

## Formation of Organic Nanodots Using Diamine Derivative and Self-Assembled Monolayer

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### 1. Introduction

In recent years, controlling nanostructures in organic semiconductor devices has been paid great attention. For example, Nakata *et al.* reported that formation of organic nanodots composed of organic semiconductor materials with low molecular weight using a vacuum deposition on SiO<sub>2</sub>/Si wafers treated with hexamethyldisilazane (HMDS) [1]. And Karthaus *et al.* reported that formation of organic (sub)micrometer-sized domes of tolyl-phenyl-diaminobiphenyl (TPD) using dewetting process on an indium-tin-oxide electrode[2]. We reported that we discover the formation of organic nanodots when we covered indium tin oxide (ITO) substrate evaporated a thin film of (bis [N-(1-naphthyl)-N-phenyl] benzidine) ( $\alpha$ -NPD) with ((hepta-decafluoro-1, 1, 2, 2-tetrahydrodecyl) triethoxysilane) (FSAM).

### 2. Experimental Procedure

ITO substrates were washed by each a ultrasonication with acetone, pure water and isopropyl alcohol for 5min. The substrates were treated with UV-ozone for 10 min. Next, a thin film of  $\alpha$ -NPD layer was evaporated on the ITO substrate under a vacuum of  $4.0 \times 10^{-4}$  Pa with the evaporation rate of 0.1nm/s. Finally, the substrate were treated with the FSAM using a gas phase method under the condition of 120°C for 2h. The characteristics of the nanostructures were measured using an atomic force microscope (AFM). Typically, AFM observation was conducted within a few hours after modifying FSAM.

### 3. Result and Discussion

Figure 1 shows AFM images ( $20 \times 20 \mu\text{m}^2$ ) and roughness profiles of the  $\alpha$ -NPD layer with thickness of 5nm, 8nm, 10nm and 15nm. Organic nanodots are observed in (a), (b) and (c) when the thickness of  $\alpha$ -NPD is smaller than 10nm. Table I shows the diameter, the height and the density

Table I Geometry parameter of nanodots

Thickness of $\alpha$ -NPD[nm]	Diameter[nm]	Height[nm]	Density of nanodots[dots/ $\mu\text{m}^2$ ]
5	500	50	3.0
8	900	80	2.0
10	1200	100	1.7

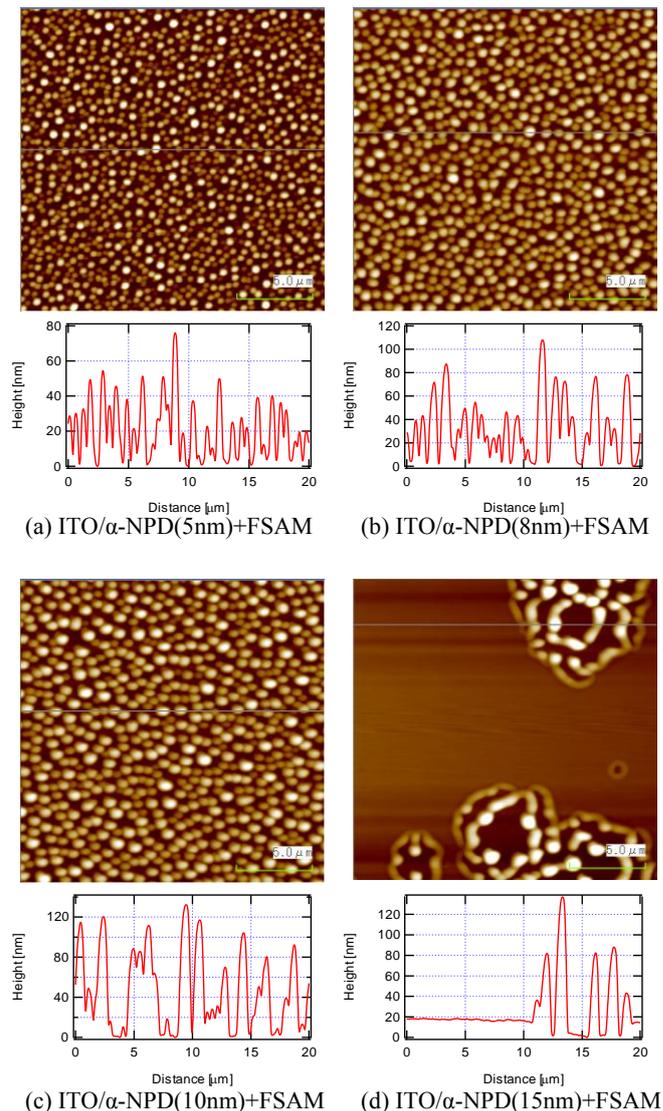


Fig. 1 AFM images ( $20 \times 20 \mu\text{m}^2$ ) show ITO substrate evaporated  $\alpha$ -NPD and afterward treated with the FSAM. (a) 5, (b) 8, (c) 10, (d) 15nm. Roughness profiles show roughness of sky blue lines in each AFM images.

of nanodots. As the thickness of  $\alpha$ -NPD layer increase, the diameter and height of nanodots also increase.

