



A theoretical study of structural and electronic properties of pentacene/Al(1 0 0) interface

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ABSTRACT

The first principle calculations within the framework of density functional theory have been performed for the pentacene molecule deposited on the aluminum Al(100) substrate to study the structural and electronic properties of the pentacene/Al(100) interface. The most stable configuration was found at bridge site with 45° rotation of the pentacene molecule on Al(100) surface with a vertical distance of 3.4 Å within LDA and 3.8 Å within GGA functionals. The calculated adsorption energy reveals that the adsorption of pentacene molecule on Al(100) surface is physisorption. For the stable adsorption geometry the electronic properties such as density of states (DOS), partial density of states (PDOS), Mulliken population analysis and Schottky barrier height are studied. The analysis of atomic charge, DOS and PDOS show that the charge is transferred from the Al(100) surface to pentacene molecule, and the transferred charge is about −0.05 electrons. For the adsorbed system, the calculated Schottky barrier height for hole and electron transport is 0.27 and 1.55 eV, respectively.

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1. Introduction

Organic opto-electronic devices such as organic light emitting diodes (OLEDs) [1,2], organic field effect transistors (OFETs) [3,4] and organic photovoltaic cells [5,6] are attracting enormous attention because of their excellent properties such as plasticity, low-cost processing and flexibility [7]. The adsorption of organic molecules on metal and dielectric surfaces has received considerable attention due to their promising role in molecular electronics. A key to design high performance molecular electronic device is to understand the function and characteristics of organic semiconducting materials while they are in-contact with metal or dielectric. The interface between organic semiconductors and metal electrodes should be studied extensively because charge transfer across the interface is crucial for the performance of organic electronic devices. Previous experimental [8–12] and theoretical [13–19] studies on the adsorption of organic molecule on the metal and dielectric surfaces show that the intermolecular interactions strongly depend on alignment of organic molecule on the metal or dielectric surface. Hence, the study of structure and property relationship is useful to understand the properties of existing devices and predict ideal material sets for electrodes, semiconductors and dielectrics with novel properties for use in next generation of optoelectronic devices. However, theoretical

calculations on interface of organic molecules on metal surface are less due to heavy computational demand.

Polycyclic aromatic hydrocarbon (PAH) is one of the most interesting classes of organic materials because of its high charge carrier mobility. Among PAHs, pentacene has recently been determined to be one of the most promising candidates for organic thin film transistors (OTFTs) [20,21], organic field effect transistors (OFETs) [22], organic light emitting diodes (OLEDs) [23,24] and organic-based photovoltaic devices [25] due to its structural stability [26] and temperature-independent high mobility of 1.3 cm²/Vs [27]. Aluminum (Al) is a simple prototype *sp* metal and is technically relevant as a contact material in organic electronic devices. The work function of aluminum is 4.28 eV, which is lower than the work function of gold and palladium by ~0.84 eV [28,29]. Previously, Simeoni et al. [17] studied the electronic properties of pentacene molecule deposited on aluminum (100) surface consisting of 7 × 2 × 2 unit cell (112 atoms) by means of *ab initio* and density functional theory (DFT) calculations. In this work the stable adsorbed geometry has been found by calculating the adsorption energy with respect to the vertical distance between the pentacene molecule and aluminum. However recent reports [13,30,31] reveal that the intermolecular interaction strongly depends on the alignment of the organic molecule on the metal surface, and the rotation of the organic molecule on the metal surface significantly affects the stability and electronic properties.

In the present work, we have investigated the adsorption characteristics of single pentacene molecule on Al(100) surface of 5 × 5 × 2 unit cell (200 atoms) using first-principle density

