Contents lists available at SciVerse ScienceDirect

Organic Electronics

Letter

Large-area non-close-packed nanosphere deposition by blade coating for vertical space-charge-limited transistor

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ARTICLE INFO

ABSTRACT

In this work, we proposed a fast and controllable blade coating process to form non-close-packed nanosphere structures. We investigated the key to obtain well-distributed non-close-packed PS spheres with blade coating. We utilized the blade-coated nanosphere structure to realize colloidal lithography and fabricate a vertical channel polymer transistor, the space-charge-limited transistor (SCLT). We demonstrated that SCLT utilizing blade-coated nanospheres delivered 13.9 mA/cm^2 at 1.8 V with an on/off current ratio as 45,000. The process of blade-coating nanospheres may facilitate the commercialization of low-cost colloidal lithography.

1. Introduction

Polystyrene (PS) spheres with well-defined diameters are common nanostructure templates. PS spheres can form 2D or 3D close-packed structures that are used commonly as photonic crystals [1]. Non-close-packed nanosphere structures are also used in numerous novel solid-state electronic devices, such as solid-state sensors with porous electrode surfaces [2], vertical channel space-charge-limited transistors (SCLTs) [3,4], and high mobility indium-gallium-zinc oxide thin-film transistors with dot-like doping [5]. These devices possess superior performance qualities when non-close-packed nanosphere structures are employed. However, current processes for forming non-close-packed nanosphere structures are unable to be commercialized. For example, ordered non-close-packed PS spheres are formed by reducing the diameter of close-packed PS spheres using reactive-ion etching techniques [6]. Forming close-packed PS spheres is a time-consuming process (e.g., 7 h for 1 cm^2 close-packed spheres). Previous

studies, including our own previous work, have used a dipping process to form disordered non-close-packed PS spheres [3,4,7]. Although it is a rapid process, it has poor reproducibility because it depends significantly on human factors.

This study proposes a fast and controllable blade-coating process to form non-close-packed nanosphere structures. This study examines key concepts for obtaining well-distributed non-close-packed PS spheres using blade coating. Finally, this paper shows that a vertical channel space-charge-limited transistor (SCLT) using blade-coated non-close-packed PS spheres delivers a current density of 13.9 mA/cm^2 at 1.8 V with an on/off current ratio of 45,000.

Fig. 1a shows a polymer SCLT, which is a 3-terminal device that functions similar to a vacuum tube triode. The carrier holes are injected into the semiconducting polymer using an emitter, passing through the openings at the base, and are finally collected by the collector. The magnitude of the potential barrier constructed between the emitter and the collector at the vertical channel controls the SCLT on/off states [3,4].

The ideal metal grid in SCLTs has a high density of separated holes. Therefore, PS spheres require a high density

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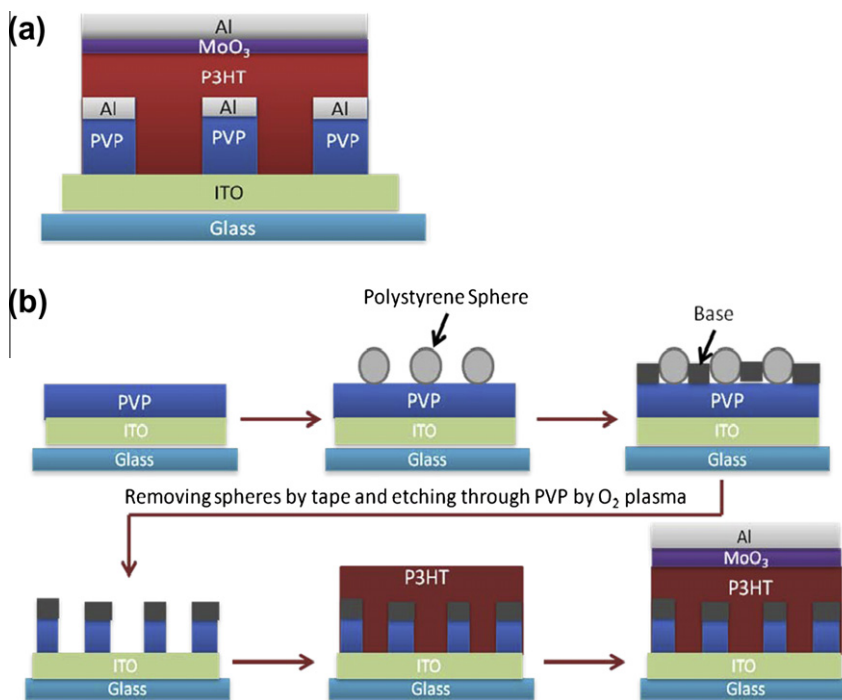   E-mail addresses: meng@mail.nctu.edu.tw (H.-F. Meng), hsiaowen@mail.nctu.edu.tw (H.-W. Zan).

