PHYSICAL REVIEW B **78**, 073305 (2008)

Microscopic mechanism of dipole layer formation at the pentacene/Si interface

Hojin Jeong, Duk Yong Jung, and Han Woong Yeom*
Center for Atomic Wires and Layers and Institute of Physics and Applied Physics, Yonsei University, Seoul 120-749, Korea

(Received 4 August 2008; published 29 August 2008)

We elucidate the microscopic mechanism of the dipole layer formation at the prototypical organic/inorganic interface of pentacene/Si(001) by first-principles calculations and photoelectron spectroscopy. Both theory and experiments indicate a positive dipole layer formation against the simple charge-transfer picture from Si surface atoms into molecules. We find that this dipole stems mainly from the distortion of the molecules, especially the C-H bonds, and partly from the intramolecular charge rearrangement. Both effects are essentially due to the Si-C bond formation, which leads to the sp^3 rehybridization on parts of the molecule. The sp^3 rehybridization offers a general concept for the dipole formation at organic/inorganic interfaces.

DOI: 10.1103/PhysRevB.78.073305 PACS number(s): 73.30.+y, 73.20.−r, 68.43.Bc, 79.60.Dp

Thin films of organic molecular semiconductors have attracted a great attention during last two decades in view of promising applications in optoelectronics and microelectronics.[1,2] The central current issues in organic electronics are mostly related to the interfacial properties of organic channel layers. In particular, the microscopic dipoles at interfaces dominate the interfacial electrostatic landscape[3] and, thus, determine the carrier injection in most of organic devices,[3] spin tunneling in magnetoresistance organic tunnel junctions,[4] resonant tunneling in organic quantum well devices,[5] and even molecular nanopatterning.[6]

However, the understanding on the microscopic mechanism of the interfacial dipole formation, which is basically due to charge transfer (or redistribution) between adsorbates and substrates, is very much limited. Although such charge transfer originates basically from electronegativity differences between adsorbates and substrates,[3,7,8] a few different charge-redistribution mechanisms for the dipole-layer formation have been suggested. For examples, in weakly interacting (or physisorbed) systems on metal substrates, the Pauli repulsion,[3] the mirror charges,[9] and the realignment of the charge neutrality level due to the metal-induced molecular density-of states[10] have been proposed as the origins of the charge redistribution. More complicated and more prevailing cases occur in strongly interacting (or chemisorbed) systems on metal or semiconductor substrates. In general, the strong chemical interaction at interfaces greatly changes both electronic and structural properties, and different charge-redistribution mechanisms can simultaneously operate,[7–9,11] such as electron donation (or acceptance) from adsorbates to substrates, electron polarization in substrate-adsorbate chemical bonds, formation of midgap states, and structural changes of adsorbates and substrates. Therefore, in order to understand the dipole formation mechanism for chemisorbed systems, a quantitative study taking into account of all these possible factors is crucial.

The pentacene (Pn, $C_{22}H_{14}$) molecule, five benzene rings fuzed linearly, on the Si(001) surface can be a prototypical model system satisfying both technological and fundamental interests. The relatively good carrier mobility, mechanical flexibility, and crystalline packing capability of Pn facilitate the development of hybrid devices combined with the processing power of Si.[1,2] The well-characterized surface structures and the well-resolved surface states of Si can serve for microscopic investigations of chemical interactions with molecules. Based on such motivations, the adsorption of Pn on Si substrates has been extensively studied.[12–16] These results show that Pn molecules initially lie flat on Si(001) through the covalent interaction between molecular π orbitals and the Si dangling bonds,[12–14] and initial Pn films grow in a quasi-layer-by-layer fashion.[15] However, the interface electronic properties of the initial Pn layers on Si(001) have not been made clear.

In this Brief Report, we investigate the electronic structures of Pn on Si(001) focusing on the dipole layer formed at the interface by first-principles calculations combined with ultraviolet photoelectron spectroscopy (UPS). The positive dipole layer is verified, against the electronegativity difference between C and Si, and its microscopic origin is disclosed. This unexpected dipole layer is a combined result of the molecular distortion and the rearrangement of molecular electronic charges due to the sp^3 rehybridization in making C-Si bonds.