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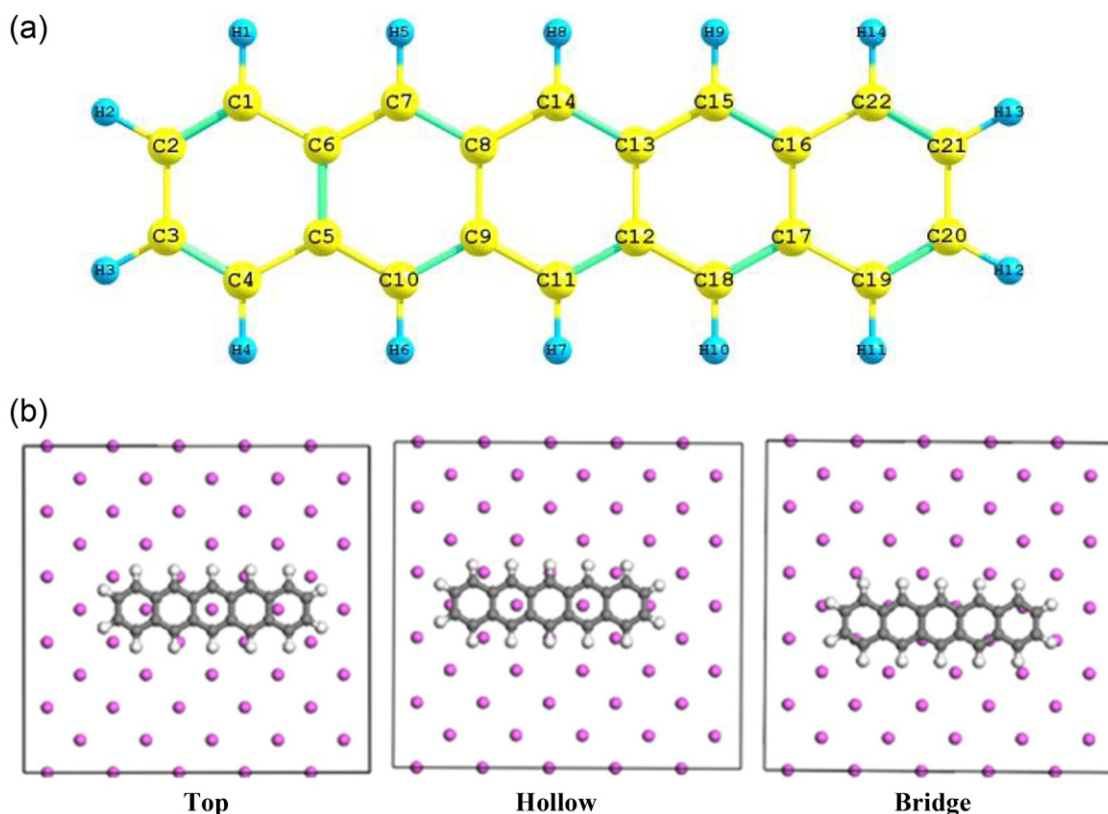


Fig. 1. (a) The optimized structure of pentacene molecule and (b) orientation of the pentacene molecule on Al(100) surface. (Only the top most Al atoms are shown for clarity). Aluminum, carbon and hydrogen atoms are shown in pink, grey and white colors, respectively.

functional theory methods. The main focus of the work is to find the most stable adsorption site and geometry of the pentacene molecule on Al(100) surface. For the stable adsorption geometry, the electronic properties like population analysis, density of states (DOS), partial density of states (PDOS) and Schottky barrier height (SBH) are calculated using density functional theory (DFT) calculations. The organization of the paper is as follows, the computation details are given in Section 2. The adsorption geometry and electronic properties such as population analysis, DOS, PDOS and SBH are discussed in Section 3. Finally, the main conclusions are summarized in Section 4.

2. Computational details

The electronic structure calculations are performed within the framework of density functional theory (DFT) using VASP (Vienna Ab initio Simulated Package) code [32–34]. In the VASP calculations, plane wave basis sets are employed to expand the electronic wave functions. The exchange and correlation functional has been parameterized according to the Perdew–Burke–Ernzerhof gradient corrected exchange functional within the generalized gradient approximation (GGA) [35] and the local density approximation (LDA) [36]. Electron-ion interactions were described by the projected augmented wave (PAW) method [37], which is a frozen-core all-electron calculation. The plane wave (PW) basis sets are independent of the atomic positions. While using plane wave basis sets any region in space is treated on an equal footing. Hence the plane wave basis sets are free from “basis set superposition error” (BSSE) [38–41]. The convergence of a calculation depends only on the number of PWs included in the expansion of the electron density. The dimension of plane wave basis set is controlled by cutoff energy

of 400 eV in our calculations. The Brillouin-zone integrations are performed using the $3 \times 3 \times 1$ k -point mesh, which is generated using Monkhorst-pack method [42]. The clean Al(100) surface is constructed using a periodically repeated slab approach with super cell geometry of $5 \times 5 \times 2$ surface unit cell. This slab consists of four layers with a vacuum region of 10 Å and each layer is having 50 aluminum atoms. A single pentacene molecule is deposited on the upper surface of the slab with the aromatic rings parallel to the surface and in total the resulting unit cell has 236 atoms. We used a conjugate-gradient algorithm in all calculations based on the reduction in the Hellman–Feynman forces on each constituent atom to less than 10 meV.

Table 1

Calculated bond lengths (in Å) and bond angles (in°) of the pentacene molecule using GGA and LDA functionals. Atomic labels are consistent with Fig. 1.

