PHYSICAL REVIEW B **75**, 153202 (2007)

Intercalation of oxygen and water molecules in pentacene crystals: First-principles calculations

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(Received 10 January 2007; published 4 April 2007)

Defect formation processes in semiconductors play an important role in controlling structural, electronic and transport properties. Here, we report the results of first-principles calculations of defect formation by oxygen and water molecules in a pentacene (Pn) molecular crystal, a prototypical system in organic electronics. We find that for both species, it is energetically favorable to enter Pn. The most stable defect structures resulting from O_2 intercalation and dissociation are either O complexes or single-O configurations. A special case is an intermolecular O bridge with levels in the energy gap of Pn, 0.33–0.40 eV above the valence-band maximum. In contrast to O_2, H_2O molecules stay preferably intact between layers.

DOI: 10.1103/PhysRevB.75.153202 PACS number(s): 72.80.Le

The interaction of impurities with pristine crystals has been an integral part of the physics of semiconductors. Defect formation may induce significant changes on the structural, electronic, and transport properties of the host crystal, especially when the defects have levels in the energy band gap. Oxygen, water, and hydrogen impurities, in particular, have attracted intense and sustained interest for traditional semiconductors such as IV and III-VI systems. Oxygen[1] and hydrogen[2] defects in silicon, for example, exhibit negative-*U* properties, are known to interact with each other,[3] and they can play a key role in the degradation of electronic devices under a variety of conditions such as bias stress,[4] aging, or irradiation.[5] Likewise, these impurities are expected to play a role in the emerging materials of organic semiconductors. These materials are typically found in the form of molecular crystals and they can demonstrate an even richer behavior in accommodating impurities in the intermolecular space.

Among the large number of organic semiconductors currently investigated for electronic applications, pentacene (Pn) stands out because of its relatively high carrier mobilities[6–9] and because it forms ordered film structures[10] on various substrates. Pentacene in solution[11] is known to photodegrade when exposed to air. Recent experimental studies have shown that controlled exposure to humidity[12] and oxygen[13] has an effect on the physical properties of a pentacene thin film. The presence of oxygen has also been suggested[14] as a possible factor in the appearance of deep gap levels in pentacene. The atomic-scale details, however, of the interaction of oxygen and water with a Pn crystal remain unknown. In particular, it is unknown whether there is an intercalation of such molecules in the crystal and how the bonding configurations differ from the ones in solution. Another question is whether O_2 and H_2O intercalation may play a role in the appearance of deep energy levels[15] and amorphous band tails[16] in the Pn band gap.

In this Brief Report, we use first-principles calculations to study the intercalation of oxygen and water molecules in a Pn crystal. We find that both species are favored to enter the crystal with a significant gain in energy as compared to vacuum. The trapping configurations, however, differ significantly for oxygen and water. In the former case, we find that the most stable configurations correspond to two atom O complexes that result after dissociation of an O_2 molecule inside a Pn layer. One of the stable configurations includes an intermolecular bridge with a single O atom. The dissociation energy of these O complexes to atomic species is about zero. Oxygen may therefore be present in a Pn crystal either as a complex or as atomic species. In the latter case, we find that the bridge configuration has a pair of levels in the Pn gap located 0.33–0.40 eV above the valence-band maximum, in agreement with experiment.[15] Other O-complex configurations have shallow levels in the gap, pointing to a possible role for oxygen in the observed[16] amorphous band tails of Pn. In contrast to oxygen, we find that water molecules prefer to stay nonbonded between Pn layers. There also exist metastable H_2O configurations in the layers that result in significant bending in the surrounding molecules. Dissociation to H and OH moieties is not favored energetically. The results point to a role of water as a scattering center between the molecular layers.

The results were obtained using density-functional theory (DFT) calculations with plane waves as a basis set and ultrasoft pseudopotentials to represent the ionic cores,[17] as implemented in the VASP code.[18] The energy cutoff was set to 400 eV, and only the Γ point was used for *k*-point sampling. Intercalation and defect formation energies were calculated for $2\times2\times1$ supercells in terms of the herringbone unit cell of Pn crystals reported by Campbell *et al.*[19] Results for density of states (DOS) are for $1\times2\times2$ supercells using the tetrahedron method with a $4\times4\times2$ *k*-point grid. Calculations with different sizes of supercells ($1\times2\times1$ and $2\times2\times2$) confirm the convergence of defect energies. DOS change only minimally for a finer *k* grid, especially regarding the key issue of defect levels in the gap. We used a local-density approximation (LDA) exchange-correlation (xc) functional[20] and included van der Waals (vdW) interactions between pentacene molecules, as described in Ref. 21. We note that LDA gives[21] an accurate description for pertinent quantities, such as pentacene and anthracene molecular cohesive energies and benzene dimerization energy. As stated

