

# Surface Modification of Organic Thin Films by Neutral Beam Irradiation

Masaya Hirade<sup>1,2</sup>, Tomohiro Kubota<sup>2,3</sup>, Yoshihiko Tsuru<sup>2,4</sup>, Masayuki Yahiro<sup>1,2,6</sup>, Koji Miyazaki<sup>2,4</sup>,  
Seiji Samukawa<sup>2,5</sup>, and Chihaya Adachi<sup>1,2</sup>

<sup>1</sup>Center for Future Chemistry, Kyushu University  
744 Motoooka, Nishi, 819-0395, Fukuoka, Japan

Phone: +81-92-802-3306, E-mail: m\_hirade@cstf.kyushu-u.ac.jp

<sup>2</sup>Beans Laboratory

67 Kandasakumakashi, Chiyoda, Tokyo, 101-0026, Japan

<sup>3</sup>Institute of Industrial Science, the University of Tokyo

4-6-1 Komaba, Meguro, Tokyo, 153-8505, Japan

<sup>4</sup>Faculty of Engineering, Kyushu Institute of Technology

1-1 Sensui-cho, Tobata, Kitakyushu, 804-8550, Japan

<sup>5</sup>Institute of Fluid Science, Tohoku University

2-1-1 Katahira, Aoba, Sendai, 980-8577, Japan

<sup>6</sup>Institute of Systems, Information Technologies and Nanotechnologies

2-1-22, Momochihama, Sawara, Fukuoka, 814-0001, Japan

## 1. Introduction

Organic devices such as organic light emitting diodes (OLEDs) are expected as next generation opto-electronic devices. They are easily prepared by low cost and low temperature device fabrication techniques. In order to enhance the device characteristics, it has been expected to introduce nano-structures into organic devices. For example, organic solar cells (OSCs) with nano-pillar structures provide a large area of a p-n heterointerface contributing efficient carrier separation and high carrier transport characteristics. [1]

Generally, construction of organic nano-structures has been used bottom-up processes such as self-organization. However, these techniques have some problems. For example, there are limitations of material's selection. Alternatively, top-down processes such as plasma etching are also very useful for the construction of nano-structures. However, since conventional plasma etching processes contain various kinds of ions and ultra-violet (UV) radiation from plasma sources, it gives severe damage to organic materials. Thus, novel processes providing low damage for organic materials have been expected.

In this study, we focus on neutral beam (NB) etching technique, allowing fabrication of nano-structures with low damage.[2] The NB process suppresses influence of ion and UV light by carbon apertures which are placed blow the plasma source. Here, we report on organic nano-structures fabrication and control of molecular orientation by NB irradiation.

## 2. Experiments

We fabricated organic thin films by vacuum evaporation or spin coating. Figure 1 shows the chemical structures of the materials, a low molecular material of 4,4'-bis[(*N*-carbazole)styryl]biphenyl (BSB-Cz) and a polymeric material of poly-(2,7-(9,9-di-*n*-octylfluorene-*alt*-benzothiadiazole) (F8BT), used in this study. These

samples were exposed to O<sub>2</sub>- or Ar-NB. Then, we studied the surface morphologies using Atomic Force Microscope (AFM), and evaluated molecular orientation using X-ray Diffraction (XRD) before and after NB irradiation.

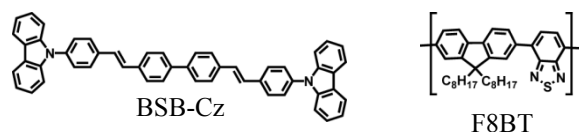


Fig. 1 Chemical structures of BSB-Cz and F8BT

## 3. Results and Discussions

Figure 2 shows AFM images of the topography of the BSB-Cz thin films before and after O<sub>2</sub>-NB irradiation.

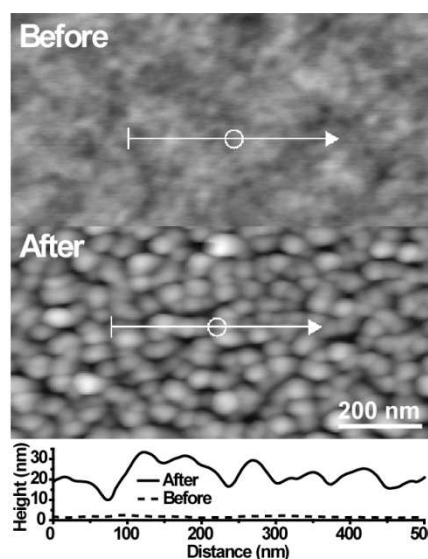


Fig. 2 AFM images of BSB-Cz surface and cross-sectional profile before and after O<sub>2</sub>-NB irradiation.

