Extended Abstracts of the 2010 International Conference on Solid State Devices and Materials, Tokyo, 2010, pp659-660

Computational Study of Electronic States around Defects in Organic Semiconductors

Toshihiro Shimada[1], Manabu Ohtomo[2] , Takashi Yanase[2] and Tetsuya Hasegawa[2]

[1] Division of Materials Chemistry
Faculty of Engineering
Hokkaido University
Sapporo, Hokkaido 060-8628, Japan
Phone: +81-11-706-6576 E-mail: shimadat@eng.hokudai.ac.jp
[2] Departiment of Chemistry
Univ. of Tokyo
Bunkyo-ku, Tokyo 113-0033, Japan

1. Introduction

Since most of organic semiconductor devices are based on direct carrier injection to HOMO / LUMO levels, their operation temperature will not be limited by thermal activation of dopant levels as in conventional semiconductors. It is expected that organic semiconductor devices will operate even at very low temperatures. However, it is often observed that organic semiconductors become insulating rather suddenly at low temperatures below ~ 100 K. It is considered that it is due to shallow traps, but their origin has not been clarified. The traps might be due to impurities, but they are observed in highly purified samples. Therefore, we suspect the contribution of defects in pure crystals.

There is a mystery in the experimentally observed trap levels. The activation energy of trap states derived from low temperature mobility is more than several tens of mV [1] but it seems that they are not active at high temperatures (>150K). A proper analysis of trap states must explain this strange behavior of defects.

2. Computational Method

We used a combination of molecular dynamics and semi-empirical quantum chemical calculation [2] to derive the energy levels around the defects. We used classical molecular dynamics package TINKER[3] with MM3 force field [4] and semi-empirical AM1[5] method implmented in MOPAC[6]. Defects are introduced in an augmented unit cell (e.g. combination of 3 x 3 x 2 unit cells) with periodic boundary condition. The crystal was first annealed and the stability of the defects are examined. Next, we took snapshots of atomic positions at 0.1 ~ 0.2 ps intervals. We calculated energy levels of clusters of nearest neighbors.

3. Results and Discussions

Figure 1 shows the histogram of electronic levels (a) without defect and (b) with point defect in pentacene. The defect was stable in periodic 3 x 3 x 2 unit cells.

It was found that thermal structural fluctuation induces time-dependent fluctuation of energy levels of molecules in both cases. This fluctuation is large enough to conceal the defect levels at room temperature. At low temperature below 100K, it was observed that the thermal fluctuation diminished and the defect levels appear separate from the valence states as indicate by arrows in Fig.1 (b). In the case of a molecular point defect in thin film phase pentacene, the defect level works as a hole-trap with the activation energy of ~ 70 meV.

4. Conclusions

We evaluated the electronic states around defects in organic semiconductor crystals. It was found that the thermal fluctuation conceals shallow trap levels originating from defects at high temperature but the trap levels suddenly become active at lower temperatures.

References

[1] V. Podzrov, *Phys. Rev. Lett.* **93**, 086602 (2004).
[2] A. Troisi, G. Orlandi, *J. Phys. Chem. B* **109**, 1849 (2005).
[3] P. Ren, J.W. Ponder, *J. Phys. Chem. B* 107, 5933 (2003).
[4] J.H. Lii, N.L. Allinger, *J. Am. Chem. Soc.* 111, 8576 (1989).
[5] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc* **107**, 3902(1985).
[6] J. J. P. Stewart, *Quant. Chem. Prog. Exch.* **10**, 86 (1990).

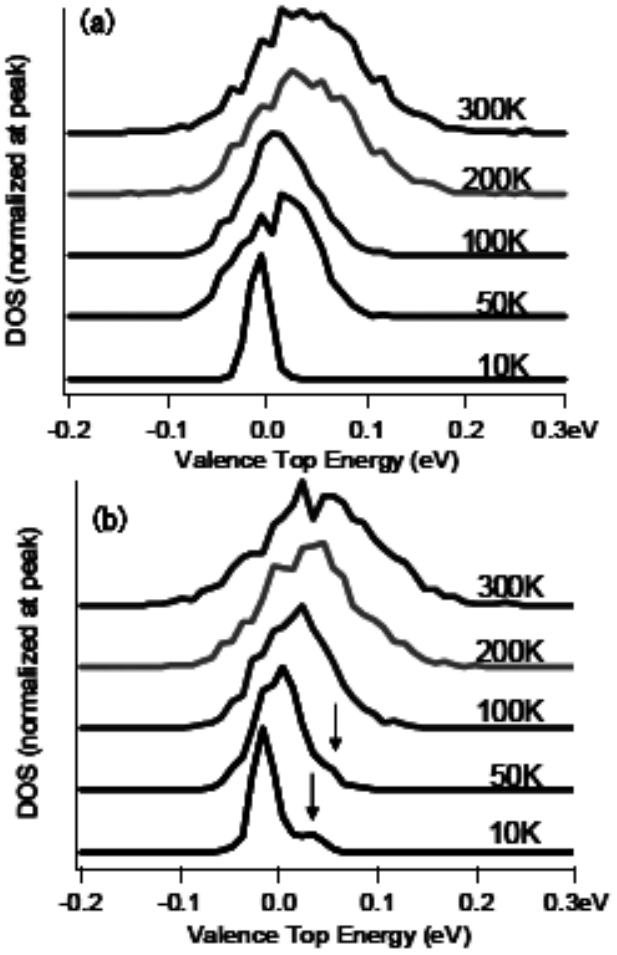

Fig.1 Energy level histogram without point defect and with point defect in thin film phase pentacene. Arrows in (b) indicate the defect levels which will work as hole traps.