Parameters	LDA	GGA
Bond lengths		
C2–C3	1.43	1.43
C3–C4	1.36	1.37
C4–C5	1.43	1.44
C6–C5	1.44	1.46
C8–C9	1.45	1.47
C5–C10	1.40	1.40
C10–C9	1.42	1.42
C9–C11	1.40	1.41
C–H	1.09	1.09
Bond angles		
C1–C2–C3	120.54	120.54
C2–C3–C4	120.54	120.54
C3–C4–C5	121.02	121.03
C1–C6–C5	118.43	118.44
H1–C1–C2	120.69	120.69

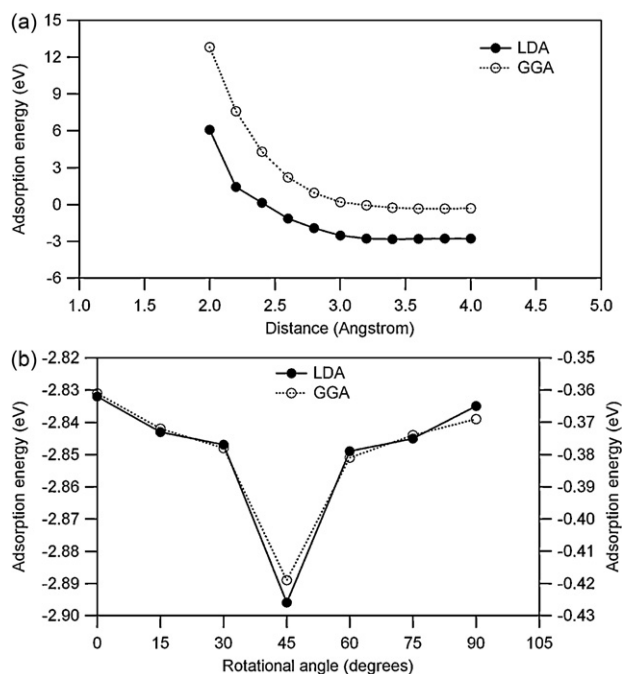


Fig. 2. The calculated adsorption energy values with respect to (a) the vertical distance between the pentacene molecule and the Al(100) substrate using LDA and GGA functionals. (b) The rotational angle of the pentacene molecule on the Al(100) substrate using LDA (left Y-axis) and GGA (right Y-axis) functionals.

3. Results and discussion

3.1. Adsorption geometry

The structure of a free pentacene molecule is optimized initially and it is shown in Fig. 1(a). The optimized geometry of pentacene molecule has a rod-like planar structure. The optimized bond lengths and bond angles of the pentacene molecule are summarized in Table 1, which are in good agreement with the experimental [43] and previous theoretical results [30]. The lattice constant (a_{Al}) of

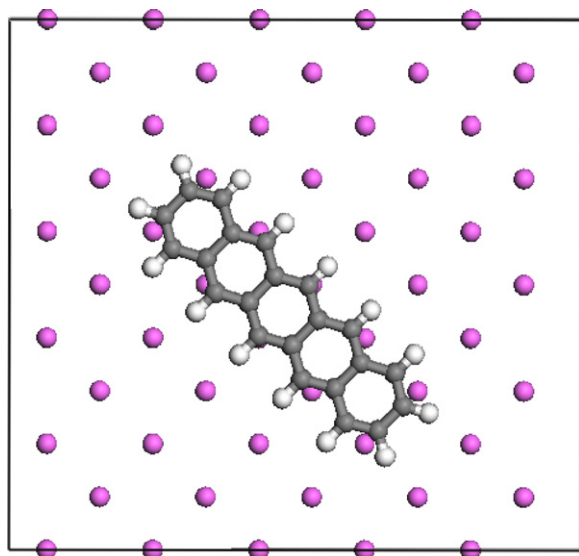


Fig. 3. The most stable geometry of pentacene molecule on Al(100) surface with the rotational angle of 45°. (Only the top most Al atoms are shown for clarity). Aluminum, carbon and hydrogen atoms are shown in pink, grey and white colors, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Table 2

Mulliken charges (in electron charge units) in the isolated pentacene molecule (q_M) and in the adsorbed system (q_{ads}).

Atom	LDA		GGA	
	q_M	q_{ads}	q_M	q_{ads}
C3	-0.145	-0.236	-0.129	-0.217
C4	-0.167	-0.238	-0.133	-0.206
C5	0.113	0.069	0.040	0.015
C10	-0.250	-0.321	-0.167	-0.241
C9	0.108	0.080	-0.040	-0.067
C11	-0.250	-0.327	-0.167	-0.244
H3	0.131	0.209	0.126	0.202
H4	0.131	0.211	0.123	0.200
H6	0.136	0.221	0.122	0.203
H7	0.136	0.224	0.122	0.206

the relaxed Al(100) system is found to be 4.03 Å, which is in agreement with the experimental value of 4.05 Å [44]. The pentacene molecule is deposited on the upper slab of the Al(100) surface. To find the adsorption geometry of a pentacene molecule on the surface, one has to consider the different orientations and the position of the pentacene molecule on the metal surface. Among the various configurations (parallel, perpendicular and tilted) of pentacene molecule on Al(100) surface, the parallel configuration is considered. Because, several experimental and theoretical works have shown that polycyclic aromatic molecules tend to adsorb on a metal surface in a flat lying geometry [45,46]. As a starting geometry, the long axis of the pentacene molecule is aligned along the [100] direction of the Al surface. As shown in Fig. 1(b), the pentacene molecule is placed at three different adsorption sites, namely top, hollow and bridge sites on Al(100) surface. For these three sites, adsorption energy (E_{ads}) is calculated using the formula,

$$E_{ads} = E_{Al-pent} - E_{Al} - E_{pent}$$

where $E_{Al-pent}$ is the total energy of the adsorbed system, E_{Al} is the total energy of the clean Al(100) surface and E_{pent} is the total energy of the isolated pentacene molecule. Among the three

