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Electronic structures and impurity accumulation around extended defects in pentacene films: first-principles study

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Abstract

Extended defects such as a grain boundary promote serious damage for carrier transport in organic molecular solids. In this work, we study electronic structures of stacking-fault and grain-boundary defects in pentacene films by the first-principles calculation. We found that these defects markedly decrease the carrier transfer across the defects, especially in case of the stacking fault in film-bending environments. On the other hand, the band offset appears at the grain boundary, which works as a large potential barrier for carriers. Moreover, we show that the grain boundary works as a sink of impurity atoms and traps carriers. These results are useful to analyze the carrier transport in granulated films.

1. Introduction

Organic semiconductors such as pentacene are fascinating materials for future devices, owing to their softness, light masses, and low-cost production. However, the grown films often include many extended structural defects like a stacking fault and a grain boundary, which are expected to work as potential barriers for carriers and promote serious degradation of carrier transport [1,2]. In addition, similar to inorganic semiconductors, the extended defects are expected to trap impurity atoms and also work as carrier traps [2]. However, there have been little theoretical studies on these properties so far. In this work, by using the first-principles calculations, we study structural and electronic structures of a stacking fault (SF) and a grain boundary (GB) in pentacene films, and clarify how these defects degrade the carrier transport and capture impurity atoms.

2. Calculation Model and Method

In this work, we adopt a (100)-faced SF and a (100)-45deg−tilted GB for extended defects in pentacene films (thin-film phase) [1]. The unit-cell models for these defects are shown in Figs.1(a) and 1(b). Atom positions in these models are fully optimized and their electronic structures are studied. In order to study the impurity-accumulation property, metal atoms (Au, Al) and non-metal atoms (H, O) are inserted at the most stable points around these defects.

Atom positions and electronic structures of the present defect systems are calculated by the standard first-principles method in the density functional theory, using the VASP code [3]. We adopt the GGA-PBE exchange-correlation functional with DFT-D3 van der Waals correction, the 500eV energy cutoff for the plane-wave expansion of wave functions, and the 1×2×2 and 1×1×2 k-points in the Brillouin-zone integration for both systems. Other calculation details are described in our previous publications [4,5].

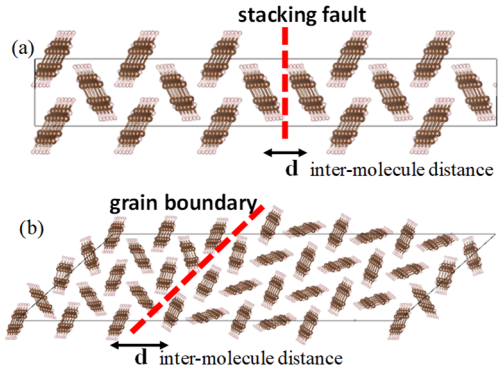

Fig.1 Schematic pictures of (a) stacking fault and (b) grain boundary in pentacene films adopted in the present calculations.

3. Results and Discussions

Structural properties of extended defects

We first consider structural properties of extended defects. Figs.2(a) and 2(b) show the formation energies of the stacking fault (SF) and grain boundary (GB), respectively, as a function of inter-molecule distance *d* shown in Fig.1. At the most stable distance, the formation energy is large, around 2.2eV/nm^2, for the GB, while the energy is small for the SF, about 0.3eV/nm^2. This result indicates that the GB is produced only in the film growth, while the SF can appear even during the device operation after the device fabrication, which might induce the progress of mobility degradation.

It is interesting to note that, when the inter-molecule distance is increased in these defects, the increase of the formation energy is small for the SF and large for the GB. This result indicates that, when the strain is applied to the film by the film bending [6], the SF is easily deformed and degrades the carrier transport as shown in the following.

Electronic properties of extended defects

Next, we consider the carrier transport property across the defects. We show the effective HOMO-band widths of the present repeated-slab SF and BG systems in Fig.3(a) and 3(b), respectively. The width is much smaller than that of the bulk pentacene solid (0.8eV) for both the SF and GB

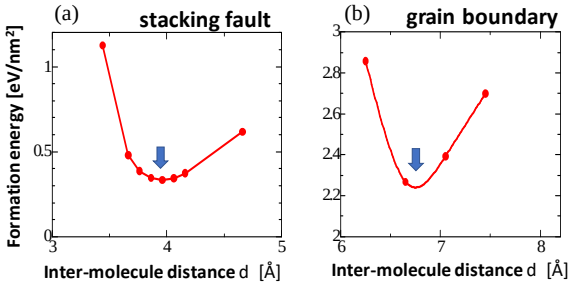

Fig.2 Formation energies of (a) stacking fault and (b) grain boundary, as a function of inter-molecule distance d around the defect shown in Fig.1. The arrows indicate the most stable distances.

