Density Functional Theory of PTCDA Adsorption on Si(111)In-8×8 at Room Temperature

현정민

숙명여자대학교 물리학과, 서울특별시 140-742, 대한민국

e-mail: todali@sm.ac.kr

Self-assembly of the molecular system of perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride (PTCDA) is of such potential importance for organic semiconductor devices that PTCDA molecule on a variety of substrates has been extensively studied. Therefore we studied the density of states (DOS), the charge densities, and intermolacular bond lengths for PTCDA, and investigated PTCDA absorptioni sites on Si(111)In-8×8 at room temperature using the density functional theory calculations.

INTRODUCTION

Self-assembly of organic molecules received scientific interest due to their potential applications in organic [1] and molecular electronic devices [2] and biosensors [3]. Especially, perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride (PTCDA) have been studied on their absorption mechanism on different metal and semiconductor substrates [4-8]. Although organic molecules on the metallic and the insulating surfaces have been extensively studied, little is known about them on nano-structured metal-semiconductor hybrid substrates such as the Si(111)In-4×1 surface at room temperature (RT) [9]. Theoretical analysis is highly required to understand issues such as the molecule-substrate interaction and the molecule-molecule interaction, which may affect the molecular adsorption mechanism and the subsequent self-assembly pattern formation on the metal/semiconductor hybrid surfaces

In this paper, we studied the electronic structure of the neutral PTCDA molecule using density functional theory (DFT) calculations and investigated adsorption sites of PTCDA molecule on RT-In/Si(111).

METHODS

We employed the density functional theory (DFT) code, the Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA), as implemented on the EDISON nanophysics web site [10]. We used the generalized gradient approximation (GGA) by Perdew, Burke, and Ernzerhof [11] and the norm-conserving pseudopotentials of Troullier and Martins [12]. A double-zeta basis set was used for all atoms. The localized basis set was made up of numerical atomic orbitals which induced an energy shift in each orbital of 0.02 Ry. We used the energy cutoff with 100Ry and a 1×1×1 mesh of *k* points for integrations over the Brillouin zone. The neutral PTCDA molecule were placed in a supercell of 27×31×20 $Å^3$, and we used In/Si(111)-8×8 supercell for PTCDA adsorption

RESULTS and DISCUSSION

PTCDA molecule is of the planar arrangement including five carbon rings, as shown in Fig. 1. This molecule consists of a perylene core and anhydride end groups. Overall dimensions of the flat molecule are 14.2 Å × 9.2 Å (length × width) for PTCDA.

We obtained the total density of states (DOS) for the PTCDA molecule and the energy levels of PTCDA molecule were aligned. The total DOS of PTCDA, as shown in Fig. 2, are made up of molecular orbitals which are generated from strongly localized *s* and *p* orbitals of the carbon (C), oxygen (O), and nitrogen (N) atoms. In case of PTCDA, the highest occupied molecular orbital (HOMO) lies 1.36 eV below the lowest unoccupied molecular orbital (LUMO). The charge densities related to the HOMO and LUMO which are depicted in Fig. 2 are mainly distributed over the perylene core and have π character. The HOMO and the LUMO orbitals of PTCDA are delocalized throughout the molecules, except for the two end anhydride groups. The distribution of charge densities for these molecules can help

understand the bonding and anti-bonding transition. Some of the C-C bonding regions of the HOMO are replaced by the repulsive nodes in the LUMO. On the other hand, the major anti-bonding nodes of the HOMO, the central anti-bonding plane along the long axis of the molecules and the C-O anti-bonding regions, are preserved in the LUMO over the entire molecule.

The calculated bond-length data are presented in Table 1 along with the previous calculations [13]. The labeling of the bonds is shown in Fig. 1. PTCDA shows C-C bond lengths between 1.41 Å and 1.49 Å and between 1.41 Å and 1.51 Å, respectively, indicating varying degrees of π conjugation and double-bond character. Since the HOMO has maxima at the C-C bonds 2 and 6, the bond character of these bonds is enhanced and the bond length is shortened by this mechanism. On the other hand, the HOMO is of antibonding character for bonds 1, 4, and 8 where the HOMO has nodes, which are elongated due to occupations of the HOMO.

We investigated PTCDA adsorption sites on RT-In/Si(111) after studying characters of a neutral PTCDA molecule. The Fig. 3 shows two case of PTCDA adsorption on In/Si(111)-8×8. The PTCDA molecule on the left (L_{PTCDA}) is rotated by 90° from PTCDA on the right (R_{PTCDA}). R_{PTCDA} is higher in energy than L_{PTCDA}, and the difference of energy is about 1 eV. PTCDA molecule on In/Si-8×8, as shown in Fig. 4, are breifed on three cases of PTCDA adsorption. That is, PTCDA molecule is adsobed on Si Seiwatz chains and In nanowires, respectively [Fig. 4(a) and (b)], and at the bundary [Fig. 4(c)]. We compared with adsorption energies (E_{adsorp}) of each case in Fig. 4. E_{adsorp} is 1.80~1.95 eV on Si Seiwatz chains, 0.78~1.27 eV on In nanowires, and 0.30 eV at the boundary. Therefore, we found PTCDA molecule on Si Seiwatz chains the most stable.

