

Chemical Trend of Atomic Impurity States in Organic Semiconductor Films; Theoretical Investigation

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1. Introduction

Organic semiconductors are promising materials for future optical and electronic devices because of their unique characteristics such as softness and light mass. During the ordinary gas/liquid-phase growth, a variety of impurity atoms, such as O, N, and Pt, are often incorporated into semiconductor films from source and catalytic materials. In device structures, on the other hand, metal atoms in electrodes, such as Al and Au, easily diffuse into semiconductor films. These impurities are believed to deteriorate semiconducting properties. However, there have been no systematic studies on what electronic states are produced by these impurities. Moreover, the understanding of essential difference of impurity states between organic and inorganic systems is also interesting from the scientific view. The purpose of this work is to clarify what impurity states are produced and how these states are categorized when a variety of impurity atoms are incorporated in organic molecular semiconductors, using the first-principles calculations.

2. Model and Method

We adopt a solid made of oligoacene molecules as a model of organic semiconductors. This is because many π -conjugated organic semiconductors have common electronic properties for impurity atoms [1, 2]. For simplicity, we construct this model solid by arranging naphthalene molecules similar to the representative crystal structure of triclinic thin-film-phase pentacene [3], as shown in Figs. 1(a) and 1(b). In this solid, naphthalene molecules form a straight line along the c-axis, while they are located staggeringly in the a-b plane.

Since the carbon skeleton of molecules is strong, impurity atoms are incorporated as interstitial atoms, as shown in Fig.1. We consider twenty kinds of impurity atoms having various valencies; such as Na, Mg, Al, Si, N, O, Ti, Au, Pt etc. Atomic and electronic structures around impurity atoms are calculated using the standard first-principles method based on the density functional theory, where all atom positions are optimized to the most stable points. The calculational details are described elsewhere [1, 2].

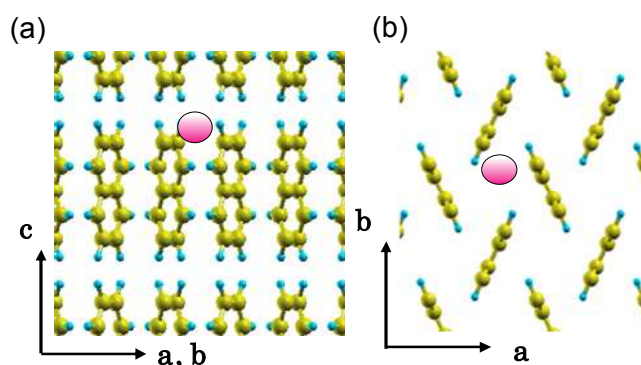


Fig.1. Schematic pictures of oligoacene model solid used in the present study; (a) side and (b) top views. Large and small balls display carbon and hydrogen atoms, respectively, while largest ball indicates the doped impurity atom.

3. Results

Figure 2 shows the schematic energy diagram of impurity states around the fundamental HOMO-LUMO gap of organic semiconductors, where the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) states are made of π and π^* states of host organic molecules, respectively. We found that impurity states are classified into at least the following four groups, (1) to (4), reflecting the electro-negativity and chemical valency (valence electron number) of impurity atoms.

(1) Cation metal atoms having small electro-negativity, such as Al, In, Mg, and Na, become donor atoms. Interestingly, as shown in Fig. 2, these donor states appear about 0.5 eV below the LUMO state of host solid, not depending on the impurity species. The reason of this feature is examined by observing the wave-function of donor state, which is shown in Fig. 3(a) for the case of Al impurity. It is seen that the donor state is mainly made of π^* -orbital states of host molecule and is weakly localized on carbon atoms near the impurity atom. This result indicates that the electron transfer occurs from impurity atom to host molecule, thus the impurity atom being positively charged and working as