Fig. 1. (a) The schematic diagram and (b) the fabrication process of P3HT SCLT.
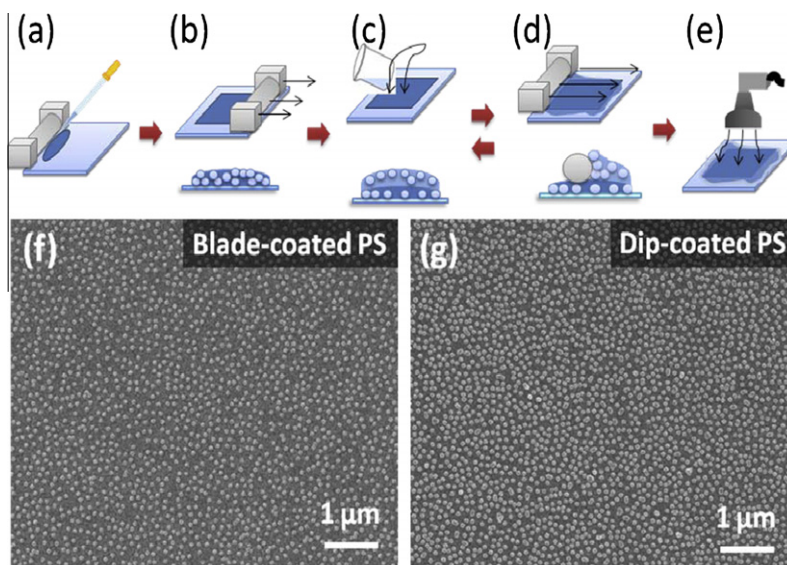

Fig. 2. The process involved in the blade method. (a) Drop the ethanol solution of PS spheres. (b) PS spheres are deposited on the substrate. (c) Boiling IPA is poured over the substrate. (d) Pushing the other spheres away. (e) Drying the remaining IPA. (f) SEM image of 100 nm blade-coated PS spheres. (g) SEM image of 100 nm dip-coated PS spheres.

and sparse distribution when used as a shadow mask for Al-based evaporation.

PS sphere aggregates cause large holes in the metal grid. Consequently, a significant transistor off-current occurs because the current passing through these holes cannot be controlled by the surrounding metal potential [8]. Commer-

cial PS spheres are a colloidal suspension in ethanol, and their surfaces are electrically charged in the ethanol solution. They recombine with counter ions in ethanol and become neutralized when ethanol evaporates. PS spheres are deposited using a dipping method during transistor fabrication. The dipping method can only be applied to small areas

and depends significantly on human factors. Therefore, this method is unsuitable for future mass production.

2. Experimental

Fig. 1b shows the SCLT fabrication process. The SCLT was fabricated on an indium tin oxide (ITO) glass substrate that is plasma cleaned and smoothed with 100 W O$_2$ plasma for 10 min. A 200 nm layer of crosslinkable polyvinyl-pyrrolidone (PVP) is spin-coated onto the ITO substrate, and then cross-linked at 200 °C for 60 min in an inert atmosphere. Methylated poly(melamine-co-formalde-hyde) is used as the cross-linking agent. The PVP is then coated with a 20 nm poly(3-hexylthiophene) (P3HT) layer and annealed at 200 °C for 10 min. Xylene is used to spin-rinse the P3HT to remove the soluble sections. The remaining P3HT has an estimated thickness of 15 nm.

