The polymeric organic-static-induction transistor (OSIT), a solid-state vacuum triode, has been extensively studied as a promising vertical organic thin-film transistor. By utilizing polymers as organic semiconductors in OSITs, important performance figures have been achieved, for example, a maximum on-current output of about 10 mA cm\(^{-2}\), on/off current ratio as high as 10\(^5\), and a large current gain of 1000. However, even though polymers with higher mobility have been developed, the performance of OSITs has not been significantly improved yet. In this work, record-high performance OSITs with small-molecule materials as organic semiconductors are demonstrated. Pentacene as a hole-transport material for p-type OSITs can be easily deposited into pinholes of the gate electrode, hence creating effective conducting channels. Excellent characteristics, such as a high on-current greater than 260 mA cm\(^{-2}\), on/off current ratio up to 3.3 \(\times\) 10\(^5\), and a large transmission factor of 99.98\% as well as high current gain of 7965, are attained. These results make the small-molecule organic semiconductor a candidate material for vertical OSITs as well as for organic electronics.

1. Introduction

Since the first report on organic thin-film transistors (OTFTs) by Tsumura et al. in 1986,[1] OTFTs are attracting tremendous attention due to their advantages for wearable and flexible electronics, low-cost, and large-area device applications.[2–5] Furthermore, based on the encouraging improvements in device fabrication and interface engineering,[6–8] the achieved charge carrier mobilities in OTFTs could exceed 10 cm\(^2\) V\(^{-1}\) s\(^{-1}\),[9] which clearly surpasses the mobility of amorphous silicon (a-Si). Still, current densities and the operating frequency of planar OTFTs are behind those of inorganic transistors suitable for flexible substrates (e.g., amorphous gallium-indium-tin-oxide).[10] One attractive alternative to overcome the limitation of planar OTFTs is vertical organic transistors. These devices offer very short channels compared to their planar counterparts because the thickness of a semiconductor layer can range from a few nanometers to several hundred nanometers.[11–16]

In the last few years, organic-static-induction transistors (OSTIs) widely known as one of the vertical organic transistors, have been developed and analyzed extensively due to great potential for high frequency and high power operation.[17–21] OSTIs mimic the concept of inorganic SITs that were initially introduced by Nishizawa et al.[22–24] In terms of operation mechanism, inorganic SIT has the exponential characteristics, but does not follow the space-charge-limited conduction law.[25] In 1998, organic SITs were first presented by Kudo et al.[19] In contrast to inorganic SITs, most of the OSTIs follow the space-charge-limited conduction law.[18,26] In the following years, a growing body of literature has emerged to improve OSTIs, like the device structure shown in Figure 1a. By using polymer semiconductors in OSITs, a maximum on-current output of about 10 mA cm\(^{-2}\), a large on/off current ratio to 10\(^5\), and a great current gain around 1000 has been reached.[20,21,27–32]

In terms of the device structure, both OSITs and inorganic SITs resemble a vacuum tube triode in which a grid-like metal film is sandwiched between a hot cathode and a cold anode.[19,20,21,22] Vacuum triodes have no background carriers in the space from cathode to anode. All carriers in the vacuum triode are emitted from the hot cathode and modified by the grid-like metal film. However, it is difficult to fill the nanometer-sized pinholes (for OSITs shown in Figure 1a) with a solvent and producing a uniform layer formation, particularly when using solution-processed polymeric semiconductors. At present, only a few publications show that small-molecule semiconductors prepared by vacuum evaporation are also promising for using in such OSIT architectures. Pentacene with low dielectric constant,[33] low depletion layer,[34] good hole mobility,[35] and producing a uniform layer formation, particularly when using solution-processed polymeric semiconductors.
as well as simple processability, is a great alternative to polymer organic semiconductors. It was first reported by Fujimoto et al. in such OSIT architectures,[36] however, only an ordinary performance was observed, for example, a low on/off ratio of 2.62. Thus, to fully exploit the application of static-induction vertical organic transistors, OSITs need to be investigated further, not only in terms of suitable device architectures and processes but also of semiconductor materials.