CONCLUSION

We have examined the electronic DOS and the HOMO/LUMO orbital characters of PTCDA using the first-principles calculations. The bonding and antibonding characters were confirmed at the HOMO and LUMO. Also, we have investigated PTCDA adsorption sites on RT-In/Si(111) and found the most stable site.

ACKNOWLEDGEMENT

We are grateful to Prof. Hanchul Kim for enlightening discussions on SIESTA code and to the contributors to the EDISON nanophysics applications.

REFERENCES

[1] Christos D. Dimitrakopoulos and Patrick R. L. Malenfant, Adv. Mater. **14**, 99 (2002).
[2] Christian Joachim and Mark A. Ratner, Proc. Natl. Acad. Sci. U.S.A. **102**, 8801 (2005).
[3] Nathaniel L. Rosi and Chad A. Mirkin, Chem. Rev. **105**, 1547 (2005).
[4] S. Antohe, N. Tomozeiu, and S. Gogonea, Phys. Status Solidi A **125**, 397 (1991).
[5] A. Hauschild, K Karki, B.C.C. Cowie, M. Rohlfing, F. S. Tautz, and M. Sokolowski, Phys. Rev. Lett. **94**, 036106 (2005).
[6] L.G. Kaake, Y. Zou, M.J. Panzer, C.D. Frisbie, and X.-Y. Zhu, J. Am. Chem. Soc. **129**, 7824 (2007).
[7] D.R.T. Zahn, G. Salvan, B.A. Paez, R. Scholz, J. Vac. Sci. technol. A **22**, 1482 (2004).
[8] G. Salvan, S. Silaghi, M. Friedrich, C. Himcinschi, D.R.T. Zahn, J. Optoelectron, Adv. Mater. **8**, 604 (2006).
[9] Zheng Wei, Heechul Lim, and Geunseop Lee, Appl. Phys. Lett. **98**, 071912 (2011).
[10] http://nano.edison.re.kr.
[11] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[12] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1992).
[13] Michael Rohlfing, Ruslan Temirov, and Frank Stefan Tautz, Phys. Rev. B **76**, 115421 (2007)

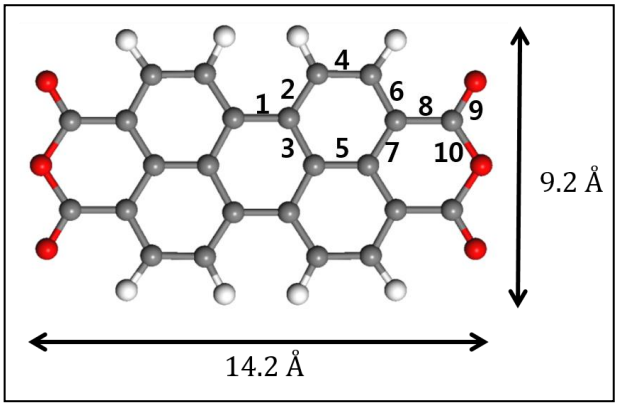

Fig. 1. The structure of PTCDA. Gray, white, red, and blue sphere correspond to carbon (C), hydrogen (H), and oxygen (O) atoms, respectively. PTCDA molecule consists of the perylene core and anhydride end groups. Each label of

PTCDA molecule refers to the interatomic bonds whose bond lengths as given in Table 1.

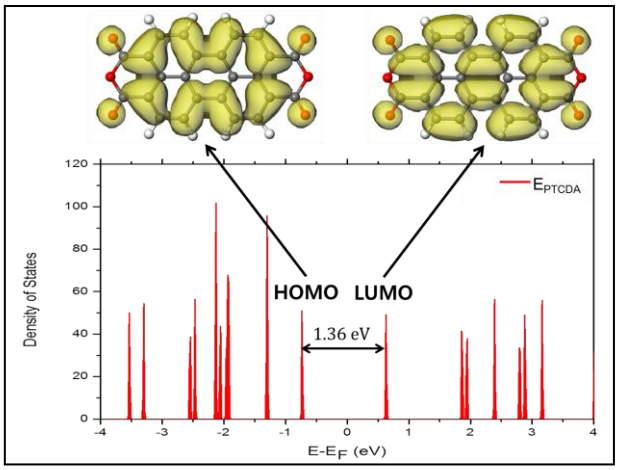

Fig. 2. Total DOS of PTCDA and the charge density contours of the HOMO and the LUMO.