PS spheres suspended in ethanol are first deposited on the substrate using a cylindrical blade (Fig. 2a and b), which is separated from the substrate by a 30 μm gap. An ethanol layer (with suspended spheres) with thickness

around the gap size is formed. Numerous PS spheres are adsorbed onto the substrate to form a monolayer while excess PS spheres are still suspended in the ethanol layer. To remove the excess spheres, boiling isopropyl alcohol (IPA) is poured onto the wet substrate (Fig. 2c) to produce a large aqueous volume with suspended spheres. Then, a 120 μm gap blade is used to quickly sweep the substrate to remove most of the IPA with suspended spheres (i.e. the blade-cleaning process shown in Fig. 2d). The cycle of pouring boiling IPA and the blade-cleaning process, named as the *IPA rinse* process, is repeated 3–4 times to remove all spheres that have not been adsorbed. Finally, as shown in Fig. 2e, a hair dryer is used to dry the remaining IPA quickly. The PS ethanol solution concentration is fixed at 0.4 wt.% for the initial deposition by blade coating. Lower concentrations produce insufficient PS sphere densities. The blade gap is 30 μm for the initial deposition and 120 μm for the *IPA rinse* process.

A 40-nm-thick layer of Al is then deposited onto the PVP layer to form the metal base electrode. The PS spheres are removed using adhesive tape and the PVP at sites with-
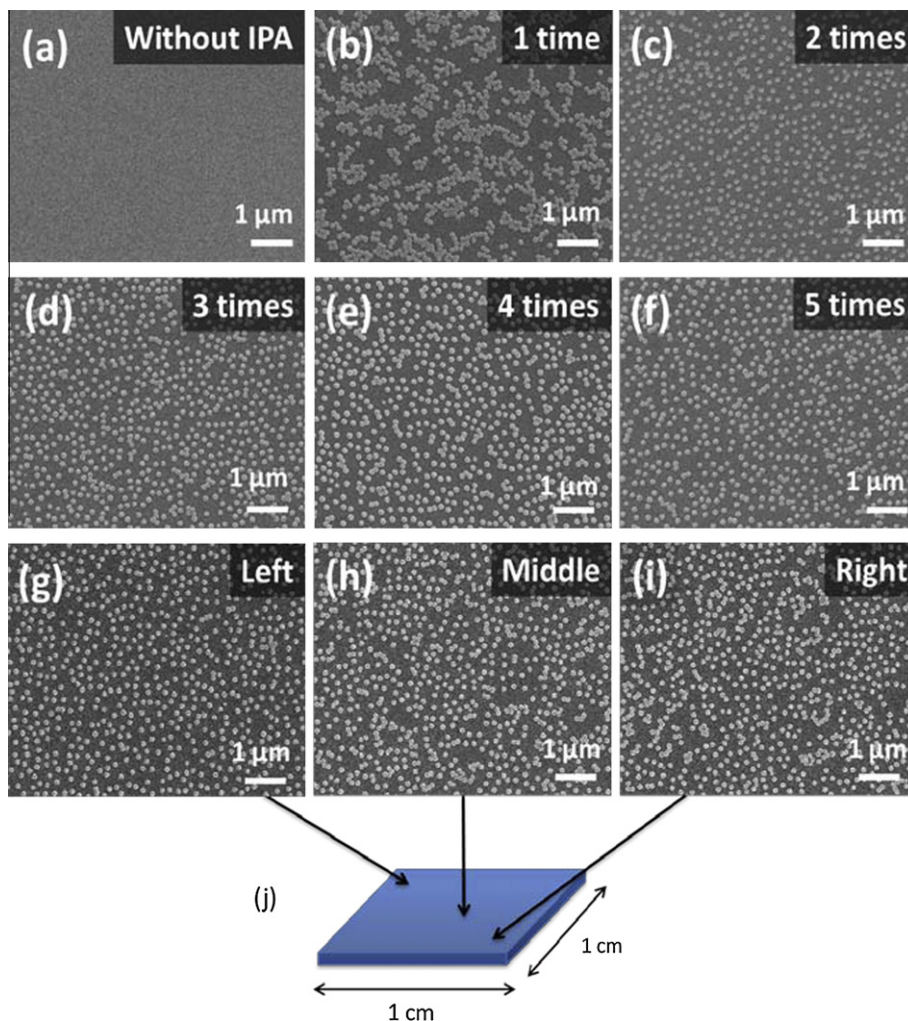

