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Metal-Atom Penetration and Clustering Processes in PTCDA Thin Films; First-Principles Study of Film Degradation

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Abstract

Penetration of electrode metal atoms into organic semiconductors often promotes serious degradation damages for devices. We studied how metal-atom impurities are incorporated in PTCDA films by the first-principles calculations. We found that metal atoms such as Al and Ti penetrate into and are uniformly distributed in films, while atoms like Ag and Au produce clusters in/on films. It was systematically shown that such difference in stable incorporation forms originates from electro-negativity difference between metal atoms.

1. Introduction

Organic molecular semiconductors are key materials for future optical/electronic devices due to their unique features such as elastic softness and low-cost production. However, there exist serious issues for applications; during the device fabrication, impurity metal atoms are often incorporated from catalysts/electrodes into semiconductor layers and destroy semiconducting properties through mobility degradation and leakage currents. In case of typical 3,4,9,10-pery- lenetetracarboxylic dianhydride (PTCDA) thin films, for example, it is well known that Al and Ti atoms easily penetrate into PTCDA substrate and react with molecules, while Ag and Au atoms prefer to locate as metal clusters in/on PTCDA substrate [1,2]. In other organic solids, the similar chemical trends were observed. However, there have been no systematic studies on how these impurities are incorporated in organic films, why metal atoms show such different forms in organic solids, and what electronic properties are produced by these impurities. The purpose of this work is to answer these questions, using the first-principles calculation.

2. Calculation model and method

We employ PTCDA solid as representative of organic semiconductors, while Al, Ti, Ag, Au, and Sn atoms are adopted as impurity metal atoms. To clarify how these atoms penetrate into PTCDA substrate and are located stable in PTCDA, a variety of atom configurations are considered as shown in insets of Fig.1, e.g., configuration where metal atoms are uniformly distributed or produce a metal cluster.

The stability of these configurations is evaluated using the formation energy, which is defined by

$$E_{\mathrm{form}}(\mu_{\mathrm{M}}) = E_{\mathrm{PTCDA}+N\mathrm{M}} - (E_{\mathrm{PTCDA}}+N\mu_{\mathrm{M}}). \quad (1)$$

Here, E_{PTCDA} and $E_{\mathrm{PTCDA}+N\mathrm{M}}$ are calculated total energies of PTCDA and metal-adsorbed PTCDA systems, respectively. N is the number of metal atom, while μ_{M} is a chemical potential of metal atom, which corresponds to the supply ratio of metal atoms. Total energy is calculated by the first-principles method based on the density functional theory using xTAPP code [3,4]. GGA-PBE is adopted for exchange-correlation functional, while plane-wave bases with less than 36Ryd is employed.

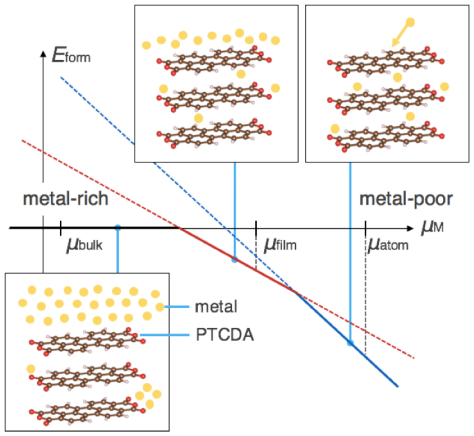

Fig.1. Schematic picture to judge stable metal-atom configurations. Formation-energy lines are shown for various atom configurations as a function of metal-atom chemical potential (supply ratio). With varying metal-atom supply, the most stable configuration changes as displayed in insets.

3. Results and discussion

Change of Atom Configurations

First, we explain the case of Al atoms. Figure 2(a) shows calculated formation energies of various Al configurations as a function of Al chemical potential (Al supply ratio). When small amount of Al atoms are supplied (Al-poor), since the formation energy is negative, Al atoms easily penetrate into PTCDA substrate and attach to molecules. With increasing Al supply (Al-rich), the formation energy is still negative, which indicates that Al atoms continue to diffuse into substrate even after Al atoms produce overlayer films on the substrate and are uniformly distributed, as shown in Fig.2(b). We found that Ti atoms also show similar feature, which is in good agreement with experiments [1,2].

Next, we show the case of Ag atoms in Fig.3(a). When

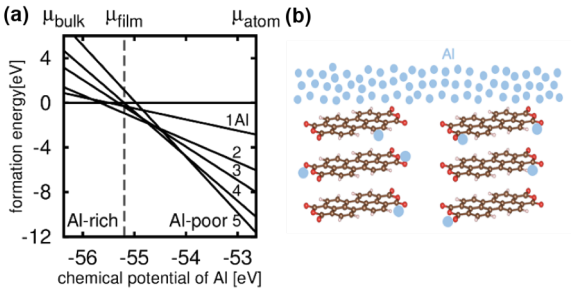

Fig.2. (a) Calculated formation energies for various Al-atom configurations, as a function of Al-atom chemical potential (Al atom supply). (b) Stable Al-atom configuration after sufficient amount of Al atoms are supplied on PTCDA surface.

