

Carrier Gas Assisted Solvent Vapor Treatment for Surface Nanostructuring of Molecular Thin Films[†]

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In this study, the variation in surface morphology of copper phthalocyanine (CuPc) thin films treated with a flow of acetone vapor assisted by nitrogen carrier gas was investigated. The CuPc nanorods with similar dimensions were well dispersed throughout the whole film surfaces after ~20 min. of treatment. However, the electronic absorption spectra only changed slightly, which indicates that molecular stacking was not altered during treatment. This treating method is simple and more advantageous compared to other solvent treating technologies such as mixed solvent spray treatment using organic solvents and water since it requires relatively mild treating conditions and does not need the presence of water.

Key Words : Solvent treatment, Surface nanostructuring, Molecular thin film, CuPc

Introduction

Over the past decades, organic semiconductors have attracted growing attention for use in a wide range of (opto)electronic device applications. The surface/interface morphology of organic semiconductor thin films is known to play a crucial role in the performance of the devices.¹⁻³ For example, a controlled nanostructure with a high contact area between the electron donating and accepting layers is advantageous in regard to improving the power conversion efficiency (PCE) of organic photovoltaic (OPV) cells.⁴⁻⁶ In this context, various methods for fabricating nanostructured surfaces of organic thin films have been developed including nanoimprint,⁷⁻⁹ solvent drop,¹⁰ and solvent vapor spray¹¹ techniques. However, the nanoimprint techniques require long and complicated nano-processes for the fabrication of template molds. In addition, although the solvent drop treatment is much simpler than the nanoimprint methods, it cannot be generally applied to a variety of organic films since the film surface is entirely covered with the solvents and the surface morphology is severely sensitive to the solubility of the film materials. Even though the solvent vapor spray treatment could address these problems to a certain extent, the use of solvent mixtures comprised of organic solvents and water is still needed to create a controlled surface nanostructure. This is the case because the use of solvents without water can easily result in over-treatment. However, the presence of water can accelerate the degradation of the device and an additional thorough drying process is needed.

In this study, we develop an alternatively simple solvent treating technology, i.e. carrier gas assisted solvent vapor flow method, and applied it to the surface nanostructuring of copper phthalocyanine (CuPc) thin films. This method could

provide relatively mild treating conditions, since the contact between solvent vapors and film surfaces was significantly reduced due to the flow of an accompanying carrier gas. This mild condition led to the formation of surface nanostructures without using water, which is expected to enhance the device performance.

Experimental

Commercially available CuPc (Aldrich Chemical, 97%) powder was purified twice using temperature gradient sublimation. The purified material was then outgassed in an ultrahigh vacuum (UHV) chamber for 15-20 h before growth and then sublimed from a miniature effusion cell onto well cleaned glass substrates held at room temperature. The cell temperature was 370 °C, which corresponded to a growth rate of ~0.3 Å/s as determined using a quartz crystal microbalance (QCM) positioned near the substrate. For solvent vapor flow treatment, the films were transferred to a privately manufactured glass chamber. Figure 1 shows a schematic diagram of the glass chamber and vapor flow system used for treatment. Nitrogen carrier gases were bubbled in acetone and flowed into the glass chamber using a vacuum pump. The pump speed was controlled by a valve attached near the pump in order to maintain the carrier gas flow rate at 2000 standard cubic centimeters per minute (scm) and solvent consumption rate at 5.5×10^{-3} mL/s. The surface morphology of the samples was analyzed using a tapping mode atomic force microscope (AFM) (SII SPA 400) and field emission scanning electron microscope (FE-SEM) (JEOL JSM 740F), and the electronic absorption (EA) of the films was recorded using an ultraviolet(UV)-visible spectrophotometer (Scinco S-3100).

Results and Discussion

CuPc, a planar phthalocyanine (Pc) molecule with 18p-

[†]This paper is to commemorate Professor Kook Joe Shin's honourable retirement.