Fig. 3. The distributions of PS spheres with IPA flush (a) 0, (b) 1, (c) 2, (d) 3, (e) 4, and (f) 5 times. The different positions SEM (g–i) are indicated in (j).

out Al coverage are removed using O_2 plasma treatment at 100 W for 10 min. The PVP is then functionalized with an octadecyltrichlorosilane (OTS) self-assembly monolayer (SAM). A 350 nm P3HT layer is spin-coated onto the substrate using a 4.5 wt.% chlorobenzene solution. Finally, the MoO_3/Al collector is deposited to complete the SCLT with active area as 1 mm^2 or 1 cm^2.

3. Results and discussions

The distribution of PS spheres deposited by blade coating with multiple boiling *IPA rinse process* (Fig. 2f) is almost as effective as the dip coating deposition process (Fig. 2g), despite producing slightly more aggregates.

As discussed the critical step during the PS sphere blade-coating is the repeated *IPA rinse* following the initial deposition of the PS spheres by blade coating in the ethanol solution. The *IPA rinse* process reduces the PS sphere aggregates. The boiling IPA redissolves the PS spheres, and the IPA is quickly removed by the blade, followed by blow drying. During this process, the aggregated PS spheres become electrically charged and move freely in accordance with

the Coulomb's Law. This process can be repeated many times to reduce the aggregates. Blow drying is performed at room temperature because high temperatures melt the PS spheres (not shown). Fig. 3 shows the number of aggregates in a specific area for the distributions with various flush times. The distribution is poor when the *IPA rinse* is not performed (Fig. 3a) or when it is performed only once (Fig. 3b). The aggregates are reduced significantly after the second rinse (Fig. 3c), and there is a slight improvement when the process is repeated 4 times (Fig. 3e). The distribution displayed in Fig. 3d is sufficient for SCLT fabrication, as shown below.