In this work, a record performance of p-type OSITs using pentacene as an organic semiconductor is demonstrated. A high on-current greater than 260 mA cm−2, an excellent on/off current ratio as high as 3.3 × 105, a large transmission factor up to 99.98%, as well as a high current gain of 7965 are achieved. Compared to solution-processed polymer films, vacuum-deposited films make it easier to control film thickness and stability. Hence, built-in parallel conducting channels allow for highly efficient charge carrier transfer from source to drain electrode, enhancing not only the transmission but also the current gain of the p-type OSIT device. Besides, the cost-effective process used in this work is looking potentially in printing organic electronics. Thus, it is expected that advances in performance and robustness in this work can enable OSITs to be used at a higher level of integration in the future.

2. Results and Discussion

To fabricate OSITs, colloidal lithography is used to create pinholes in poly(methyl methacrylate) (PMMA) and aluminum (Al) films as shown in Figure 1a. Detailed fabrication procedures are summarized in the Experimental Section and Figure S1, Supporting Information. Pinholes in PMMA (dark brown) and Al film (grey) provide an ideal template for the formation of nanoscale devices with a density of the pinholes around 108 cm−2 for a solution density of the polystyrene spheres of 1.5 wt%. Moreover, PMMA also acts as an insulator to isolate adjacent conducting channels in an OSIT (cf. Figure 1a). Pentacene (sky blue) is used as organic semiconductor material offering good hole conduction properties.[37] The channel length of the OSIT is determined by the film thickness of the pentacene. Using the common source configuration in Figure 1a, the vertical current that flows between the two external electrodes is modulated by changing the voltage of a mesh-like gate (VGS). Hence, the transmission factor relies upon the number of pinholes, which allow current from the source to flow through and reach drain (D) electrode by applying a drain-source voltage (VDS) (Figure 1a). With a positive gate-source voltage (VGS > 0) applied, holes cannot transmit through the thin gate layer, and consequently are not able to arrive at the drain. When gate-source is applied to a negative voltage, charge carriers will accumulate at the gate electrode, and OSITs will turn on. Once accumulated, charge carriers diffuse through the pinholes and finally are collected by the drain. Apart from a slight current that flows into the gate electrode (causing gate leakage current Ig), the source current Is is transmitted through the openings and injected into the drain electrode as drain current Id. Figure 1b shows a photograph of a glass substrate including four independent OSITs (the active area is 0.6 × 0.6 mm2), which are labeled by numbers and corresponding red squares, respectively.

To make sure the device can be turned off, it is better if the openings in the gate of the OSIT are not too big, however, if the openings in the gate are very small, on-current might be limited. In this regard, the density of unintentional dopants in the semiconductor is of great importance, since it defines whether a pinhole can be still fully depleted by the gate-source voltage. Diameters of 100–200 nm are a good choice of the channel size.[21] Hence, 100 nm diameter polystyrene spheres are utilized as evaporation masks. On the other hand, a device with high performance needs uniform surface coverage of polystyrene spheres, avoiding large-scale aggregation which leads to the formation of the undesired wide channels. Thus, negatively charged spheres are selected to exploit the electrostatic interaction between substrate and particle surface. As a result, the adsorption generally produces single dispersed particles. To restrain polystyrene particle aggregation, the film is dipped into a container of hot (90 °C) isopropanol for 15 s. This is an effective method to overcome the capillary forces, which are developed by the menisci among particles during solvent evaporation, and keep the dispersed nanoparticles in place. In this step, the nanoparticles on the surface are slightly out of shape and increase the contact area between particles and substrates.[38] Therefore, a film covered by well-distributed high-density polystyrene spheres is formed, as proven by the scanning electron micro-

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**Figure 1.** a) Cross-section scheme of the built-in channels in OSITs and circuit diagram. b) Photograph of a glass substrate including four OSITs (edge length: 2.5 cm).
scope (SEM) image in Figure 2a. The particle size distributions are also obtained by atomic force microscopy (AFM), as shown in Figure 2b. The gate layer of 30 nm-thick Al is subsequently deposited and then the spheres are removed with tape.