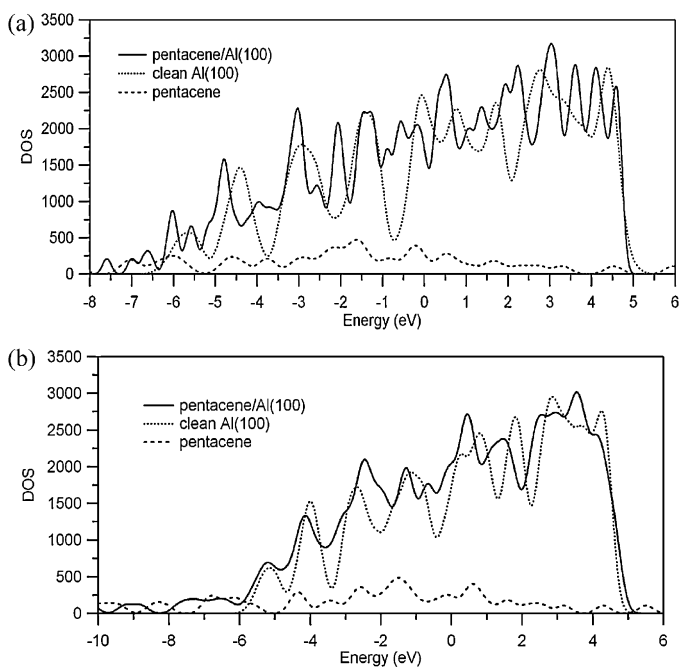


Fig. 4. Total density of states of the isolated pentacene molecule, clean Al(100) surface and pentacene/Al(100) calculated at LDA and GGA functionals. The Fermi energy of the adsorbed system is -4.53 eV at LDA and -4.21 eV at GGA level, and is taken as the reference energy for the total DOS.