Compared with the dip coating method, the advantage of blade coating PS spheres is that large and uniform distributions can be obtained easily. Scanning electron microscopy (SEM) is used to examine several positions in the 1 cm^2 area (Fig. 3j). Fig. 3g–i shows similar distributions of average PS sphere density and aggregate level. Specifically, the average PS sphere densities in Fig. 3g–i are 17.8, 20.0, and 19.6 numbers per μm^2. A 10% variation is obtained. Such uniformity cannot be achieved using the dip coating method. The blade-coated sphere density vari-
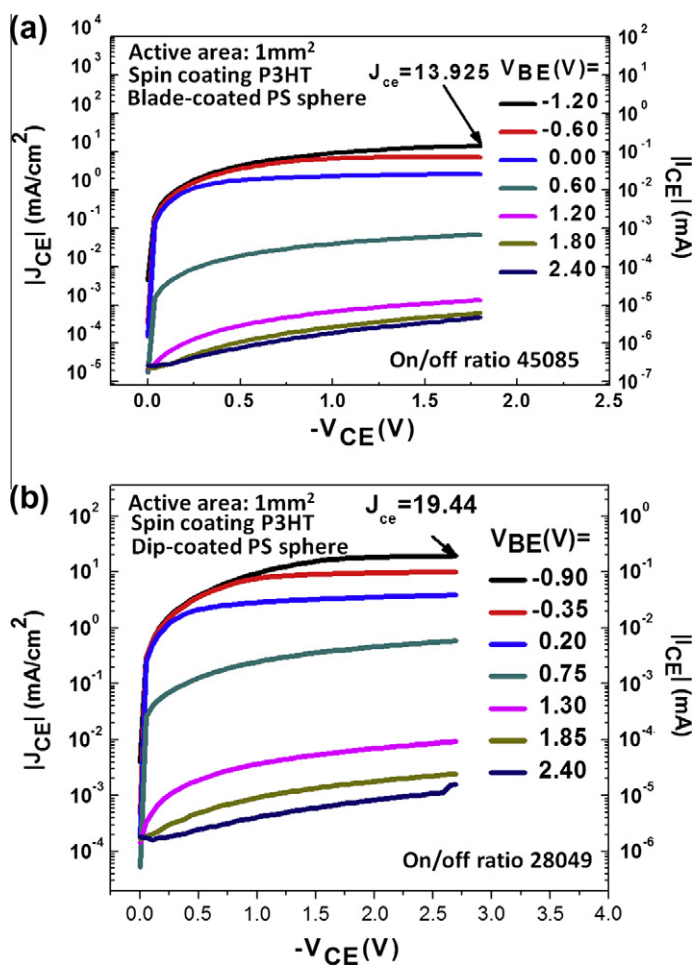

Fig. 4. The output characteristics for P3HT SCLT fabricated with (a) blade-coated PS spheres and (b) dip-coated PS spheres. The current density and the total output current are labeled by the left y-axis and right y-axis, respectively.
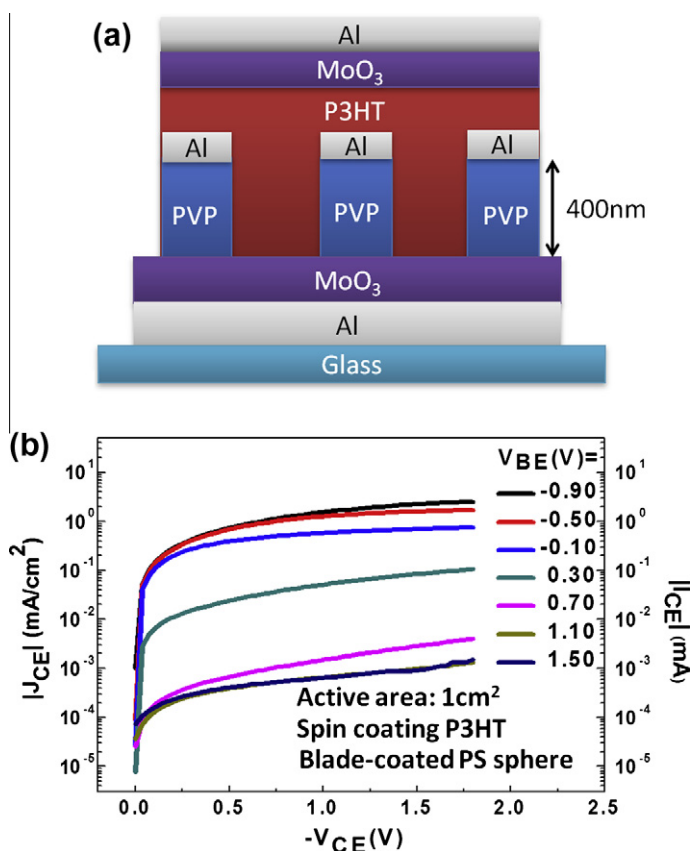
Fig. 5. (a) The schematic diagram of a large-area low-cost SCLT without using an ITO electrode. (b) The output characteristics for the large-area low-cost SCLT.

ation is due to the disturbance of IPA flushing process. In this experiment, IPA flushing is realized by pouring boiling IPA directly on blade-coated PS sphere region. In future work, the disturbance of IPA flushing may be avoided by smoothly flowing IPA through the blade-coated PS sphere region. Furthermore, it is anticipated that this process can be scaled up to 10 cm if a larger blade is used. Therefore, blade coating is shown to be suitable for cost-efficient mass production of nanogrid structures over large areas.

