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Large-Area Nano-patterning and Fabrication of Vertical Transistor Array by Non-close-packed Polystyrene Spheres

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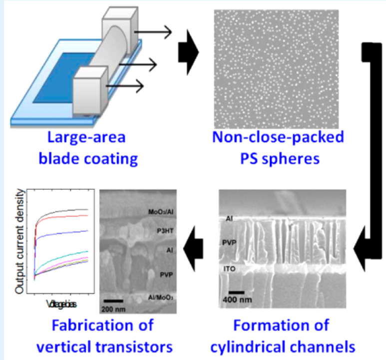
Supporting Information

ABSTRACT: We demonstrated a large-area nanopatterning technique with the help of a non-close-packed PS sphere layer over a large-area substrate. The non-close-packed PS sphere layer is fabricated by blade coating method. It was demonstrated that non-close-packed PS spheres can be achieved within an area of 18 cm × 25 cm on a rigid glass substrate and within an area of 10 cm × 10 cm on a flexible substrate. We also demonstrated that the blade-coated non-close-packed PS sphere layer was suitable for the mass production of vertical organic transistors over a large area.



KEYWORDS: *large-area nanopatterning, vertical transistors, polymer transistors, organic transistors, nanosphere lithography*

Patterning at the nanometer scale has been at the center of the whole nanoscience and technology field. In addition to the conventional electron-beam lithography, there are many other alternative approaches including laser interference lithography[1,2] and self-assembled colloid lithography by polymer nanospheres.[3,4] The e-beam and interference methods have intrinsic limit on the area of exposure and are not suitable for a direct large area patterning. However, from the application point of view a reliable large-area fabrication of nanopatterns with high throughput is necessary. Colloid lithography depends on the assembly of polymer spheres into either periodic hexagonal close-packed structure or random non-close-packed structures. If such spheres are used as the shadow mask for thermal evaporation, the deposited region for the former case are made of disconnected triangles whereas the deposited region is a connected network for the latter. Their applications are therefore complementary. The large area fabrication of the close-packed polymer spheres have been demonstrated but the assembly usually takes a long time[3,4] and the reproducibility is not good. For non-close-packed polymer spheres, deposition by dipping[5] as well as blade coating[6] have been reported, but the largest area is also limited. Because of the strong tendency for the nanospheres to aggregate by hydrostatic pulling during the final stage of solvent drying, the drying process for nonclose packed spheres is extremely sensitive. In earlier works the polystyrene (PS) sphere are deposited by vertically dipping the substrate into sphere solution followed by vertical dipping into boiling isopropanol alcohol (IPA) to achieve a rapid drying which may prevent sphere aggregation (vertical−vertical).[5] Such vertical−vertical method gives uniform sphere distribution only in the millimeter scale. In the recent work the PS sphere are deposited on a horizontal substrate by blade coating follower by drying done by pouring boiling IPA over the horizontal substrate (horizontal-horizontal).[6] Such horizontal-horizontal method improves the size of uniformity but no more than about 1 cm by 1 cm. Such an area is still too small for most of the real applications.

In this work, we employ a horizontal-vertical method for the nonclosed-packed PS spheres, where the spheres are first deposited on a horizontal substrate by a large blade coater, then the substrate is dipped vertically into the boiling IPA followed by rapid drying by the hot wind, as shown in Figure 1. In this way, the nonuniform IPA drying by the pouring over horizontal substrate is avoided and the good nonclosed packed distribution of PS spheres are achieved for A4-size substrate (20 cm by 30 cm) except for the edge regions. This horizontal-vertical method can in principle be scaled up to the meter scale. It has a high yield and high fabrication throughput as it does

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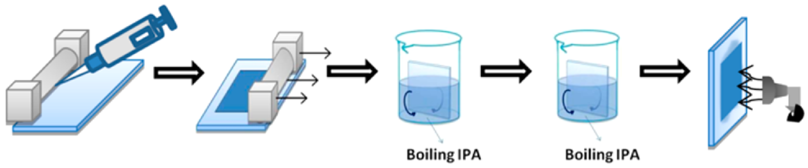

Figure 1. Processes involved in the blade-coating method. The PS suspension is blade-coated on the substrate, and then the substrate is dipped into a beaker of boiling isopropanol to remove the PS spheres in the bladed ethanol layer. The substrate is moved to another beaker of boiling isopropanol and blown dry after 10 s.

not require any slow self-assembly process. Furthermore, it consumes little amount of sphere solution. Such large area patterning at the 100 nm feature size may find applications in many areas, including the antireflection for solar cell, the formation of interpenetrating p−n junction for the active regions of solar cell, large surface areas for chemical sensor and catalysis, as well as vertical transistors. Here we use the vertical transistor array as an example to show the large-area uniformity of the nanostructures made by the horizontal-vertical method.