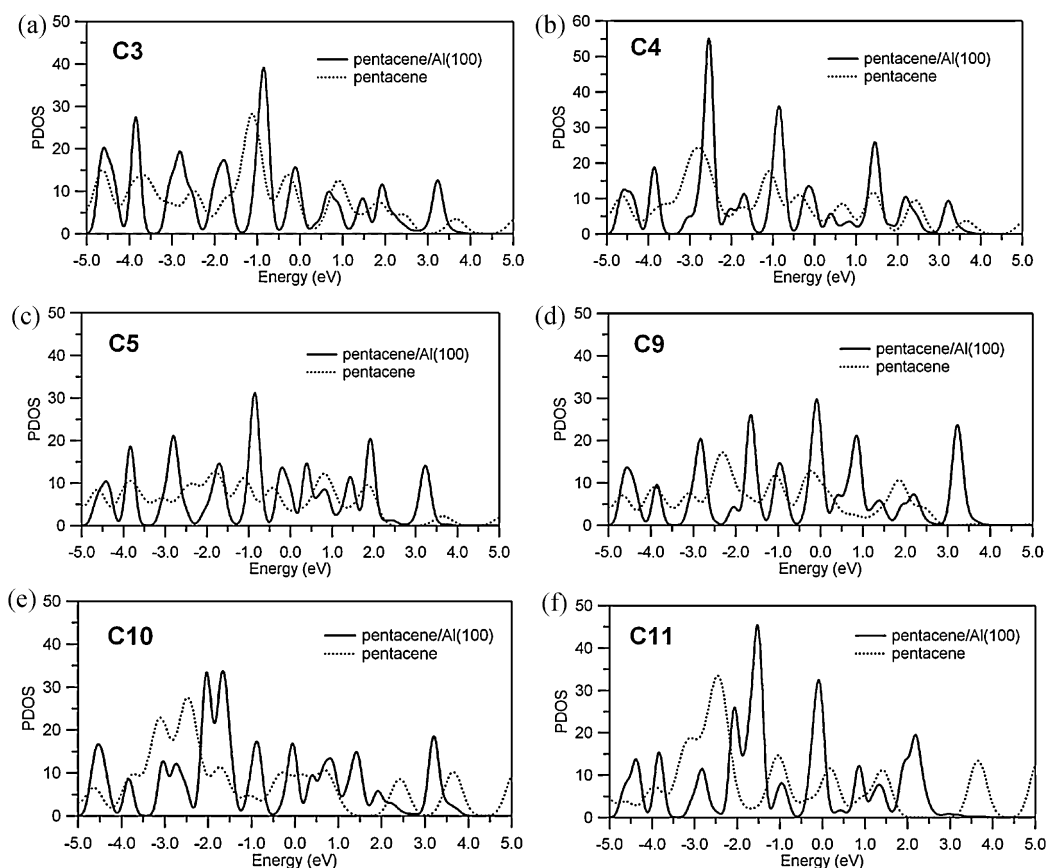


Fig. 5. (a–f) Partial density of states on the different carbon atoms in the isolated pentacene molecule and in the adsorbed system calculated using LDA functional. The Fermi energy of the isolated pentacene molecule is -3.66 eV at LDA and -3.65 eV at GGA level, and is taken as the reference energy for the PDOS.

adsorption sites, the bridge site orientation is the stable orientation with the adsorption energy value of -2.53 eV.

To find the most stable adsorption geometry, with respect to the vertical distance between the pentacene and Al(100) surface, the adsorption energy calculation has been carried out with bridge site configuration. The calculated adsorption energy values using LDA and GGA functionals are plotted with respect to the vertical distance and is shown in Fig. 2(a). From Fig. 2(a), it has been observed that the maximum adsorption energy of -2.83 eV is found at a distance of 3.4 Å at LDA level and maximum of -0.36 eV is observed at a distance of 3.8 Å at GGA level of calculation. With these vertical distances, the pentacene molecule is rotated on the Al(100) surface from 0° to 90° in the steps of 15° and the adsorption energy is calculated. As shown in Fig. 2(b), from 0° to 30° , the variation of adsorption energies is 0.02 eV only. The adsorption energy is maximum at 45° of rotational angle, the maximum value is -2.90 and -0.42 eV at LDA and GGA level of theories, respectively. The most stable geometry of pentacene molecule on Al(100) surface with the rotational angle of 45° is shown in Fig. 3. The calculated adsorption energy and vertical distance between pentacene and Al(100) surface show that the interaction between the pentacene molecule and the Al(100) surface is physisorption. Previously, Simeoni et al. [17] studied the pentacene/Al(100) interface using DFT methods and reported the adsorption energy value of -2.42 eV within LDA and -0.32 eV within GGA functionals. Recently, Mete et al. [13] have reported the adsorption energy value for pentacene/Ag(111) surface as -1.93 eV and -0.16 eV within LDA and GGA functionals, respectively. These results reveal that LDA functional substantially overestimates the binding energy of the physisorbed system. On the other hand, GGA functional strongly underestimates the binding energy. For the stable adsorption geometry, the electronic

properties like density of states (DOS), partial density of states (PDOS), Mulliken population analysis and Schottky barrier height (SBH) are studied using LDA and GGA functionals.

3.2. Electronic properties

3.2.1. Population analysis

The charge transfer between the pentacene molecule and the Al(100) metal substrate is studied by calculating the atomic charge on the individual systems and on the adsorbed system using a Mulliken charge analysis of bond population [47]. Table 2 summarizes the calculated Mulliken charges in the single molecule (q_M) and in the adsorbed system (q_{ads}) using LDA and GGA functionals. From the tabulated atomic charges it is observed that the carbon atoms of the pentacene molecule acquire charge from metal surface, whereas the hydrogen atoms release a small amount of charge to the metal surface. In comparison with the isolated pentacene molecule, the total Mulliken charge on the pentacene molecule in the adsorbed system is increased by -0.051 electrons within LDA and -0.046 electrons within GGA functional, indicating that there is a net charge transfer from the Al substrate to the pentacene molecule and the charge transfer leads to a positively charged metal and a negatively charged pentacene overlayer, suggesting a strong electrostatic interaction between pentacene and Al surface. The HOMO energy of pentacene molecule (-4.32 eV) is slightly larger than the work function of aluminum. This is the reason for the negative potential on pentacene molecule and positive potential on aluminum surface. The similar results have been reported earlier by Babajanyan et al. [28]. In a previous study, Simeoni et al. [17] reported that in the adsorbed system, the charge is transferred from the pentacene molecule to aluminum surface and the