Table 1. The intramolecular bond lengths (in Å) of PTCDA in the gas phase. Our calculations were performed within DFT-GGA. The bond labels are indicated in Fig. 1.

Label of bond	Bond length (Å)	
	This work	DFT (LDA) (Ref. 13)
C-C (1)	1.473	1.463
C-C (2)	1.424	1.405
C-C (3)	1.448	1.431
C-C (4)	1.422	1.400
C-C (5)	1.435	1.427
C-C (6)	1.411	1.392
C-C (7)	1.420	1.414
C-C (8)	1.494	1.475
C-O (9)	1.234	1.214
C-O (10)	1.440	1.384

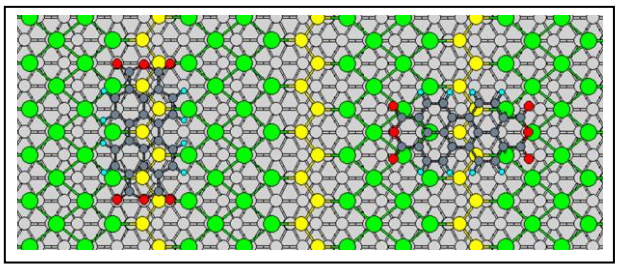

Fig. 3. Two PTCDAs on RT-In/Si(111). PTCDA on the left (L_{PTCDA}) is rotated by 90° from PTCDA on the right (R_{PTCDA}). Green, yellow, and gray sphere correspond to In nanowire, Si Seiwatz chain, and Si substrate, respectively.

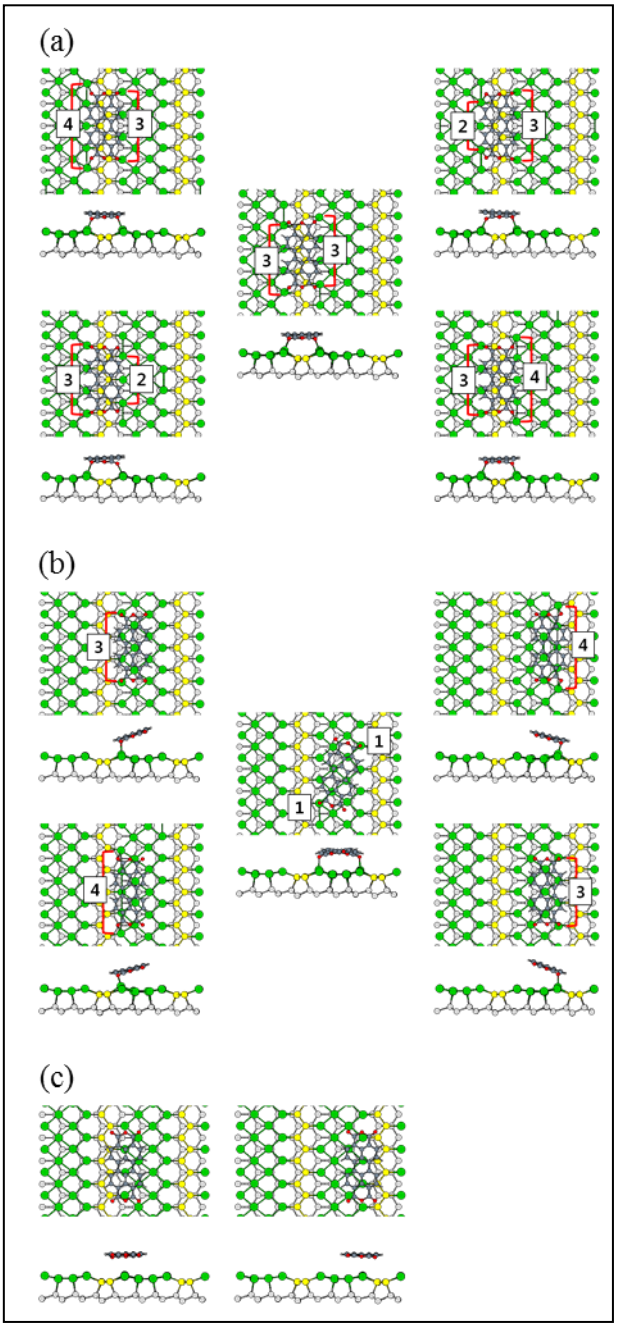

Fig. 4. A variety of adsorption positions for PTCDA on Si(111)In-8×8. PTCDA is adsorbed (a) on Si Seiwatz chain, (b) on In nanowire, and (c) at the boundary.