All calculations are performed using the VASP code[17] with ultrasoft pseudopotentials[18] and the generalized-gradient approximation for the exchange-correlation energy.[19,20] The Si(001) surface is modeled by $p(8\times4)$ periodic slabs including six Si layers and a H layer terminating each slab bottom. The 300 eV cutoff energy for the plane-wave expansion and only the Γ point for the surface-Brillouin-zone integration are sufficient for converged results. All the atoms, except for the bottommost Si and H atoms, are fully relaxed. The work function (Φ) is obtained from the difference between the electrostatic potential (V_{ES}) in vacuum and the Fermi energy (E_F). The electrostatic dipole (μ) normal to the surface is calculated as

$$\mu = \int_0^c z\rho(z)dz, \tag{1}$$

where c and z are the height of the supercell and the vertical position from the supercell bottom, respectively, and $\rho(z)$ is the charge density including both nuclei and electrons at height z, integrated over the surface-parallel plane. In order to obtain an accurate dipole moment from Eq. (1), the charge density of a slab is fully enclosed by a supercell [or integration boundaries of Eq. (1)] and each slab is separated far

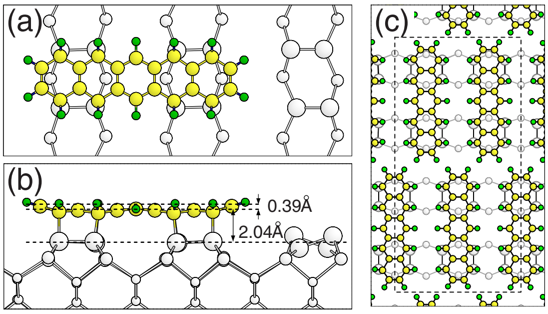

FIG. 1. (Color online) [(a) and (c)] Top and (b) side views of the optimized geometries of Pn on Si(001) at [(a) and (b)] 0.25 and (c) 1 ML. The white, yellow (medium-sized), and green (small) balls represent Si, C, and H atoms, respectively. The horizontal dashed lines in (b) indicate the average heights of H, C, and Si-dimer atoms, and the dashed box in (c) indicates the $p(8\times4)$ surface supercell.

enough to avoid an artificial interaction with imaginary charges of neighboring slabs. Thus, we position the slab at the middle of the supercell and include a thick vacuum space of 20 Å.[21] We also apply the dipole-correction scheme to compensate the imaginary dipoles of neighboring slabs.[22]

UPS measurements are performed using He discharge radiation and high-resolution photoelectron analyzer (SES-100, Gamma data). Pn vapor is dosed onto the clean Si(001)2×1 surface from a graphite effusion cell. The Pn coverage is calibrated through the intensity decay of the dangling-bond surface state. The Φ is measured by well-defined secondary cutoffs of photoelectron spectra.

The fully optimized geometry of a Pn molecule on Si(001) is displayed in Figs. 1(a) and 1(b), which has been established as the most stable and the most popular adsorption structure by the previous investigations.[13,14] In other, minor, adsorption structures, the molecules are 90° rotated or laterally translated. However, the qualitative nature of the Si-Pn bonding, and, thus, the essential part of the following discussion, does not change among different adsorption structures. The molecule symmetrically lies across two Si dimer rows; eight C atoms are fourfold coordinated through the chemical interaction with four Si dimers, which leads to a large adsorption energy of 5.38 eV and to important structural changes in the molecule and the substrate. The molecule loses its planar geometry upon adsorption with the average height difference between C and H atoms of 0.39 Å, and asymmetric Si dimers underneath the molecule are symmetrized. The bond angles ($\sim$108.7°) at the fourfold-coordinated C atoms are very close to the ideal tetrahedral angle (109.5°), indicating the sp^3 hybridization, while other C atoms still preserve the sp^2 hybridization with their bond angles of $\sim$120°. One $p(8\times4)$ surface supercell can accommodate four molecules at most by saturating all Si dimers as shown in Fig. 1(c), which is defined as the 1 monolayer (ML) coverage. This definition is consistent with the experimental one mentioned above. The adsorption structure and energy are nearly unchanged with increase in the number of the molecules per supercell from one (0.25 ML) to four (1 ML), indicating only a negligible interaction between adsorbed molecules.