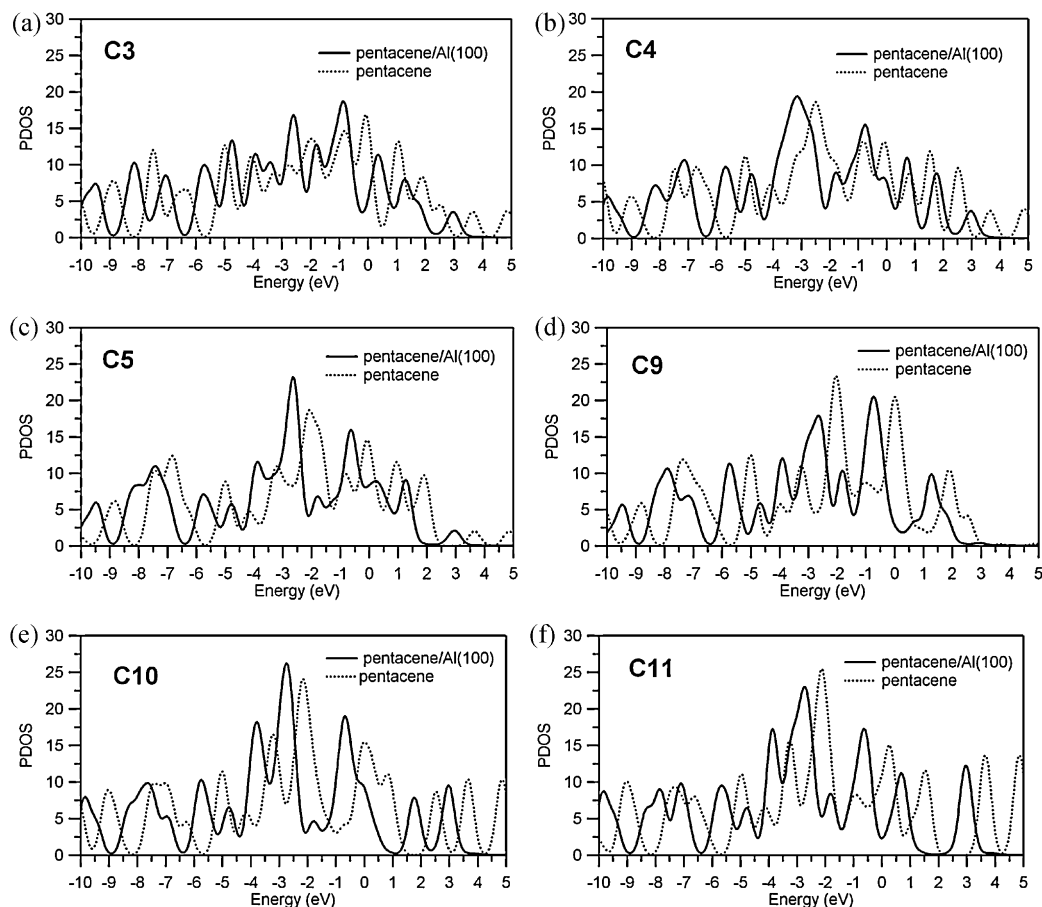


Fig. 6. (a–f) Partial density of states on the different carbon atoms in the isolated pentacene molecule and in the adsorbed system calculated using GGA functional. The Fermi energy of the aluminum is -4.46 eV at LDA and -4.11 eV at GGA level, and is taken as the reference energy for the PDOS.

central carbon atoms C7 and C11 suffer more than other carbon atoms. Whereas in the present study, the charge is transferred from the Al(100) surface to pentacene molecule, and the amount of charge on all the atoms in the pentacene molecule significantly modified by the adsorption. This is due to the large surface area of the aluminum substrate and the position of the C atoms on the Al substrate considered in the present investigation.

3.2.2. Density of states

In order to study the charge transfer and the contribution of a particular atomic orbital or atom to the molecular energy levels of the adsorbed system, we have calculated the density of states (DOS) and partial density of states (PDOS) on the atoms of pentacene molecule in the adsorbed system and are compared with the isolated pentacene molecule. Fig. 4 shows that the total DOS for the isolated pentacene, clean Al(100) surface and pentacene/Al(100) calculated from DFT calculations. The calculated Fermi energy of the adsorbed system is -4.53 eV at LDA and -4.21 eV at GGA level, which is taken as the reference energy for the total DOS. The observed DOS of the overall system is approximately the sum of the DOS of isolated systems. The slight variations in the total DOS confirm the nature of interaction between the pentacene molecule and Al(100) surface.

The PDOS on carbon atoms in isolated pentacene molecule and in the adsorbed system are shown in Figs. 5a–f (LDA) and 6a–f (GGA). The PDOS for the specific carbon atoms C3, C4, C5, C9, C10 and C11 (see Fig. 1 for labeling of atoms) are considered and all the remaining carbon atoms follow the similar trend due to symmetry. The calculated Fermi energy of