Vertical organic transistors have attracted lots of attentions recently because of their excellent device performances, such as high on/off current ratio,[7,8] low operation voltage,[9,10] and high output current density.[11,12] Contrary to the organic field-effect transistors in which the source and drain electrodes are in the same plane, the channel length in vertical organic transistors is determined by the thickness of the organic layer which vertically separates the electrodes for carrier injection and collection. The short vertical channel length can be easily achieved by reducing the organic layer thickness between electrodes. On/off current ratio of 1×10^5 and operating voltage of 0.6 V have been demonstrated[8,10] by a vertical organic transistor, named as the polymer space-charge-limited transistor (SCLT). In the SCLT, a base electrode with random openings is embedded in an organic layer, which is sandwiched by emitter and collector electrodes. The holes are injected into the organic layer by the emitter electrode, passing through the openings on the base electrode, and finally being collected by the collector electrode. The potential barrier inside the vertical carrier channel is controlled by the base voltage (V_{BE}) applied on the base electrode. The openings on base electrode are fabricated by using a layer of non-close-packed polystyrene (PS) spheres as the shadow mask while metal deposition. If the experimental conditions of dipping method are not well controlled, the PS sphere aggregates will form and lead to large openings on the base electrode after metal base deposition. Large openings on base electrode in the SCLT will result in large off-current and poor on/off current ratio.[13] Here it was demonstrated for the first time that the non-close-packed PS nanosphere layer can be achieved in an area of 18 cm × 25 cm above a rigid glass by the blade-coating deposition process. The non-close-packed PS nanosphere layer was also realized in an area of 10 cm × 10 cm on a flexible polyethylene terephthalate (PET) substrate by blade-coating method. The scanning electron microscopy (SEM) was utilized to inspect the distribution of PS spheres on the surface, and it is observed that the non-close-packed PS sphere layer was achieved at different locations over the substrate. The SCLTs were fabricated in different locations to demonstrate the capability of blade-coating method for the fabrication of SCLT over a large-area substrate. The output current densities and on/off current ratios of these SCLTs are 5.04 ± 2.01 mA/cm^2 and 1×10^3 to 1×10^4, respectively. Such a large-area distribution of high performance SCLTs demonstrates that the blade-coating method with vertical IPA rinsing is suitable for mass production.

To demonstrate the blade-coating method shown in Figure 1 is capable of distributing non-close-packed PS spheres over a large area, the PS spheres were bade-coated on a large glass substrate with area of 20 cm × 30 cm. Because the organic materials on the edge of the glass substrate were removed to expose the glass substrate serving as the bearing face between blade coater and substrate, the effective area with organic materials and PS spheres was reduced to about 18 cm × 25 cm. The SEM images were taken at 12 positions (Figure 2a) to inspect the distribution of PS spheres blade-coated on a large substrate. Only a few PS sphere aggregates were observed in these SEM images (Figure 2b and Figure S1). The average particle number in a 5 um × 5 um area is estimated to be 310 ± 39. These results demonstrate that a layer of non-close-packed PS spheres can be achieved over a large area by the blade-coating method proposed in this work. If the fabrication processes shown in Figure 1 is not followed, but pouring or blade-coating boiling IPA over the substrate, aggregates usually forms in many locations (Figure 2c). This is because there are still PS spheres suspended in the upper ethanol solution before drying. If there are still PS spheres in the upper ethanol solution, spheres will settle on the surface during drying and result in aggregates. In the processes shown in Figure 1, the immersion in boiling IPA helps in remove PS spheres in the ethanol solution and prevents the formation of aggregates. Besides, by using the method presented in this work, a repeated IPA rinse process is prevented, which is however essential in previous work to achieve a non-close-packed PS sphere layer.[6] The fabrication processes demonstrated in this work is much easier and cost-efficient.

