaxed to obtain optimized values of the different parameters.

The most stable site for Cu adatom adsorption has been found to be A_N site which is consistent with previous works [17] while A_B site have been found to be the most favorable for Pd and Au adatom adsorption. Optimized stable adsorption distances of 2.147 Å (Fig. 2a) were obtained for Cu in case of adsorption atop A_N site. It was also found that if Cu adatom is placed at a separation distance lower than 2.147 Å and the system is optimized, the atom is found to move away from h-BN sheet and if it is optimized by placing it at a distance greater than 2.147 Å, the adatom is found to move towards h-BN surface. Also if the adatom is placed at a much larger separation distance than 2.147 Å and is optimized, the position of adatom changes negligibly with respect to the unoptimized position due to lack of any interaction. By similar calculations we obtained optimized separation distances of 2.287 Å for Cu (Fig. 2b), 2.607 Å for Au (Fig. 2e) and 2.150 Å for Pd (Fig. 2f) adatom adsorption on A_B site. The optimized adsorption energy of Cu adatom adsorption on A_N site have been found to be −0.244 eV, while −0.75 eV and −0.11 eV adsorption energies on A_B site have been calculated for Pd and Au adatom. A negative value of adsorption energy (−0.091 eV) has been calculated for Cu adatom adsorption in M site of h-BN sheet while the value of adsorption energy (0.274 eV) has been found to be positive in case of Pd adatom adsorption in same configuration. Au adatom on M site of h-BN sheet have been found to be grossly unstable and when placed in similar configuration, the adatom tends to move towards other stable positions. Optimized adatom-h-BN plane equilibrium distance, adsorption energy, magnetic moment per supercell and Mulliken charge of metal adatom were calculated for Cu, Pd, and Au adatom for A_N, A_B and M sites and have been shown in Table 1. It is readily seen that optimized adsorption energies of all the most favorable sites have negative value. Displacement of nearest N/B atom from the h-BN plane due to adsorption