Since BSB-Cz forms amorphous morphology, their deposited films have very smooth surface (RMS  $\sim 0.30$  nm). However, after O<sub>2</sub>-NB irradiation, the morphology of the surface was significantly changed. The nano-sized grains appeared on its surface, and the grain size was increased by enhancing exposure time of O<sub>2</sub>-NB irradiation. The grains with about 80 nm diameter and several 10 nm height were obtained by O<sub>2</sub>-NB irradiation for 10 min (RMS  $\sim 5.93$  nm).

In the case of O<sub>2</sub>-NB irradiation for F8BT, the morphology transition also occurred. During NB irradiation, organic thin films would be heated, resulted in the enhancement of the molecular orientation. We evaluated the orientation of them by XRD. Figure 3 shows the out-of-plane XRD patterns of the F8BT thin films before and after NB irradiation. There were no remarkable differences in all of these samples.

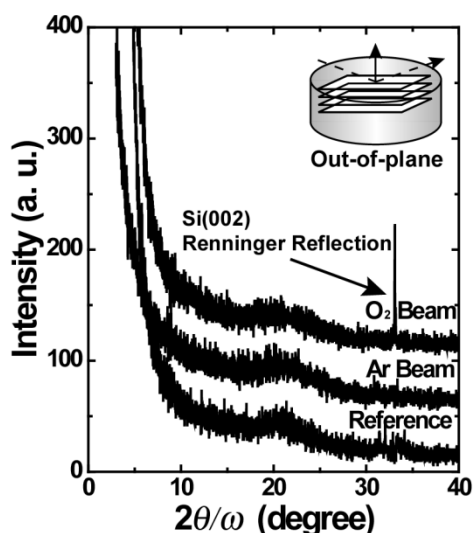


Fig. 3 Out-of-plane XRD patterns of F8BT thin films before and after O<sub>2</sub>- or Ar-beam irradiation.

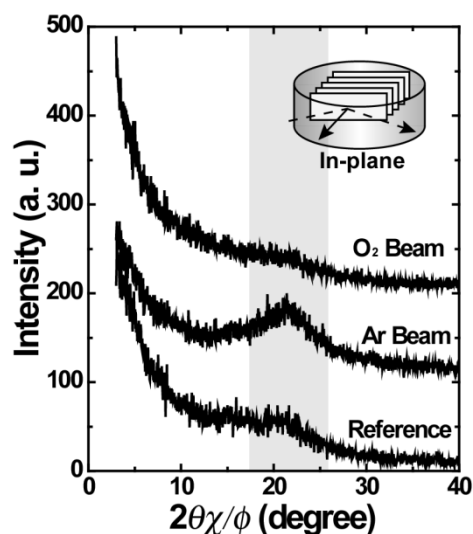


Fig. 3 In-plane XRD patterns of F8BT thin films before and after O<sub>2</sub>- or Ar-beam irradiation.

Figure 4 shows the in-plane XRD pattern of F8BT. In the case of O<sub>2</sub>-beam irradiation, the diffraction pattern was almost same with that of the reference. However, the enhancement of the diffraction peak, at  $2\theta=22^\circ$ , was observed by the Ar-NB irradiation. This peak corresponds to  $\sim 0.42$  nm, indicating enhancement of the orientation of the polymer chain. [3]

#### 4. Conclusions

We applied the NB technique to organic thin films. In the case of low weight molecules such as BSB-Cz, the nano-scaled grains with 80 nm diameter and several 10 nm height were obtained by O<sub>2</sub>-NB irradiation. Further, enhancement of the orientation of the polymer chain was observed in the F8BT thin films by Ar-NB irradiation. We expect this modification will provide high mobility in organic field effect transistors.

#### References

- [1] M. Aryal, F. Buyukserin, K. Mielczarec, X. M. Zhao, J. Gao, A. Zakhidov, and W. Hu, *J. Vac. Sci. Technol. B* **26** 2562 (2008)
- [2] S. Samukawa, *Jpn. J. Appl. Phys.* **45** 2395 (2006)
- [3] C. L. Donley, J. Zaumseil, J. W. Andreasen, M. M. Nielsen, H. Sirringhaus, R. H. Friend, and J. S. Kim, *J. Am. Chem. Soc.* **127** 12890 (2005)