This study now focuses on SCLTs with an Al base fabricated using PS spheres deposited by blade coating. First, the results for a small active area of 1 mm^2 are discussed, and transistors with 1 cm^2 active areas are shown later. All the discussed devices use P3HT as channel material and the PVP is functionalized with an OTS SAM. For SCLT fabricated with blade-coated PS spheres, a collector current density (J_c) as a function of collector voltage (V_{CE}) is shown in Fig. 4a. The output current density J_c is approximately 13.9 mA/cm^2 when V_{CE} = 1.8 V and the on/off current ratio is approximately 45,000. Fig. 1a shows the device structure. The transistor is in top-emission mode when the holes are injected from the top MoO$_3$/Al emitter into the P3HT valence band and subsequently collected by the bottom ITO collector. Fig. 4b shows the transistor characteristic for SCLTs fabricated using conventional dip-coated PS spheres under identical

conditions. The collector on-current is approximately 17.9 mA/cm^2 when V_{CE} = 1.8 V and the on/off current ratio is approximately 28,000. These results are similar to those of devices that are fabricated using blade-coated PS spheres.

Therefore, this verifies the feasibility of using blade-coated PS spheres to fabricate vertical polymer SCLTs. The cost efficiency and high current output of SCLTs with blade-coated PS sphere technology are also shown. To increase the output current, the SCLT active region is increased to 1 cm^2. To reduce the production cost, the expensive ITO electrode is replaced by a dual-layer Al/MoO$_3$ electrode. To improve the DC bias endurance ability, the PVP and P3HT thickness are increased to 400 and 550 nm, respectively. The device structure and the J_c–V_{CE} characteristics of such a large-area low-cost SCLT are shown in Fig. 5a and b, respectively. The output current density is 2.5 mA/cm^2 when V_{CE} = 1.8 V, and the on/off current ratio is approximately 2400. Compared to the device performance shown in Fig. 4a, the slightly reduced output current density and on/off current ratio in Fig. 5b are potentially caused by the increased channel length (i.e., P3HT thickness) and the minor oxidation of the bottom Al electrode during oxygen plasma etching. However, the total output current of the large-area SCLT is as high as 2.5 mA. This high output current generated from a low-

cost organic transistor facilitates the development of cost-efficient power devices. Specifically, the proposed colloidal lithography with blade-coated PS spheres does not require expensive conventional lithography processes and is compatible with roll-to-roll processing. We anticipate that the process can be scaled up to 10 cm by using a larger blade. Therefore, blade coating is shown to be suitable for the cost-efficient mass production of SCLTs with nano-grid structures over large areas.

4. Conclusion

This study successfully showed a colloidal lithography process using a blade-coating deposition process. A solution with PS spheres is deposited onto the substrate by blade coating. Excess PS spheres are removed by rinsing with boiling IPA followed by blade coating. A non-close-packed PS sphere structure with uniform distribution is obtained by controlling the initial PS sphere density and the frequency of IPA rinsing. The proposed blade-coated PS spheres were then used to fabricate a vertical channel polymer SCLT. This study showed that SCLTs fabricated with blade-coated PS spheres and those fabricated with conventional dip-coated PS spheres possess similar characteristics. Furthermore, this paper showed that a large-area cost-efficient SCLT delivers a total output current as high as 2.5 mA, thereby facilitating

the development of cost-efficient organic power devices. We anticipate that the proposed colloidal lithography formed by blade-coated PS spheres can be scaled up to an area approximately 100 cm^2 by increasing the blade size. This study provides a potential foundation for achieving cost-efficient colloidal lithography in real production environments.

Acknowledgements

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