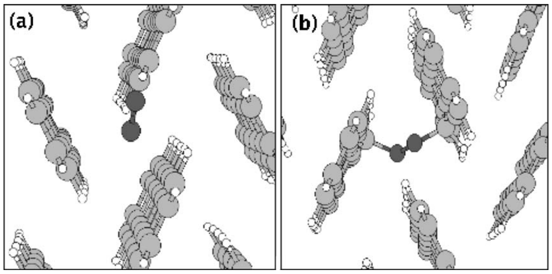

FIG. 1. Insertion of an O_2 molecule in a pentacene crystal (a) between layers and (b) as a peroxy bridge. The insertion is energetically favored by (a) 0.13 eV and (b) 0.55 eV compared to O_2 in vacuum (C: gray, O: dark gray, and H: white spheres).

in selected cases below, the use of a generalized-gradient approximation (GGA) xc functional[22] gives different energies, but the main conclusions stay qualitatively the same.

We investigated an extensive number of possible configurations of O_2 molecules in a Pn crystal, either between or inside Pn layers. We hereafter denote with E_i the energy difference for an O_2 molecule in Pn and in vacuum. Positive E_i favors insertion of species in the Pn crystal. We found that transfer of an O_2 molecule from vacuum to a configuration between the layers, as shown in Fig. 1(a),[23] results in an energy drop of 0.13 eV. The triplet state is more stable than the singlet by 0.48 eV. The molecule interacts with the network, without, however, forming covalent bonds and it does not dissociate. In contrast, attempts to probe an O_2 molecular configuration inside Pn layers resulted always to the formation of C–O bonds. One possible state is an intermolecular peroxy bridge, shown in Fig. 1(b), with an E_i energy of 0.55 eV. It is a transient state before breakup of the O_2 molecule inside the layer, which leads to further decrease in energy.

Interaction of an O_2 molecule with a single Pn molecule, as in gas phase or solution, results in the formation of transannular endoperoxides.[24] In the case of the crystal, we found that other structures are the most stable. They contain either a pair of triangular C–O–C bonding configurations or an intermolecular O bridge and a dangling O atom (all C–O bonds are on the sixth C atom of Pn viewed from the top), as shown in Figs. 2(a) and 2(b), respectively. We term these configurations $\mathrm{O_I}$ for (a) and $\mathrm{O_{II}}$ for (b). The formation of C–O bonds in the epoxy complexes of $\mathrm{O_I}$ results in a large E_i of 1.88 eV with the singlet state being more stable than the triplet. $\mathrm{O_{II}}$ is almost as stable with an E_i of 1.78 eV and the triplet marginally (by 0.07 eV) lower in energy than the singlet. Results for these E_i's are the same for a finer $2\times2\times2$ k mesh, confirming convergence with respect to k-point sampling. We note that the variation and eventual reversal of the spin splitting for O_2 between layers, as an intermolecular peroxy bridge, $\mathrm{O_I}$, and $\mathrm{O_{II}}$, follow the overstretching and breakup of the O–O bond. We note that the use of GGA also indicates that intercalation in the form of $\mathrm{O_I}$ and $\mathrm{O_{II}}$ is energetically favorable. GGA E_i's are smaller at 1.0 eV and 0.6 eV for $\mathrm{O_I}$ and $\mathrm{O_{II}}$, respectively. A variant of $\mathrm{O_I}$ with the O atoms on neighboring Pn molecules in the same layer has a lower E_i of 1.5 eV. When either of the O atoms or both form similar pairs of bonds with C atoms toward the center of the molecule, the energy rises further by 0.3–1.0 eV.