The utilization of the procedure shown in Figure 1 on a flexible substrate is also demonstrated in Figure 3. The non-close-packed PS sphere layer can be formed by blade-coating method shown in Figure 1 on a flexible substrate without remarkable aggregates. The densities of the PS spheres at nine different positions are similar (Figure 3b and Figure S2). The average particle number in a 5 um × 5 um area is estimated to be 243 ± 20. The PS sphere distribution situations on flexible and rigid glass substrates are similar (Figures 2b and 3b and Figures S1 and S2), which makes us believe that the size of the area of non-close-packed PS sphere layer could be easily scaled up by the method proposed in this work.

To demonstrate the nanoscale patterning over a large area by using the procedure shown in Figure 1, a film with many nanometer-sized channels was fabricated. The non-close-packed PS array is first formed on a rigid ITO substrate coated with a thick poly(4-vinylphenol) (PVP) layer (Figure 4a), then the aluminum is thermally deposited serving as etching mask. The diameter of the PS spheres is 100 nm. After removing the PS spheres with tape and etching the PVP at sites without Al coverage, many cylindrical channels can be observed

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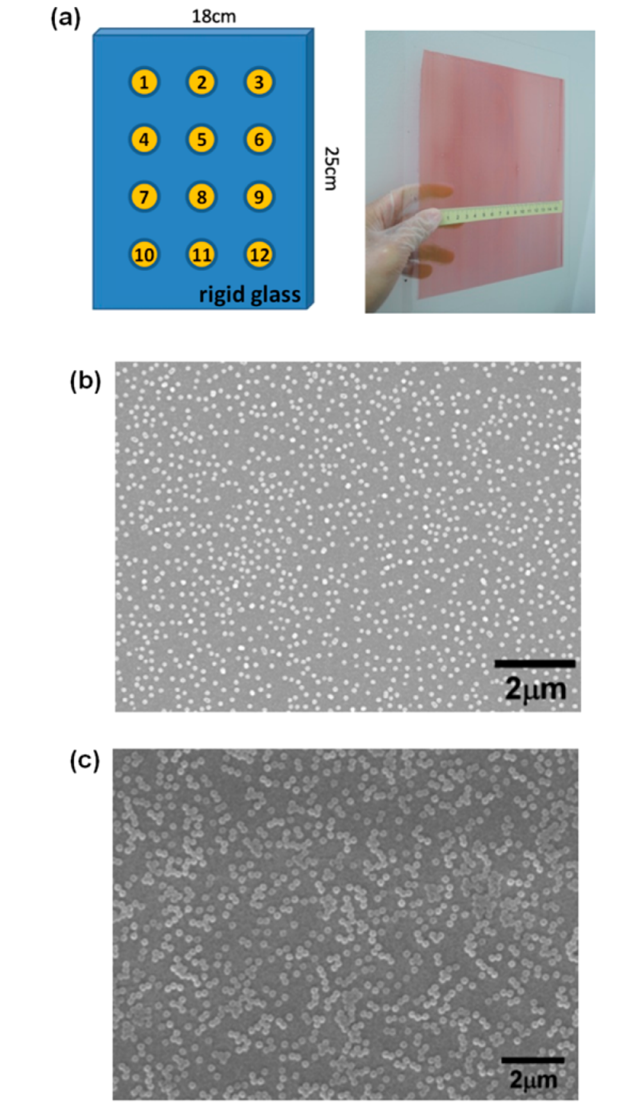

Figure 2. (a) Twelve positions on a large glass substrate are selected for taking SEM images. Photographic image of the substrate. (b) Representative SEM image of the distributions of PS spheres at positions #6. (c) SEM image of the surface of the substrate when the blade-coating method is not followed.

no matter the thickness of PVP film (Figure 4b, c). Even for a thick PVP film, long cylindrical channels can be formed with diameter and length of about 100 and 1200 nm, respectively. The realization of such a nanopatterned film proves the possibility of this method for large-area nanoscale patterning.