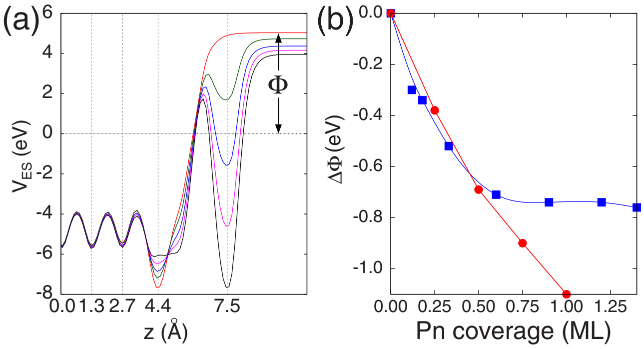

FIG. 2. (Color online) (a) Calculated electrostatic potential (V_{ES}) of the Si(001) surface with Pn coverages from 0 (top) to 1 ML (bottom). The vertical dashed lines indicate, from right to left, the average heights from the fourth Si layer of Pn molecules and top three Si layers. The energy zero is the E_F at each coverage. The Φ of the clean Si(001) surface is indicated. (b) Measured (boxes) and calculated (circles) work-function changes ($\Delta\Phi$) as a function of the Pn coverage.

The direction and the magnitude of an interface dipole are often extracted from the work-function changes ($\Delta\Phi$). The $\Delta\Phi$ of Si(001) upon the Pn adsorption is measured using UPS [boxes in Fig. 2(b)]. The Φ decreases gradually up to the Pn coverage of 0.6 ML and then saturates at $\Delta\Phi\sim-0.75$ eV at higher coverages. This suggests the formation of a *positive* dipole layer at the interface below 0.6 ML. The early saturation must be due to the growth of physisorbed multilayers at higher coverages, as reported in the previous microscopy study.[15]

The calculated $\Delta\Phi$ [circles in Fig. 2(b)], obtained from V_{ES} shown in Fig. 2(a), reproduces quantitatively well the measured Φ decrease below 0.6 ML [$\Delta\Phi=-0.39$ (-0.69) eV at 0.25 (0.5) ML in theory versus $\Delta\Phi=-0.34$ (-0.69) eV at 0.23 (0.60) ML in experiment]. This implies that the origins of the Φ decrease are successfully captured in the calculation. The overestimation of $\Delta\Phi$ in theory at higher coverages is reasonable since an ideal monolayer cannot be obtained experimentally above 0.6 ML.[15]

Between two energy levels, the E_F and the vacuum level (VL), associated with $\Delta\Phi$, the calculated V_{ES} seen in Fig. 2(a) shows that E_F is almost unchanged upon adsorption, which is checked from the change in energy difference between V_{ES} at center Si layer of the slab. On the other hand, the VL is gradually decreased with the Pn coverage. These verify that the Φ decrease is entirely due to the positive dipole layer formed by the Pn adsorption, which lowers the vacuum level. Indeed, the dipole-moment change ($\Delta\mu$) per supercell by a single Pn adsorption (0.25 ML) is calculated by Eq. (1) to be 0.99 eÅ, in fully accord with the calculated $\Delta\Phi$ of -0.39 eV through $\Delta\Phi=e\Delta\mu/\epsilon_0 A$ with elementary charge e, permittivity of vacuum ϵ_o, and unit-cell area A.

Then, one should clarify how the surface charge redistributes microscopically to form the positive dipole. Among the phenomenological mechanisms for the charge-redistribution suggested earlier, we claim that the donation of molecular electrons to surface states as well as the carrier exchange mediated by midgap states cannot be the case here. The former is ruled out by the invariance of E_F upon the Pn