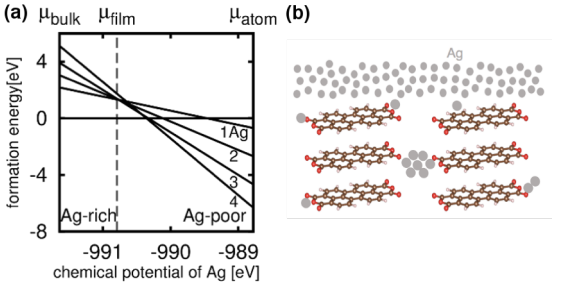

Fig.3. (a) Calculated formation energies for various Ag-atom configurations as a function of Ag-atom chemical potential (Ag atom supply). (b) Stable Ag-atom configuration after sufficient amount of Ag atoms are supplied on PTCDA surface.

Ag-atom supply is small, Ag atoms penetrate into PTCDA substrate and attach to molecules, similar to cases of Al and Ti. When Ag supply increases, however, Ag atoms show quite different configurations from Al and Ti. Because the formation energies become positive in Ag-rich region, Ag atoms prefer to aggregate as Ag clusters in PTCDA substrate as shown in Fig.3(b), together with producing Ag film on the substrate. We also found that Au atoms show similar feature, which well explains the observations [1].

Origin of Different Incorporation between Metal Atoms

In order to understand the origin of different configurations between Al and Ag atoms, we show the adsorption sequences of Al and Ag atoms to a single PTCDA molecule in Figs.4(a) and 4(b), respectively. In addition, averaged ionization charges of adsorbed metal atoms and those of PTCDA-O atoms are shown in Figs.4(c) and 4(d) for Al and Ag adsorptions, respectively.

From these figures, we know that small electro-negativity atoms like Al and Ti are ionized by releasing valence electrons and strongly attached to O atoms of host molecules with ionic bonding. Therefore, the diffusion is difficult to realize once they are bounded to molecules [3,4]. Correspondingly, these metal atoms prefer to locate in a scattered manner both around a single molecule and between molecules in organic solids owing to long-range Coulomb repulsive interaction between metal atoms (Fig.4(a)). This ionized and scattered configuration is expected to induce the degradation of carrier mobility.

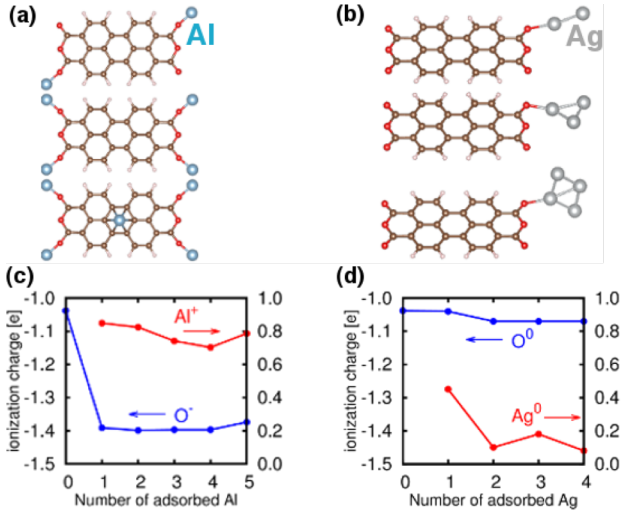

Fig.4. (a) and (b): Stable adsorption sequences of Al and Ag atoms on PTCDA molecule. (c) and (d): Averaged ionization charges of adsorbed Al and Ag atoms and O atoms in molecule, as a function of the number of metal atoms.

On the other hand, large negativity atoms such as Au and Ag are almost neutral when attached to molecules (Fig.4(b)), thus weakly bound to molecules by orbital hybridization. Therefore, their diffusion is easily realized when they are poorly supplied. However, when these atoms approach to each other even nearby molecules, they produce clusters with strong short range metallic interaction (Fig.4(b)). Such clusters work as step stones to induce leakage current in semiconductors.

4. Conclusions

Penetration and clustering processes of electrode metal atoms in PTCDA films are studied by the first-principles calculations. We found that small negativity atoms like Al and Ti are uniformly distributed in films, while large negativity atoms such as Ag and Au produce clusters in/on films. Such difference is expected to induce different degradation of carrier transport in devices.

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