Another demonstration of the flexibility of this large-area nanoscale patterning technique is to realize SCLTs over a large area. The fabrication procedure and the cross-sectional SEM image of a SCLT are shown in Figure 5. Because the sample holder size of our thermal evaporation system for metal is limited to be 10 cm × 10 cm, the substrate size used for further demonstration was reduced. The non-close-packed PS sphere layer was formed on a rigid glass substrate with area of 10 cm × 10 cm and the SCLTs were fabricated at nine different positions, as shown in Figure 6a. The thickness of insulating PVP is about 350 nm, and the thickness of P3HT, which is also the channel length, is about 750 nm. The representative output characteristics for the SCLTs are shown in Figure 6b, and the output characteristics for nine SCLTs are shown in Figure S3

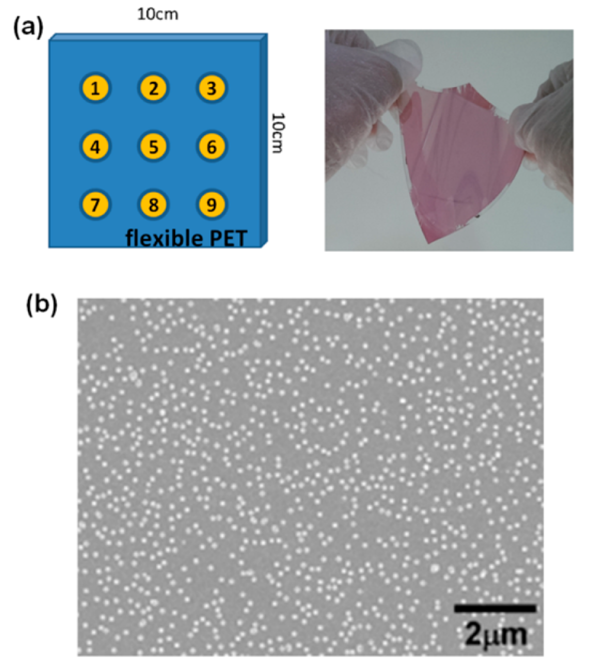

Figure 3. (a) Nine positions on a flexible substrate are selected for taking SEM images. Photographic image of the flexible substrate. (b) Representative SEM images of the distributions of PS spheres at positions #6.

and Table S1. The top MoO_3/Al emitter was commonly grounded and the bottom Al/MoO_3 collector was negatively biased at V_{CE}. The V_{BE} was varied to modulate the output current density J_C. The devices were turned on when $V_{BE} = -0.9$ V, whereas the devices were turned off when $V_{BE} = 0.9$ V. For these nine SCLTs, the average output current density is 5.04 ± 2.01 mA/cm^2 and the on/off current ratios are 1×10^3 to 1×10^4. The on/off current ratio is inferior to our previous result[8] because of the differences in many experimental conditions. For instance, there was a SiO insulating layer of 50 nm deposited above Al base electrode in the SCLT in previous report.[8] The leakage current between electrodes was prevented and breakdown voltage was increased. As a result, the range of V_{BE} was wide in previous report,[8] leading better device performance. In this work, instead of trying to optimize the characteristics of the SCLTs, the main goal in this work is to demonstrate a large-area nanopatterning technique and its application in the fabrication of SCLTs over a large area. The demonstration of the blade-coating method is suitable for distributing PS spheres for mass production of SCLTs is a good start for future applications. Besides, we have recently demonstrated the performance of the vertical organic transistor on polyethylene naphthalate (PEN) flexible substrate is similar to the performance of the one on glass substrate.[14] After bending 1000 times, no remarkable change of the characteristics of the vertical organic transistor on PEN flexible substrate can be observed. We believe the performance of SCLTs fabricated over a large area no matter on rigid or flexible substrate will be improved as long as the previous experimental processes are followed.

In conclusion, a blade-coating method was demonstrated to be able to form a large-area non-close-packed PS sphere layer on rigid glass or flexible PET substrates. The area covered with non-close-packed PS spheres can be as large as 18 cm × 25 cm on glass substrate and 10 cm × 10 cm on PET substrate. Nine

