

# NOVEL ORGANIC CRYSTAL THIN FILM GROWTH TECHNIQUE USING SUPERCRITICAL FLUID CAPABLE OF FILLING HIGH-ASPECT-RATIO FEATURES

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We have successfully developed a novel organic thin-film fabrication technique, which enables filling organic materials onto high-aspect-ratio features using supercritical CO<sub>2</sub>. This technique allowed complete filling of an organic photovoltaic material, anthracene, onto Si trenches (1- $\mu$ m-width and 10- $\mu$ m-depth). In contrast to poor step coverage by conventional coating methods, such as spin-coating and vacuum evaporation, this technique alone leads to realization of a 3D organic photovoltaic cell (OPVC) for higher energy conversion efficiency.

## INTRODUCTION

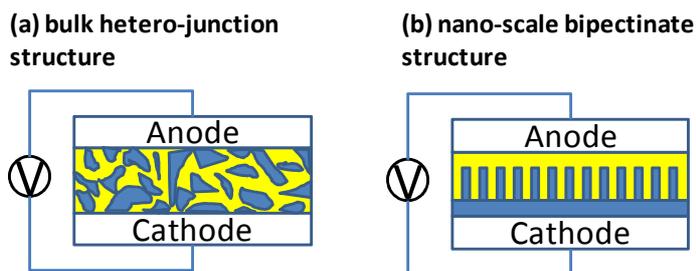
Organic photovoltaic cell (OPVC) is attractive due to inexpensive manufacturing cost, flexibility, and light weight [1]. Power conversion efficiency (PCE) of OPVC is a bottleneck for commercial products, and has been quickly improved to 10.1% by Mitsubishi Chemical Corporation in these last few years. However, it is still insufficient compared to 25% in Si-based inorganic photovoltaic cell [2]. A strategy for further PCE improvement is proposed to facilitate charge carrier separation at the donor/acceptor interface and charge carrier transportation from above interface to the corresponding electrodes through each photovoltaic material. Sariciftci et. al, formed bulk hetero-junction structure consisting of nano-scale donor/accepter material domains, which enabled nano-scale phase separation having large interfacial area, and improved to PCE of 3.5% from about 1% in planar structure [3]. However, discontinuous material network in bulk hetero-junction inhibited efficient charge carrier transportation. Highly ordered nano-scale interpenetrating hetero-junction structure, i.e., nano-scale bipectinate structure is supposed to be beneficial for superior PCE because continuous network of photovoltaic materials guarantee efficient charge carrier transportation with sustaining efficient charge carrier separation by large interfacial area [4]. Nevertheless, OPVC device using this ideal structure has, so far, not been reported mainly due to process difficulties. Conventional thin film fabrication methods, such as spin-coating and vacuum

evaporation, could not fill the photovoltaic material onto pectinate structure because of its poor step coverage.

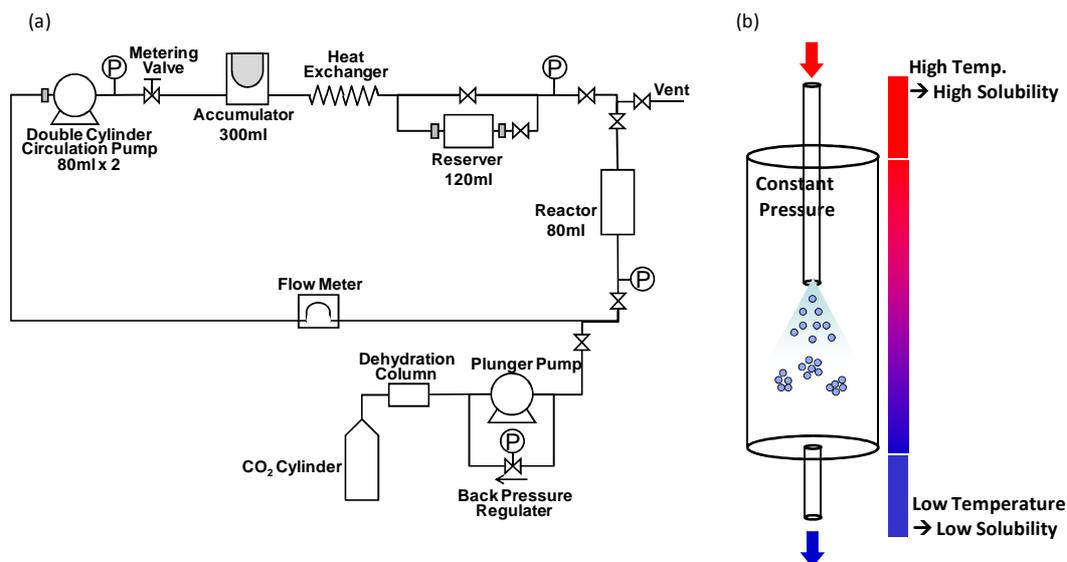
In this study, we developed a novel organic thin-film fabrication technique using supercritical CO<sub>2</sub> (scCO<sub>2</sub>), called temperature-driven supercritical fluid deposition (TSFD), which enables filling organic materials onto high-aspect-ratio features. This technique allowed complete filling of an organic photovoltaic material, anthracene, onto Si trenches (1-  $\mu$ m-width and 10- $\mu$ m-depth).