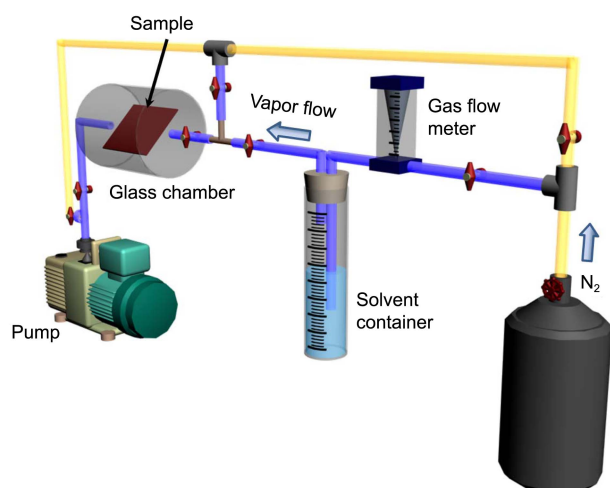


Figure 1. Schematic diagram of the carrier gas assisted solvent vapor flow system used in this study.

electrons in its aromatic system, is one of the most widely used electron donor materials in small-molecular based OPV device applications due to its thermal and chemical stability, large absorption coefficient, and high hole mobility.¹²⁻¹⁴ CuPc thin films with a thickness of 50 nm were grown on glass substrates using organic molecular beam deposition (OMBD). The film was flat with a root mean square (rms) roughness of 1.74 nm and characterized by tiny spherical grains as shown in Figure 2(a), which is typical of the α -phase planar Pc polymorph.^{15,16} Acetone vapors were then flowed through the films at room temperature for various periods of time. Figures 2(b)-(d) show surface AFM images of CuPc thin films treated for 5 min., 10 min., and 50 min., respectively. All images were taken with the same scan area

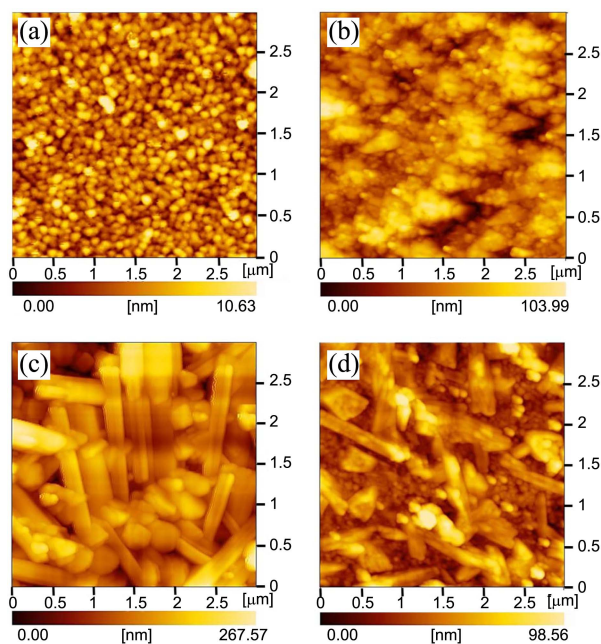


Figure 2. AFM images of the 50 nm thick CuPc films (a) as-deposited and treated using acetone vapor flow for (b) 5 min., (c) 10 min., and (d) 50 min.

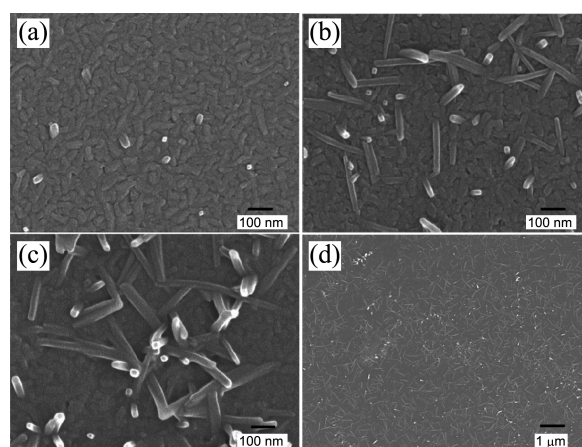


Figure 3. FE-SEM images of the 50 nm thick CuPc films treated using acetone vapor flow for (a) 5 min., (b) 10 min., (c) 15 min., and (d) 20 min.