The dramatic change of appearance is observed at the

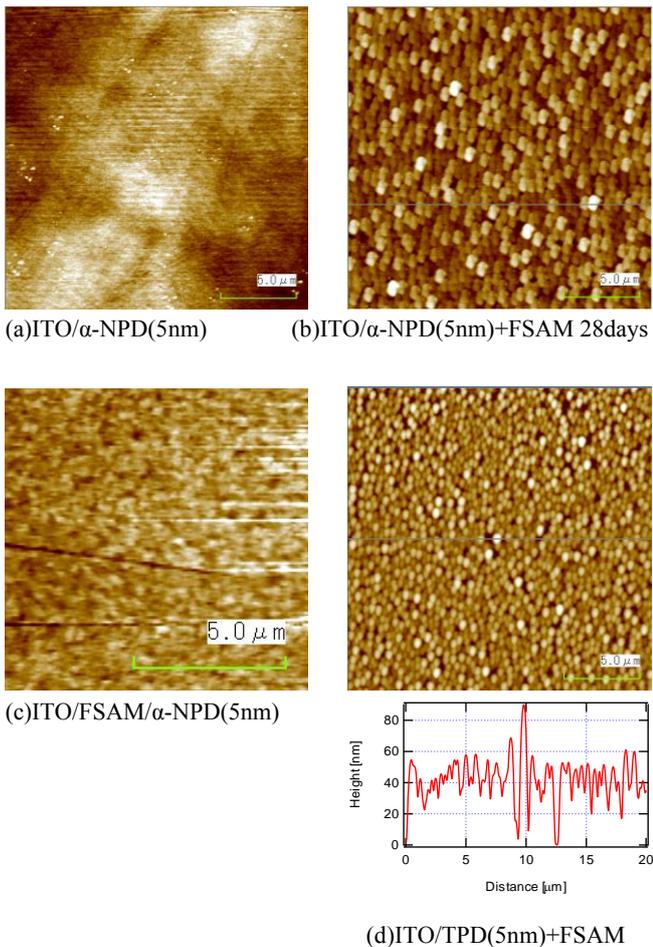


Fig. 2 AFM images ( $20 \times 20 \mu\text{m}^2$ ) shows (a) ITO substrate evaporated  $\alpha$ -NPD (5nm) (b) organic nanodots that passed 28days. (c)  $\alpha$ -NPD on ITO substrate treated with the FSAM and afterward annealed. (d) ITO substrate evaporated TPD (5nm) and afterward treated with the FSAM.

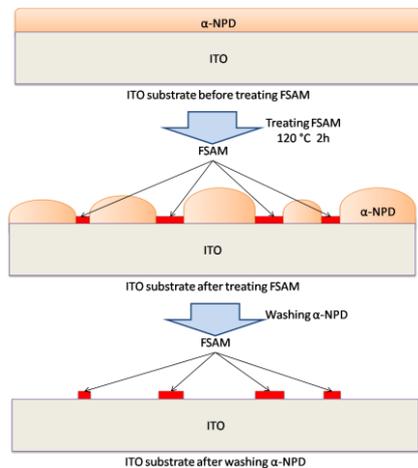


Fig. 3 Sketch of nanodots. The above figure is ITO substrate before modifying the FSAM. Middle is ITO substrate after modifying FSAM. Below is ITO substrate after washing  $\alpha$ -NPD.

$\alpha$ -NPD thickness of 15nm [Fig. 1(d)]. The crystallization of  $\alpha$ -NPD is observed partly. However, most part was flat. All area of substrate became flat when the thickness of the  $\alpha$ -NPD layer increased larger than 15nm. So, 15nm is boundary point of formation of organic nanodots. Fabricated organic nanodots is stable. Fig.2 (a) shows AFM image of organic nanodots that passed 28days. A preservation atmosphere is low level vacuum of  $1 \times 10^{-1}$  Pa.

Organic nanodots are not observed when we evaporated  $\alpha$ -NPD on FSAM modified ITO substrate and afterward annealed the substrate[Fig. 2 (b)]. The anneal condition are  $120^\circ\text{C}$  for 2h. Covering a  $\alpha$ -NPD thin film with FSAM is formed to be necessary for the formation of organic nanodots.

After we washed organic nanodots ( $\alpha$ -NPD thickness is 5nm) by ultrasonication with isopropyl alcohol for 5min, we measured the work function of organic nanodots substrate washed isopropyl alcohol by an ultraviolet photoelectron spectroscopy (AC-2, Riken Keiki Co.). The work function is estimated to be 5.2eV. The work function of bare ITO substrate and FSAM-modified ITO substrate are estimated to be 5.0eV and 5.4eV, respectively. We consider FSAM partially remained on this substrate.

Figure 3 shows the schematic sketch of the forming organic nanodots. ITO substrate evaporated  $\alpha$ -NPD thin film is flat before treating the FSAM. During fabricating the FSAM,  $\alpha$ -NPD aggregate and bare ITO areas show up. The FSAM is fabricated on bare ITO area. The nanodots of  $\alpha$ -NPD molecules are formed being squeezed by FSAM areas.

In addition, we cover ITO substrate evaporated a TPD thin film with FSAM. The nanodots are observed in this case. An average diameter of nanodots was approximately 550nm and an average height of nanodots was approximately 80nm.

### 3. Conclusions

We discovered a new formation of organic nanodots when we covered ITO substrate evaporated a  $\alpha$ -NPD thin film with FSAM. The thickness of  $\alpha$ -NPD at 15nm is a boundary point of formation of organic nanodots. Nanodots are not composed only  $\alpha$ -NPD. The FSAM causes the aggregating of  $\alpha$ -NPD and TPD and makes organic nanodots.

### References

- [1] M. Nakata et al. , *Appl. Phys. Exp.* **3** (2010) 055201.
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- [3] T. Mori et al., *Appl. Phys. Exp.* **4** (2011)