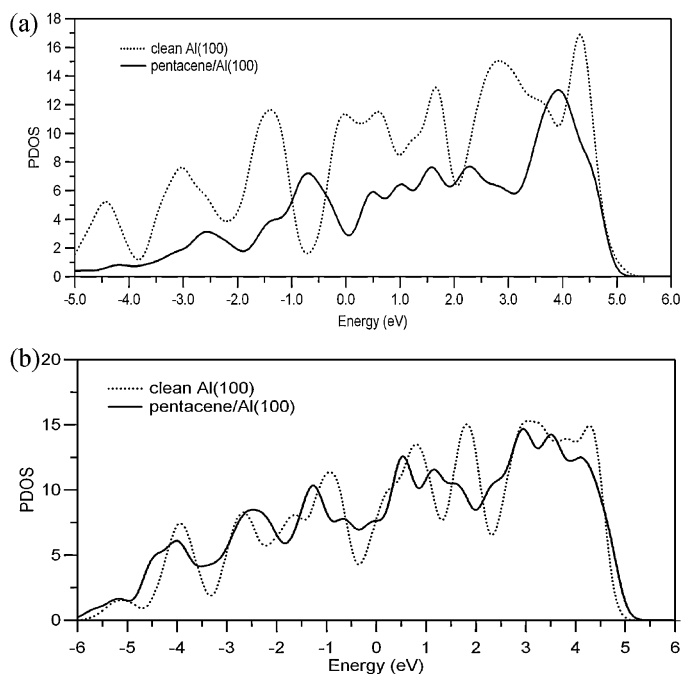


Fig. 7. Partial density of states of the aluminum atom in the clean Al(100) surface and in the adsorbed system calculated using (a) LDA and (b) GGA functionals. The Fermi energy of the aluminum is -4.46 eV at LDA and -4.11 eV at GGA level, and is taken as the reference energy for the PDOS.

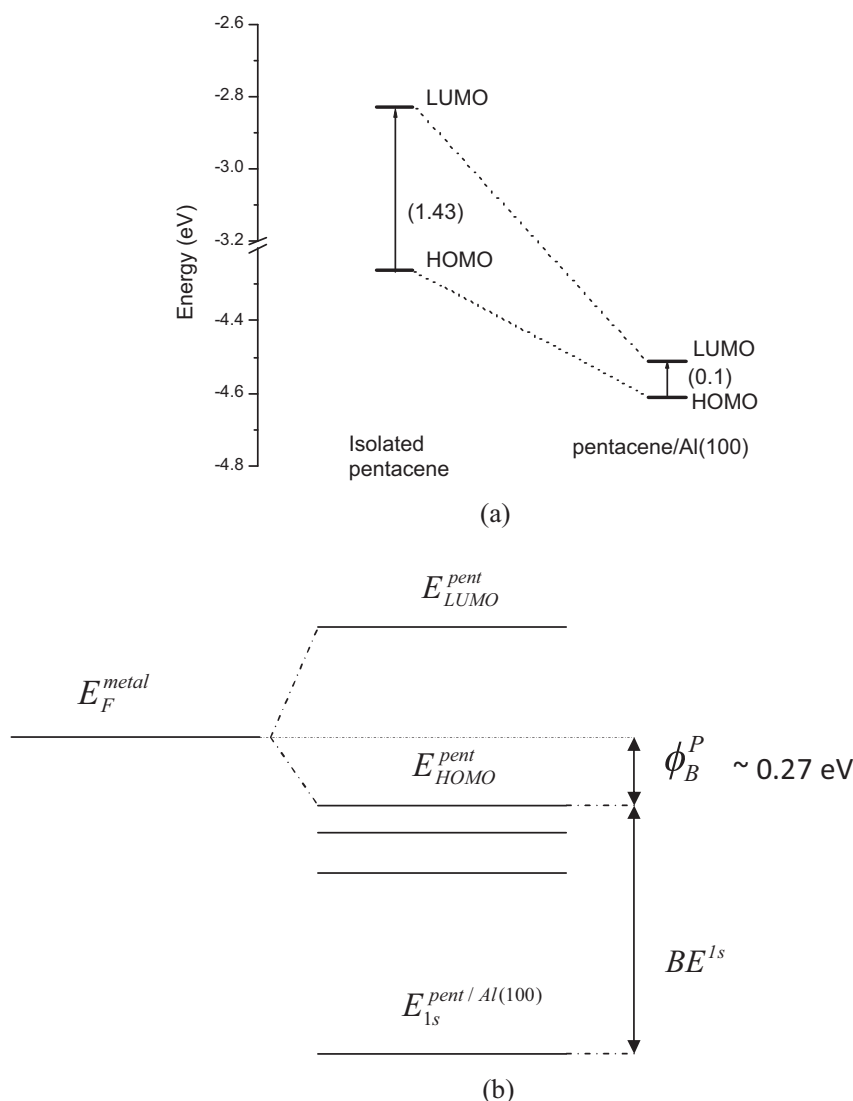


Fig. 8. (a) Energies of frontier molecular orbitals of pentacene molecule and pentacene/Al(100) interface. Energy gap value (in eV) is given within the parenthesis. (b) Schematic diagram showing calculation of Schottky barrier height.