After removing the polystyrene spheres, a lot of nano-holes are left on the Al film without destroying the film as shown in Figure 2c. For one square centimeter, it has about $10^9$ well-distributed holes, which is essential to acquire great reliability of device operation over a large area. According to the size distribution in the inset of Figure 2c, 87.8% of the nano-holes are between 90 and 100 nm, 9.5% of the nano-holes are between 100 and 200 nm, and 2.4% are between 200 and 300 nm. There are only 0.3% of the nano-holes larger than 300 nm because of aggregations of the polystyrene spheres. The size distribution provides good conditions for forming pinholes in the PMMA later, and is promising to achieve good gate control over the source to drain. Afterward, the PMMA without Al coverage is etched out by using a reactive ion etching system with a power of 20 W and a volume ratio of 2:1 for O$_2$ and Ar. Consequently, pinholes are left in the PMMA, as shown in Figure 2d. On the SEM image, the pinholes in PMMA seem larger than 100 nm because charging occurs when we are scanning with SEM, which makes the pinholes in PMMA look larger than they are. Finally, a 350 nm-thick film of pentacene and a layer of gold as a source electrode are deposited using a vacuum evaporation system.

The electrical properties of the OSIT are then characterized in the common source configuration with the electric circuit given in Figure 1a. Figure 3a shows the output curves of the p-type OSITs. The drain current densities are plotted against the drain-source voltage at different applied gate-source voltages.
Considering the leakage from the drain to the gate, positive drain currents are clipped since they show an unreal situation for device operation. According to the output curves, an on/off ratio larger than $10^5$ is achieved at low working voltages ($<1.5\,\text{V}$). The gate-source voltage can effectively modulate the drain current of OSITs. However, the saturation behavior (in Figure 3b) is lost in OSITs due to short channel effects.[39]

A transfer curve of the p-type OSIT is shown in Figure 3c. The gate-source voltage sweep gives a current–voltage characteristic with excellent rectifying behavior as $V_{GS}$ ranges from 0.5 to $-1.5\,\text{V}$. The off-state of the drain current contains two contributions, the leakage of charges from source to drain which is not controllable by the gate and the reverse biased gate-drain diode. The current–voltage curves for the gate-drain diode are demonstrated in Supporting Information (Figure S2, Supporting Information). By comparing the off-current of gate-drain diode with that of OSITs, it is evident that the former one governs the off-state of the OSIT ($\approx 10^{-3}$–$10^{-4}\,\text{mA cm}^{-2}$). Particularly, only a few charge carriers leak from the source if the gate-source voltage is positive. For the forward bias, the drain current shows an exponential increase as the gate voltage increases, until $V_{GS} = -0.5\,\text{V}$; in this region, the drain current is limited by the potential of the pinholes determined by the gate, producing an exponential curve. At higher gate potential ($-0.5\,\text{V} < V_{GS} < -1.0\,\text{V}$), the drain current increases with a lower slope because the charge channel around the gate is forming. When the gate potential larger than $-1.0\,\text{V}$, externally applied gate potential does not affect anymore because of the shielding effect of the charge accumulation around the gate. The conductive channel is effectively depleted with applied gate-source potential. The operation mode is similar to that of bipolar junction transistors, which incorporate two back-to-back connected p-n diodes, contrary to the Schottky diodes as illustrated here. Finally, a great current density up to 260 mA cm$^{-2}$ and the highest on-off current ratio about $3.3 \times 10^5$ are achieved for the best device at $V_{GS} = -1.5\,\text{V}$ and $V_{DS} = -3\,\text{V}$. The performance is better than in most previous studies in similar structured OSITs, for example, the maximum current density of $\approx 10\,\text{mA cm}^{-2}$ observed for polymer SITs.[27,29,40,41] Because of the nanostructures on the surface, the surface energy cannot be considered as a constant parameter but rather becomes a quantity that varies on the nanometer scale. This effect may cause local variations in the surface wetting of semiconductor inks. In particular, nanometer-sized pinholes might not be filled sufficiently with the semiconductor ink during solution-based processing, or the microstructure of the polymer within the pinholes. For vacuum-deposited small-molecule pentacene, the film formation appears to be more uniform, which probably contributes to the effective filling of the conducting channels.[42–44]