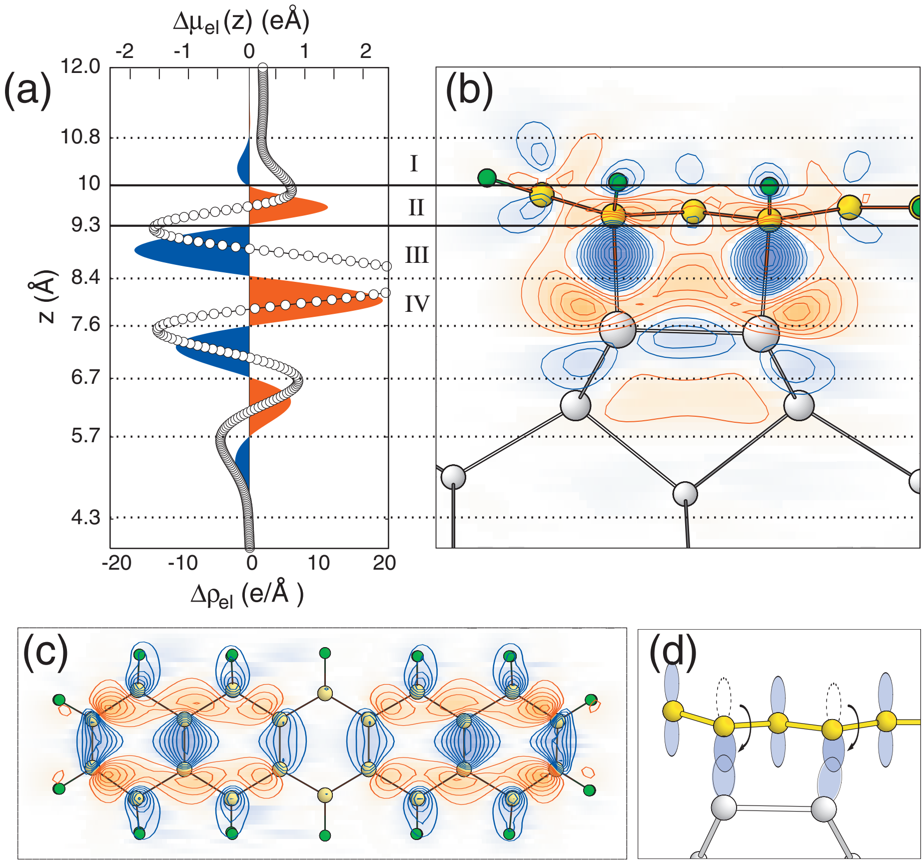

FIG. 3. (Color) (a) Variations of the in-plane electron-density change $\Delta\rho_{\mathrm{el}}$ upon the Pn adsorption (filled curve) and $\Delta\mu_{\mathrm{el}}(z)$ (open circles) with height z from the slab center. See text for the definitions of $\Delta\rho_{\mathrm{el}}$ and $\Delta\mu_{\mathrm{el}}(z)$. [(b) and (c)] Contour map of $\Delta\rho_{\mathrm{el}}$. In (b), all charges are projected onto a surface-normal plane, while in (c) only the charges within the Pn molecule [layers I and II in (a) and (b)] are projected onto a surface-parallel plane. (d) Schematic representation of the origin of the intramolecular charge rearrangement upon adsorption. See text for details. Blue and red colors represent the electron excess and depletion, respectively.

adsorption. That is, *the Pn molecule is neither an electron donor nor an electron acceptor*. The latter mechanism is not consistent with the measured valence-band spectra and the calculated density of states (data not shown here), where no midgap state is found. A consistent experimental result was reported earlier.[12] Thus, the formation of chemical bonds at the Pn/Si interface is the only possible charge-redistribution mechanism to be considered further. However, in contradiction to the present observation, the formation of C-Si bonds at the interface is generally expected to produce the negative dipole because of the larger electronegativity of C than Si (2.55 vs 1.90 in Pauling scale). That is, the positive dipole formation cannot simply and trivially be explained by any phenomenological description discussed in the literature.

In order to elucidate the physical origins for such unexpected dipole formation, a more comprehensive analysis of the charge redistribution upon adsorption is necessary. Since both atomic (ionic) and electronic structure changes contribute to the dipole formation, we consider these effects separately.

To this end, we split the net charge density (ρ) of the Pn-adsorbed surface into three parts of ρ_{sub}, ρ_{pc}, and $\Delta\rho_{\mathrm{el}}$. In which, ρ_{sub} and ρ_{pc} are the charge densities of isolated Si(001) and the isolated Pn (but keeping the optimized atomic positions in the adsorption configuration), respectively, for the contribution of atomic reconstruction. On the other hand, $\Delta\rho_{\mathrm{el}}$, defined as $\Delta\rho_{\mathrm{el}}=\rho-(\rho_{\mathrm{sub}}+\rho_{\mathrm{pc}})$, purely reflects the electron-density change due to chemical interaction between the molecule and the substrate.

The atomic reconstruction of the substrate upon adsorption is characterized by the symmetrization of Si dimers underneath the adsorbed molecule [see Fig. 2(b)]. However, this reconstruction increases the dipole moment only by 0.02 eÅ (2% of the total $\Delta\mu$) compared to that of the clean Si(001) substrate. In sharp contrast, the distortion of the Pn molecule produces a substantial positive dipole moment of 0.68 eÅ as calculated from ρ_{pc}. This explains 69% of the total $\Delta\mu$. That is, *the molecular distortion is the major origin of the positive dipole-layer formation*. This huge dipole is simply due to the tilt of strongly polarized C-H bonds in the adsorbed molecule; electropositive H atoms are lifted up by 0.39 Å in average from electronegative C atoms [see Fig. 1(b)].