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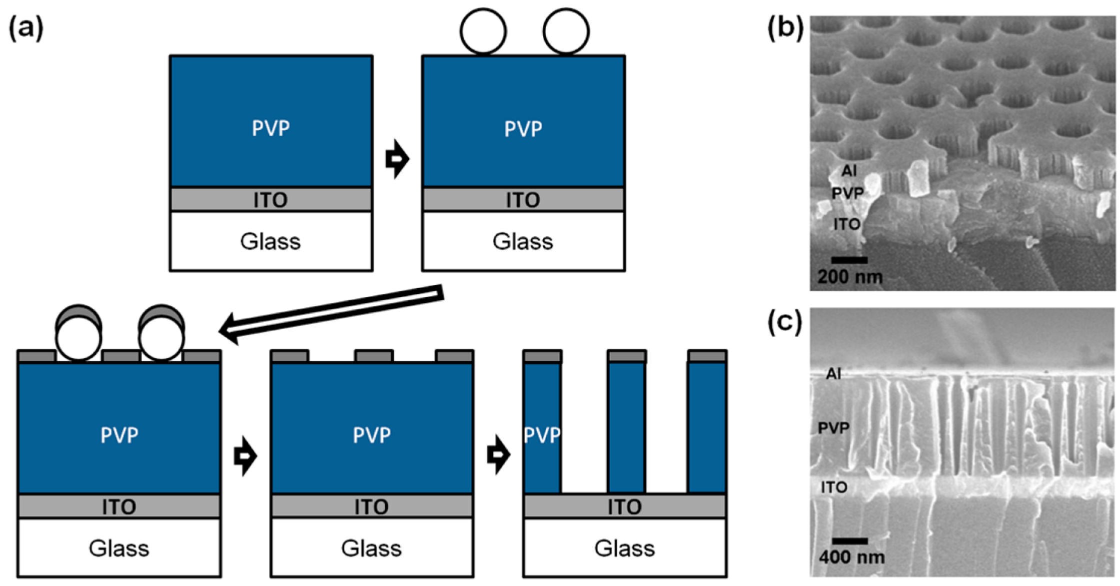

Figure 4. (a) Fabrication processes for cylindrical channels. (b) SEM image taken with tilt angle of 60° of a thin PVP film with many nanometer-sized channels. (c) Cross-sectional SEM image of a thick PVP film with many nanometer-sized channels.

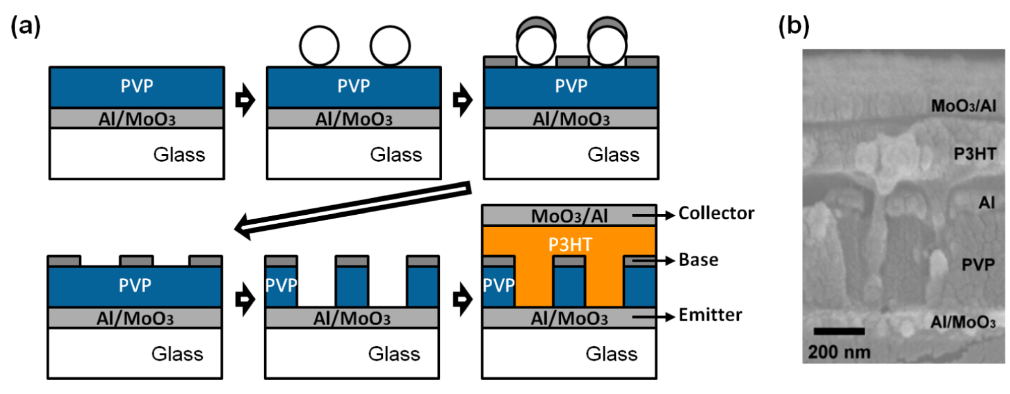

Figure 5. (a) Fabrication processes for a SCLT. (b) Cross-sectional SEM image of a SCLT.

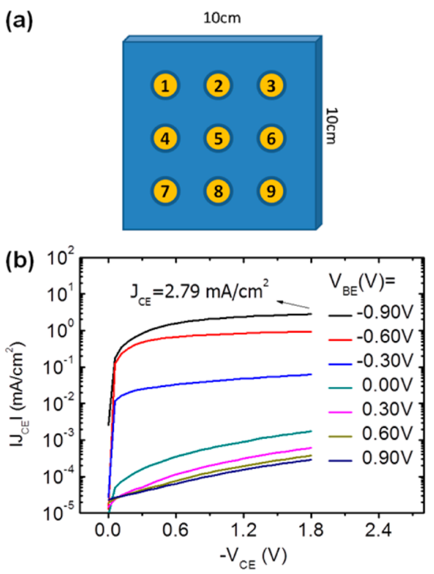

Figure 6. (a) Nine positions on a rigid substrate are selected for SCLT fabrication. (b) Representative output characteristics for SCLTs fabricated on a large glass substrate.

SCLTs fabricated at different locations showed output current densities of about 5 mA/cm^2 and on/off current ratios of 1×10^3 to 1×10^4.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b03724.

Device fabrication details, Figures S1–S3, and Table S1 (PDF)

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Notes

The authors declare no competing financial interest.

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