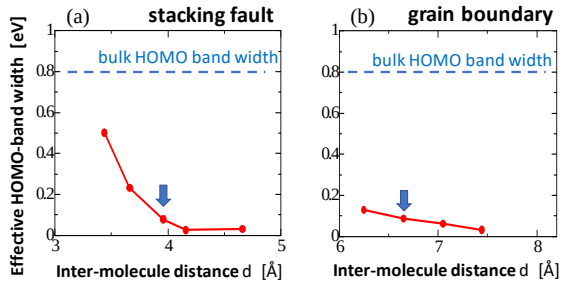

Fig.3 Effective HOMO-band width of the present repeated-slab system in cases of (a) stacking fault and (b) grain boundary, as a function of inter-molecule distance d around the defect. The arrows indicate the cases of the most stable distances.

reflecting the small hole transfer across the defects. It is interesting to note here that, with increasing the inter-molecule distance, the width of the SF system shows the exponential decay, which reflects the carrier transfer by the overlap of electronic orbitals on both sides of the SF. On the other hand, the width of the GB system shows small changes, which occurs due to the incommensurate staggered arrangement of molecules on both sides of the GB. This result indicates that the carrier transfer across the defect is quite different between the SF and GB.

The most remarkable feature is the appearance of the band offset at the GB. Figs.4(a) and 4(b) respectively show the LUMO and HOMO wave functions of the present GB system. The LUMO state is confined in the right molecular layers, while the HOMO state is localized in the left layers. By analyzing the local density of states, we can obtain the

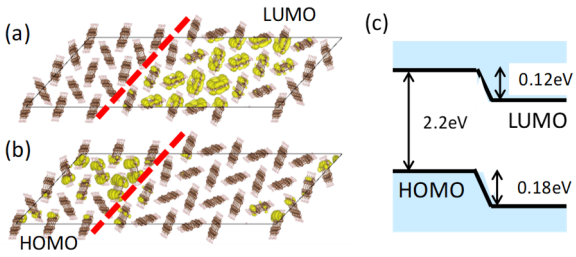

Fig.4 Wave functions of (a) LUMO and (b) HOMO states around the grain boundary. (c) Calculated band alignment around the present grain boundary.

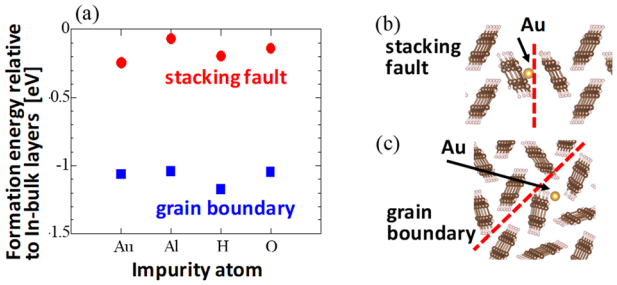

Fig.5 (a) Formation energies of impurity atoms around defects. (b) and (c): Stable Au-atom positions around the stacking-fault and grain boundary.

band alignment as shown in Fig. 4(c). Such alignment appears owing to the difference of molecular density on both sides of the GB originating from the incommensurate lattice-mismatch along the GB. This feature is generally expected at any GB's and becomes one of important origins to prevent the carrier transfer across the GB's.

Impurity accumulation and carrier trap around defects

Finally, we consider the impurity accumulation around the defects. Fig.5(a) shows the formation energy of various impurity atoms around the SF and GB, where the energy is relative to the case of in-bulk layers. The formation energy is small for the SF, indicating no preference of impurity accumulation. On the other hand, the energy is negative and large for both metal and non-metal atoms in case of the GB. This is because the GB has the incommensurate staggered molecule arrangement as in Fig.5(c) and the insertion of additional atoms is easily realized. From this, we can expect that the impurity atoms easily precipitate from bulk layers to the GB. Moreover, we found that these impurity atoms, except O atom, produce gap states about 0.4-0.5 and 0.1-0.2eV above the HOMO bands for the SF and GB, respectively, and becomes electron/hole carrier traps.

4. Conclusions

By the first-principles calculations on extended defects in pentacene films, we showed that the stacking fault is easily deformed under the film-bending condition, which prevents the carrier transfer and progresses the carrier-mobility degradation. The grain boundary markedly decreases the carrier transfer between grains by not only the staggered molecule arrangement but also the band offset at the boundary. We also showed that the grain boundary traps impurity atoms and such atoms produce the carrier traps.

Acknowledgements

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