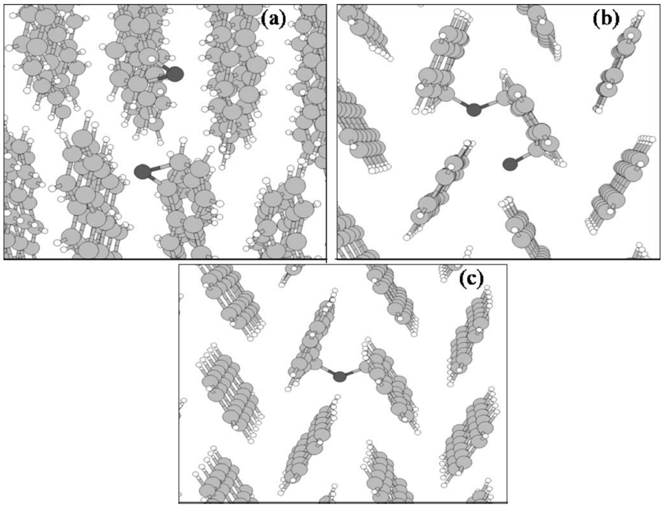

FIG. 2. Stable defect configurations resulting from O_2 incorporation into a pentacene crystal: [(a) and (b)] breakup of O_2 in vicinal O defects with insertion energies of 1.88 and 1.78 eV, respectively, and (c) dissociation in atomic species (C: gray, O: dark gray, and H: white spheres).

We also probed the energetics of dissociation of the $\mathrm{O_I}$ and $\mathrm{O_{II}}$ complexes in atomic species. We considered three cases of single-O configurations by removing one atom from $\mathrm{O_I}$ and $\mathrm{O_{II}}$. The dissociation energy of either $\mathrm{O_I}$ to a single O at the end of a Pn molecule or $\mathrm{O_{II}}$ to an intermolecular bridge [shown in Fig. 2(c)] is very small, 0.0–0.1 eV. Compared to these structures, the single-O configuration with only the dangling O of $\mathrm{O_{II}}$ is less stable by 1.0 eV. Assuming that the corresponding barriers are small enough, oxygen species are expected to enter a Pn crystal and either form complexes such as $\mathrm{O_I}$ and $\mathrm{O_{II}}$ or dissociate into the corresponding single-O configurations.

The presence of oxygen, in complex or atomic form, is expected to alter the properties of the Pn semiconductor, because the formation of C–O bonds disrupts the pristine π-π^* bonding character. Indeed, DOS calculations for the most stable defect structures mentioned above reveal that O induces changes in the vicinity of the Pn energy band gap. For example, the single-O intermolecular bridge of Fig. 2(c) has a pair of levels in the gap 0.33 and 0.40 eV (these values are essentially the same when a GGA xc functional is used) above the valence-band maximum (VBM). The corresponding DOS is shown in Fig. 3 where we juxtapose it with the LDA DOS of the pristine Pn crystal. We note that the calculated energy gap (0.76 eV) is in agreement with previous DFT studies,[25] but smaller than the experimental value[26] (2.20 eV) due to well-known limitations of DFT. We also investigated the electronic structure for the other stable configurations of oxygen in Pn. Configuration $\mathrm{O_I}$ does not contain levels in the gap; rather there are molecular resonances present inside the Pn valence and conduction bands. The $\mathrm{O_{II}}$ complex, on the other hand, has shallow levels in the gap at the edges of the Pn bands.

In addition to configurations resulting from a single dissociation step of an O_2 molecule in Pn, there are stable struc-

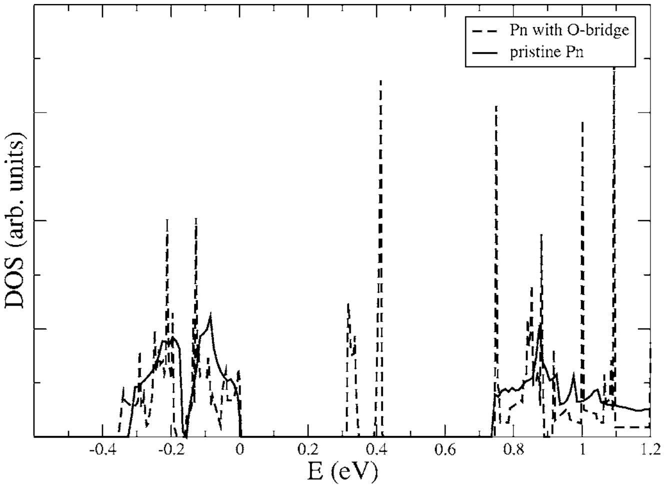

FIG. 3. LDA density of states for pristine Pn (solid line) and for the O-bridge defect (dashed line) of Fig. 2(c). Zero of energy at valence band maximum. Levels in the Pn band gap appear for the O-bridge defect structure.

tures for which C–H bonds are replaced by C–O and C–OH bonds. Such structures, especially the ones at the end of Pn molecules, are more stable than the configurations discussed above by up to 2 eV. Their creation, however, entails the dissociation of the very stable C–H bonds and it should be suppressed due to high barriers.