the isolated pentacene molecule is -3.66 eV at LDA and -3.65 eV at GGA level, and is taken as the reference energy for the PDOS analysis. Figs. 5a–f and 6a–f show the change in energy states of pentacene molecule on Al(100) substrate. It has been observed that the PDOS on the carbon atoms of pentacene molecule in the adsorbed system increases and shifted toward the lower energies, in comparison with that of the isolated pentacene molecule. Fig. 7 show the PDOS for a specific Al atom in the clean Al(100) substrate and in the adsorbed system. This is located at the bridge site, that is nearer to the C11 atom of the pentacene molecule. The calculated Fermi energy of the aluminum is -4.46 eV at LDA and -4.11 eV at GGA level, which is taken as the reference energy for the PDOS analysis. PDOS calculated for a particular Al atom show that the PDOS on the Al atom decreases while interacting with pentacene molecule, indicating the transfer of charge from Al substrate to the pentacene molecule. This is in agreement with the results obtained from Mulliken population analysis and PDOS on carbon atoms.

As shown in Fig. 8(a), the adsorption of pentacene molecule on Al(100) surface shifts the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) toward the lower energies compared with that of the isolated pentacene molecule. The calculated HOMO energy of pentacene is -4.26 eV,

which is closer to the work function of aluminum. The HOMO (H) and LUMO (L) levels are shifted by 0.24 and 1.59 eV, respectively. As shown in Fig. 8(a), the H–L gap of isolated pentacene molecule is 1.43 eV, whereas in the adsorbed system the H–L gap is 0.1 eV. That is, the adsorption of pentacene molecule on the Al(100) surface reduces the H–L gap of pentacene molecule. Recently, Hahn and Kang [11] reported that the H–L gap of pyridine molecule decreases about 1 eV while interacting with Ag(110) surface.

3.2.3. Schottky barrier height

One of the most important properties in the study of organic molecule–metal interface is the Schottky barrier heights (SBHs). The SBH is calculated from first principle calculations taking into account both the charge rearrangement at the interface and the bulk contributions of the separate constituents [48,49] based on core level energy as reference energy [50,51]. In the case of the metal/molecule interface, as shown in Fig. 8(b) for pentacene/Al(100) interface, the p-type Schottky barrier height (SBH) is estimated using the following equation:

$$\phi_B^p = E_F - E_{1s}^{\text{int}} + BE^{1s}$$

That is, the contribution from charge rearrangement at the interface is calculated as the difference in energy between the Fermi energy of the adsorbed system (E_F) and the energy of the 1s orbital of carbon atom in the interface (E_{1s}^{int}). The bulk contribution is added as the binding energy term calculated as the difference between the energy of the highest occupied molecular orbital (E_{HOMO}) of the isolated pentacene molecule and E_{1s}^{int} . The bulk contribution of the metal surface is built-in with E_F , since it is expected that the Fermi level of the interface coincide with the Fermi level of clean Al slab. The calculated p-type SBH value for the adsorbed system is equal to 0.27 eV within LDA and 0.15 eV within GGA. The n-type SBH (ϕ_B^n) is calculated as,

$$\phi_B^n = E_{\text{gap}}^{\text{pent}} - \phi_B^p$$

where $E_{\text{gap}}^{\text{pent}}$ is the band gap of the pentacene molecule. The calculated band gap for the isolated pentacene molecule is about 1.43 eV. Using this band gap, the calculated n-type SBH is 1.16 eV within LDA and 1.28 eV within GGA. The experimental band gap value reported by Park et al. is 1.82 eV [52]. That is, the DFT method underestimates the band gap by about 0.4 eV. With the experimental band gap value, the calculated n-type SBH is 1.55 eV. The calculated SBH values are comparable with the previous theoretical results [17]. The calculated SBH values reveal that the hole transport is favorable in the studied adsorbed system, because the p-type SBH is lower.

4. Conclusions

The first principle calculations have been performed to study the geometry and electronic properties of the interface formed by a pentacene molecule and Al(100) surface. The most stable configuration was found at bridge site with 45° rotation of the pentacene molecule on Al(100) surface and a vertical distance of 3.4 Å within LDA and 3.8 Å within GGA functional. The calculated adsorption energy reveals that the adsorption of pentacene molecule on Al(100) surface is physisorption.

For the stable adsorption geometry the electronic properties such as density of states (DOS), partial density of states (PDOS), Mulliken population analysis and Schottky barrier height are studied. The analysis of atomic charge calculated from Mulliken population analysis reveal that the charge is transferred from the Al(100) surface to pentacene molecule and the transferred charge is about −0.05 electrons. The energy states at the pentacene–aluminum interface have been studied through DOS analysis. The PDOS results reveal that the charge is transferred from Al(100) surface to pentacene molecule. For the adsorbed system, the calculated p-type Schottky barrier height is 0.27 eV, and the n-type SBH is 1.55 eV. Since, the p-type SBH is lower, the hole transport is favorable in the adsorbed system.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jmngm.2012.06.008>.

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