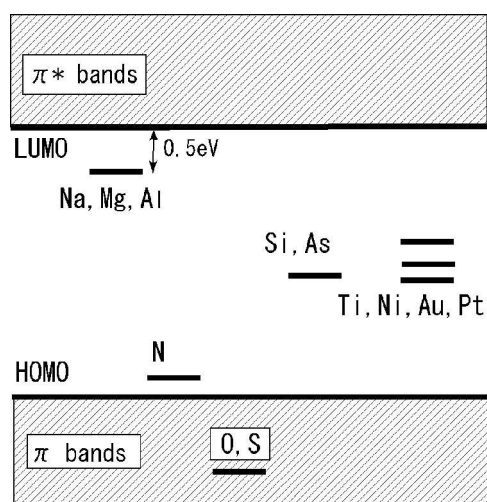


Fig.2. Schematic energy diagram of various impurity states around the HOMO-LUMO fundamental gap of π -conjugated organic semiconductors.

a positive point charge for π^* -orbital electrons. This is the reason why most donor states have almost similar energy positions, irrespective of metal-atom species. Correspondingly, since the impurity atoms are tightly bounded to the molecule by the strong ionic interaction, the impurity atoms are located near a specific single molecule and are difficult to move through the organic solid.

(2) Anion atoms having large electro-negativity and even-number of valence electrons, such as O, S, and Se, produce isolated electron-occupied levels far below the HOMO state of host molecular solid. Thus, there appear no impurity states within the HOMO-LUMO fundamental gap.

(3) Nitrogen atom becomes an acceptor and produces an acceptor state 0.3 eV above the HOMO state of host solid. This acceptor state is produced by the hybridization between π -orbital states of host molecules and p-orbital states of N atom. On the other hand, middle-valency atoms like Si and As generate deep-level states made of p orbitals around the center of the HOMO-LUMO gap.

(4) d-orbital metal atoms produce deep-level states around the center of HOMO-LUMO gap. Figure 3(b) shows an example of such deep-level state in the case of Au impurity atom. These deep-level states are strongly localized around impurity atoms and are made of the orbital hybridization between s and d orbitals of Ti, Au, and Pt atoms and π -orbital states of host molecules. However, since there is little electron transfer between impurity atoms and molecules, the d-orbital metal atoms are weakly bounded to host molecules and easily move within the organic solid. Moreover, since these deep-level states are partially electron occupied, they are expected to work as active deep-level states for carrier transport. In fact, we found that these d-orbital metal atoms prefer to stick with each other and produce a cluster, which is expected to induce carrier-conductive paths in organic solids.

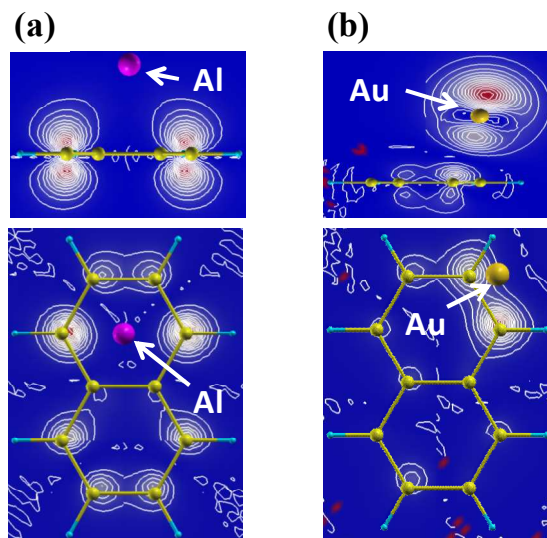


Fig.3. Calculated wave-function densities of impurity states; (a) donor state by Al impurity and (b) deep-level state by Au impurity. Upper and lower panels show the side and top views, respectively.

4. Conclusions

Chemical trend of atomic impurity states in organic semiconductors are studied using the first-principles theoretical calculations. We found that impurity states are classified into at least four groups, depending on the electro-negativity and chemical valency of impurity atoms. Cation metal atoms having small electro-negativity, such as Mg and Al, produce donor states about 0.5 eV below the π^* -orbital LUMO state of host molecule, while N atom produces an acceptor state 0.3 eV above the π -orbital HOMO state. However, anion atoms having large negativity and even number of valence electrons, such as O and S, produce isolated levels far below the HOMO state, thus appearing no impurity states within the HOMO-LUMO gap. On the other hand, d-orbital metal atoms, like Ti, Au, and Pt, produce active deep-level states within the HOMO-LUMO gap, thus expected to induce the electron conductive paths in organic solids.

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