Water molecules can also be incorporated in Pn crystals. Unlike oxygen, however, the most stable configuration (with an E_i of 0.55 eV) we found for H_2O is an intact molecule between Pn layers, as shown in Fig. 4. In this form, the H_2O molecule does not induce any considerable structural change in the embedding medium and DOS calculations show no significant change inside or at the edges of the band gap. An H_2O molecule could nevertheless affect carrier mobilities by acting as a scattering center.

Migration of H_2O molecules inside the layers results in configurations higher in energy by more than 0.5 eV. Starting with the same initial configurations as found to result in the formation of C–O bonds in the case of an O_2 molecule, an H_2O molecule stays intact. In this case, however, considerable bending is induced on the Pn molecules that encapsulate the H_2O species, a feature that could affect polaron hopping and therefore the transport properties of a Pn device. Dissociation of an H_2O molecule to extra CH and COH moieties in vicinal molecules raises the energy considerably, by 1.2 eV compared to Fig. 4. We note again that, at least for the cases considered here, the most stable water-related configuration in Pn is that of an H_2O molecule between the layers.

The above results for oxygen and water intercalations are in agreement with several experimental observations. In particular, the observation that H_2O and O_2 species enter a Pn crystal[12,13] is confirmed in our calculations. The appearance of levels in the gap is in agreement with the experimental findings of Lang *et al.*,[15] and the formation of other complexes may account for at least part of the amorphicity observed in Ref. 16. We should stress that although the DFT values for the levels in the gap are in excellent agreement with experiment,[15] a more elaborate calculation based on the GW approximation is needed to determine the position of the levels with higher accuracy. A GW approach, which obtains the self-energy in terms of the Green function G and the screened interaction W, has been used for the ideal bulk case,[25] but its employment for the larger defect supercells is computationally demanding and will be considered elsewhere. Likewise, future studies can address other interesting points that require intensive calculations. In particular, kinetics is another important factor in deciding ultimately the relevance of the defects discussed in this work. Key questions are, for example, whether oxygen intercalation leads to formation of a self-protecting native oxide on Pn, and the role of light in aiding oxygen migration and dissociation.

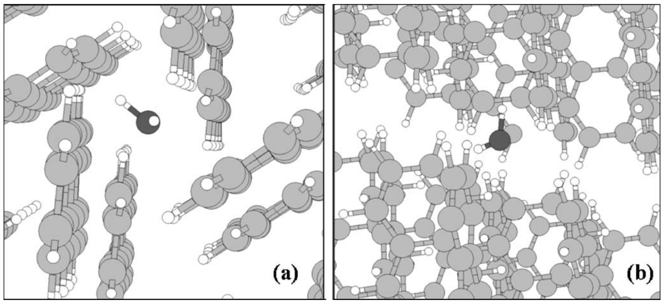

FIG. 4. Incorporation of an H_2O molecule between pentacene layers: (a) top and (b) side view (C: gray, O: dark gray, and H: white spheres).

Let us also stress that our results do not preclude other species or mechanisms contributing to a modification of the electronic and transport properties of a Pn crystal. For example, excess H in the form of CH_2 configurations has also been suggested[27] as an explanation of the observed[15] 0.38 eV gap level. Our results confirm that a CH_2 defect in a Pn crystal has a level in the gap, albeit at a slightly higher position (0.47 eV above VBM) than the 0.34 eV reported in Ref. 27. Finally, structural defects, such as vacancies,[28] can also play a role in determining crystal properties, and perhaps aid the defect formation processes discussed in this work.

In summary, we have shown that intercalation of oxygen and water molecules in pentacene crystals is favored energetically. The most stable configurations for O are either complexes or single atomic species. Distinct levels in the gap are found for intermolecular O bridges, in agreement with experiments. Other complex configurations have levels close to band edges that may account for recently observed amorphous band tails. In contrast to oxygen, H_2O stay in intact molecular form between molecular layers.

We acknowledge useful discussions with G. G. Malliaras and support by the William A. and Nancy F. McMinn Endowment at Vanderbilt University and by DOE under Grant No. DEFG0203ER46096. The calculations were performed at ORNL’s Center for Computational Sciences.

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