## EXPERIMENTAL

Deposition by TSFD was carried out by continuously supplying an organic precursor dissolved in high-temperature scCO<sub>2</sub> to a cooled substrate. Schematics of the TFD system and of the chamber were shown in Fig. 2(a) and (b), respectively. The system consists of scCO<sub>2</sub> supplying part (downside in Fig.2(a)) and closed-looped line part for deposition (upside in Fig.2(a)). ScCO<sub>2</sub> was circulated clockwise in the closed-loop line by circulation pump and the circulation rate of scCO<sub>2</sub> was regulated by the metering valve. The apparatus from heat exchanger to the chamber inlet was heated to high temperature, typically 200 °C, and that from the chamber outlet to the heat exchanger was heated to relatively low temperature, typically 100 °C. The downside of the chamber was chilled to keep the substrate temperature to relatively low temperature, typically 100 °C. The deposition was carried out as follows. First, the organic precursor was stored in the reserver and the substrate was placed on the stage in the chamber. Then, all the apparatus was pressurized to a process pressure such as 15 MPa by scCO<sub>2</sub> and heated to corresponding set temperatures, while circulating scCO<sub>2</sub> with diverting the reserver. After the pressure and the temperature were settled, circulation rate was regulated to a process circulation rate of 3.5 g/min. Deposition was started by circulating scCO<sub>2</sub> through the reserver for dissolving the organic precursor like anthracene.



**Figure 1:** Schematics of 3-dimensional OPVC structure

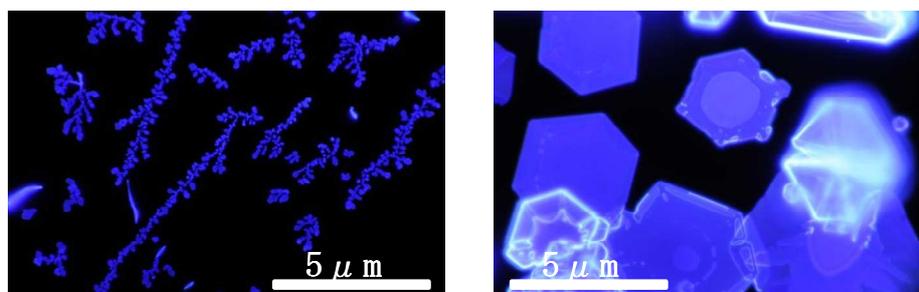


**Figure 2:** Schematics of (a) the apparatus and (b) the deposition chamber.

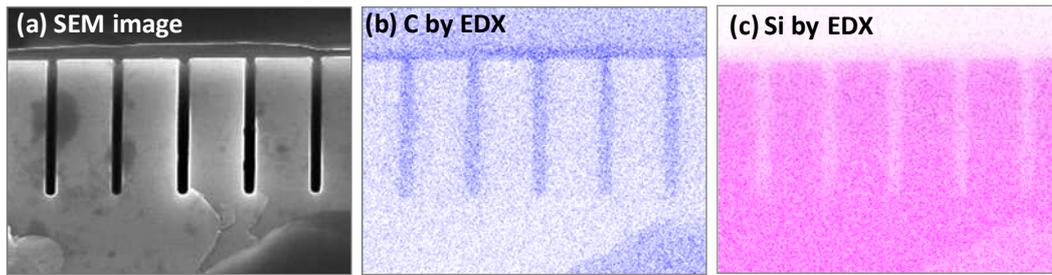
## RESULTS

In this technique, an organic material is dissolved in high-temperature  $scCO_2$  and continuously supplied to a cooled substrate through an inlet nozzle. Typical temperatures are 200 and 100 °C for the nozzle and the substrate, respectively. In this configuration, the temperature-dependent solubility of the organic material on  $scCO_2$  causes supersaturation of the solute near the substrate, which were then transported to the substrate surface through a boundary layer. There are two mechanisms for excellent filling capability. One is high supersaturation in the vicinity of the substrate due to large and temperature-dependent solubility, and rapid mass transfer in the boundary layer. These reflect liquid-like density and gas-like diffusivity of the fluid, respectively. The other is fast surface migration of molecules impinging on the substrate by keeping a substrate at moderate temperature while cooling the substrate to obtain a sufficient temperature difference between the nozzle and the substrate. Both of these favour isotropic 2D island growth over dendritic growth as shown in Fig. 3, and ensure enough transportation of molecules from the top surface to the inner surface of 3D features via surface migration as shown in Fig. 4. In addition, a large velocity of the fluid from the nozzle and a small distance between the nozzle and the substrate prevent homogeneous nucleation above the substrate, in spite of a large supersaturation.

(a) Surface-migration-limited      (b) Crystallization-limited



**Figure 3 :** Plain view optical image of the substrate.



**Figure 4 :** Cross-sectional (a) SEM image, (b) Carbon and Si composition mapping by EDX after filling..

## CONCLUSION

Novel organic thin-film fabrication technique, which enables filling organic materials onto high-aspect-ratio features using supercritical CO<sub>2</sub> was developed, and complete filling of an organic photovoltaic material, anthracene, onto Si trenches with aspect ratio of 10 was successfully demonstrated. This methodology can be applied to widespread functional organic substances, and contributes a realization of 3D organic electronic devices.

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