The current gain is plotted against current density in Figure 3d. The calculation of the current gain is similar to the bipolar junction transistor, which is performed by $I_D/I_G$.[45] To
evaluate the maximum amplification factor of OSITs as $V_{GS}$ is smaller than $V_{DS}$, the differential current transmission factor ($\alpha$) and current gain ($\beta$) are calculated by following equations,

$$\alpha = \frac{dI_D}{dI_G}$$  \hspace{1cm} (1)

$$\beta = \frac{I_D}{I_G}$$  \hspace{1cm} (2)

The highest differential gain ($\beta_{\text{MAX}}$) is 7965 when the current density is 40 mA cm$^{-2}$. Even in the maximum on-state (260 mA cm$^{-2}$), the gain value remains close to 340. Besides, the differential transmission is as high as 99.98%. The large differential gain is not only a result of the low gate leakage current but also the high on-current density achieved for the device structure demonstrated here. Oxygen ion etching during the fabrication process is expected to create a high-density aluminum oxide film on the surface and the side edge of the gate electrode, which can effectively reduce the gate leakage.

To verify the reliability of the colloidal lithography technique, we compare the following transistors prepared with three different particle solution densities such as 0.5, 1.0, and 1.5 wt%. Figure 4a–c shows the SEM images of the PMMA surface coated with polystyrene spheres, which are prepared by immersing the samples in different solutions with corresponding particle densities. According to the SEM images, polystyrene spheres are uniformly distributed on the surface of PMMA. The particle concentrations calculated by Image J are $1.32 \times 10^9$, $9.15 \times 10^8$, and $5.50 \times 10^8$ cm$^{-2}$, respectively. The concentration ratio of the polystyrene spheres is very close to the ratio of solution density 3:2:1, which also indicates a quite uniform distribution of the polystyrene spheres. However, the particle aggregation phenomenon (more than three particles together) is very apparent in Figure 4a because of the higher particle solution density. On the contrary, only a few particle aggregations are present in Figure 4c due to lower particle solution density. Typically, if many aggregations occur, the device will not be easily turned off due to large pinholes, so the solution density of the polystyrene should not be too high.

The electrical properties of OSITs prepared with different solution densities are also investigated, as shown in Figure 4d,e. According to the gate voltage sweeps, the OSITs prepared with the highest solution density of 1.5 wt% and lowest solution density of 0.5 wt% also show the highest and lowest current densities in on-state at fixed gate-source voltage, respectively. Then, the current in every conducting channel is further calculated, assuming that all the polystyrene spheres are individually dispersed, and the current densities are divided by the corresponding particle densities for each solution density. Theoretically, the current in the conducting channels of three devices should be the same for each drain-source voltage and gate voltage. Figure 4e shows the
average current in the pinholes, which is plotted according to the current densities divided by pinhole densities. The average current per hole curves for the OSITs with three different particle densities coincide surprisingly well. A small difference occurs because not all the polystyrene spheres are individually dispersed in the experiment. Overall, the colloidal lithography used here is a reliable technique.