of $3 \mu\text{m} \times 3 \mu\text{m}$. After 5 min. of treatment (Fig. 2(b)), the surface morphology started to change and the rms roughness increased rapidly to 16.5 nm. The formation of nanorods was clearly observed on the film treated for 10 min. Surface nanostructures on the films treated for longer than 20 min. were likely to aggregate and shape changes were observed. Figure 2(d) shows the film surface after 50 min. of treatment. Some of the surface nanorods disappeared or lost their initial shapes at this longer treatment time. Variations in surface nanostructures were observed more clearly in FE-SEM images (Fig. 3). For the CuPc film treated for 5 min. (Fig. 3(a)), the surface was covered with slightly elongated grains and a small number of nanorod nuclei. After 10 min. of treatment, longer nanorods were clearly observed on the film surface as shown in Figure 3(b). As the treatment proceeded, the number and dimension of the nanorods

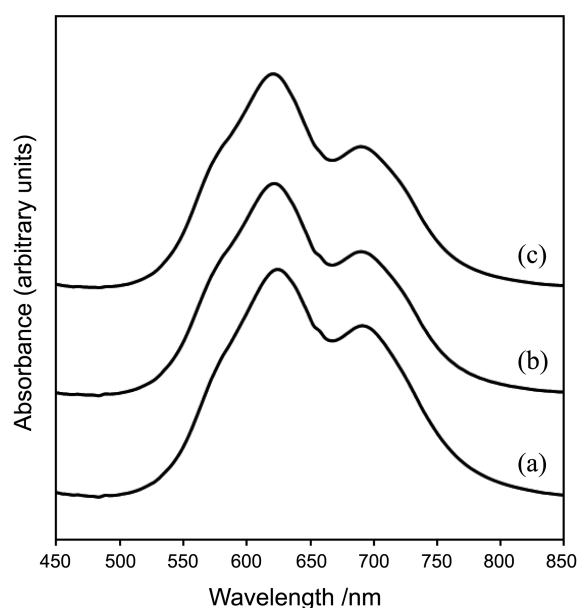


Figure 4. Electronic absorption spectra recorded for the 50 nm thick CuPc films (a) as-deposited and treated using acetone vapor flow for (b) 10 min. and (c) 50 min.

tended to increase. When the film was treated for 15 min., the average width and length of the nanorods were ~ 45 nm and ~ 270 nm, respectively (Fig. 3(c)). Figure 3(d) shows the film surface treated for 20 min. in a larger scan area of $18 \mu\text{m} \times 13 \mu\text{m}$. Nanorods with similar dimensions and aspect ratios were well dispersed throughout the whole surface. EA spectra recorded for the as-deposited CuPc film (Fig. 4(a)) contained the characteristic features of the α -phase Pc polymorph.^{15,17} The absorption maxima centered at 623 nm and 694 nm were mainly attributed to the Q-bands of planar Pc films, Q_S and Q_L band, respectively.^{15,18} The existence of these sub-Q-bands could be explained by molecular stacking within the Pc films. The Q_S and Q_L sub-band are known to correspond to face-to-face (H-aggregates) and edge-to-edge (J-aggregates) molecular stacking, respectively.^{11,19} Solvent treatment of the organic thin films may alter the stacking of the surface molecules and consequent EA spectra. A considerable decrease in Q_S sub-band and increase in Q_L sub-band was recently observed after solvent spray treatment.²⁰ In contrast, there was no apparent change in EA spectra for CuPc films treated with solvent vapor flow as shown in Figure 4. The peak positions and relative intensities were retained irrespective of treatment time, which indicates that CuPc molecules barely altered their stacking during acetone vapor flow treatment.

In conclusion, we developed a novel surface nanostructuring technique, i.e. carrier gas assisted solvent vapor flow method, for organic thin films. The method involves using acetone as a solvent and can be applied to the fabrication of surface nanostructures on CuPc thin films. Nanorods with regular dimensions and aspect ratios were formed and well dispersed throughout the whole surface. However, the EA spectra of the films only changed slightly, indicating that the treatment did not alter the molecular stacking. This method is simple and has many advantages compared to other solvent treatments since it does not require the presence of water.

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