Then, the remaining 29% contribution in $\Delta\mu$ (0.29 eÅ) must be due to the electron-rearrangement effect or the chemical interaction represented by $\Delta\rho_{\mathrm{el}}$. At a first glance, this is surprising since the positive dipole moment of 0.29 eÅ seems to indicate the electron transfer from C to Si, contrary to the electronegativity picture. To solve this puzzle, we define an additional function $\Delta\mu_{\mathrm{el}}(z)$ as

$$\Delta\mu_{\mathrm{el}}(z)=\int_0^z z'\Delta\rho_{\mathrm{el}}(z')dz'. \tag{2}$$

This corresponds to the dipole moment due to the electronic charge within $0-z$ and $\Delta\mu_{\mathrm{el}}(z)\rightarrow\Delta\mu_{\mathrm{el}}$ when $z\rightarrow c$.[8] The calculated $\Delta\mu_{\mathrm{el}}(z)$ is plotted in Fig. 3(a) along with the in-plane integrated $\Delta\rho_{\mathrm{el}}$. These show in detail which part of the electronic density change is responsible for the electronic dipole formation. Figure 3(b) is the contour map for $\Delta\rho_{\mathrm{el}}$, where all charges in $\Delta\rho_{el}$ are projected onto a surface-normal plane. As shown in Figs. 3(a) and 3(b), $\Delta\rho_{el}$ oscillates with z and the formation of covalent bonds is obvious between C and Si atoms. These bonds are strongly polarized with the electron depletion and accumulation appearing in regions III and IV of Fig. 3(a), respectively. This verifies clearly the partial electron transfer from Si to C atoms in making the bonds, in accord with the electronegativity picture. However, there exists another subtle electron-depletion layer (II) at the molecular plane, and we find that this charged layer determines the direction of the dipole moment over the charge transfer from Si to C; the $\Delta\mu_{el}(z)$ is changed to positive from negative in passing the depletion layer II and converges to the macroscopic dipole of 0.29 eÅ over the shallow electron-excess layer I. That is, *the intramolecular charge redistribution is another major mechanism for the positive dipole formation*.

The electron redistribution within the Pn molecule is further visualized in Fig. 3(c), where parts of $\Delta\rho_{el}$ within layers I and II are projected onto a surface-parallel plane. When Pn is adsorbed on Si(001), 4 of 11 π bonds of the molecule are broken and rehybridized to eight C-Si σ bonds. As seen in the figure, the intramolecular electron rearrangement of Pn is closely related with this rehybridization; the electrons are depleted along the bonds between C atoms containing the fourfold-coordinated C atoms bonded to Si while accumulate along other bonds not involved in the direct C-Si bonds. This rehybridization compresses the spatial distribution of p_z electrons toward the substrate, as illustrated in Fig. 3(d), leaving effective positive charges above the molecular plane. Although, the amount of this positive charge induced on the molecule is small [see the charge densities of layers II and III in Fig. 3(a)], it dramatically determines the dipole moment of the surface, since its contribution to the dipole is weighted by z [see Eq. (1)].[7,8]

As discussed above, both the molecular distortion (a structural effect) and the intramolecular charge rearrangement (an electronic effect) are crucial in forming the positive dipole layer. We emphasize that both contributions come essentially from the same origin, the sp^3-like local rehybridization of the molecule, which is due to the C-Si bond formation. Since the C-Si σ-bond formation occurs ubiquitously for organic molecular adsorbates on Si or semiconductor surfaces, the present mechanism of the dipole formation can widely be generalized. To check this idea, we also calculate the dipole formation upon the adsorption of benzene on Si(001). The results, indeed, show that the single benzene molecule within a 4×4 supercell of Si(001) with di-σ ("butterfly")- and with tetra-σ ("tight-bridge")-bond configurations[23] increases the dipole moments by 0.40 and 0.56 eÅ, respectively. Considering that the sp^3 hybridization also takes place at Si(111),[24] the previously reported positive dipole layers on the benzene/Si(111) (Ref. 11) and the Pn/Si(111) (Ref. 16) surface can straightforwardly be understood. In addition, in contrast to the general argument of the physisorption of organic molecules on metal surfaces, Ferretti *et al.*[25] recently reported that the Pn molecule does chemically interact even with a nonreactive noble-metal (Cu) surface. It would be interesting to apply the present analysis method of the dipole formation to the cases of strongly interacting molecule/metal interfaces.

This work was supported by MOST through Center for Atomic Wires and Layers of the CRi program.

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*yeom@yonsei.ac.kr

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