Moreover, taking the average current value of $2 \times 10^{-7}$ mA (max. current density divided by pinhole density) and the size of 100 nm for the pinhole in Figure 4e, the current density in the pinhole is 2.5 A cm$^{-2}$. In the following, we use the SCLC equation

$$J = \frac{9}{8} \varepsilon_0 \mu \frac{(V - V_0)^2}{d^3}$$

(3)

where $d$ is the semiconductor film thickness, $V$ the applied voltage, $\mu$ the charge mobility, $\varepsilon$ and $\varepsilon_0$ the relative and vacuum permittivity of the semiconductor, respectively. When $V = V_{def} = -3$ V, and assuming $\mu = 0.1$ cm$^2$ V$^{-1}$ s$^{-1}$, the current density in the pinhole is 7.5 A cm$^{-2}$, which is in the same range as the estimated value of 2.5 A cm$^{-2}$. Because of the Schottky contacts between the metal and semiconductor, not all applied voltages are used to form the SCLC. Thus, some voltages drop across the contacts and will not contribute to the SCLC. Accordingly, the $V - V_0$ should be smaller than 3 V, and the experimental current density in the pinholes should be smaller than 7.5 A cm$^{-2}$. Therefore, the current is limited by the SCLC in each channel of an OSIT.$^{[21,22]}$

3. Conclusions

In summary, vertical OSITs based on p-type small-molecule organic semiconductors with record-high performance have been demonstrated. In addition to a large on/off ratio ($3.3 \times 10^5$) and a large on-current density (260 mA cm$^{-2}$), OSITs exhibit an excellent transmission factor of 99.98%. Colloidal lithography is used to build vertical conducting channels. Afterward, oxygen ion etching is used to remove the PMMA without Al coverage. During the process, a layer of aluminum oxide is formed on the gate electrode, effectively reducing the gate leakage current. Pentacene as the organic semiconductor is deposited by a vacuum vapor deposition system, which can easily tune the depositing rate and control the film thickness by changing heated temperature during deposition. Our results show that pentacene can be filled into the pinholes and creates excellent conducting channels for OSITs. This work establishes the foundation for further research on high-performance OSITs with small-molecule semiconductors, and the improved fabrication process also enables the realization of OSITs to be used in integrated circuits.

4. Experimental Section

The glass substrates were first cleaned with N-methyl pyrrolidone, ethanol, and deionized water followed by an ultraviolet ozone cleaning system. In the ultra-high vacuum ($<10^{-7}$ mbar) evaporation system, the bottom electrode including 5 nm Cr and 50 nm Au layer stack was realized by continuous deposition through stainless-steel shadow masks. Then, a layer of ~200 nm-thick PMMA was prepared by spin-coating a blend solution of anisole with PMMA on the Cr/Au coated glass substrate and dried with increasing temperature from 30 to 200 °C, finally kept at 200 °C for 3 min, so that uniform PMMA films were obtained. The 100 nm diameter negatively charged polystyrene spheres were adsorbed on the surface of PMMA by immersing in an ethanol suspension of polystyrene spheres for 3 min. The densities of the ethanol suspension of polystyrene spheres were 0.5, 1.0, and 1.3 wt%, respectively. After the spheres were adsorbed, a gate electrode (Al) was prepared by thermal evaporation on top of the particles at 1 Å s$^{-1}$. After that, the particles were peeled off by a tape (3M Scotch). Then, the PMMA at the location without aluminum coverage was removed by reactive ion etching with 20 W power and a volume ratio of O$_2$:Ar equals 2:1, and consequently, the pinholes were formed. Then, the organic semiconductor pentacene (purchased from Sensient Technologies) was deposited atop with a rate of 0.3Å s$^{-1}$ and a thickness of 350 nm. Finally, the top electrode was deposited. The complete devices were subsequently encapsulated in a nitrogen glove box. The electrical transport performance was characterized using a parameter analyzer Keithley 4200-SCS. The scanning electron microscope images were captured using a Zeiss GeminiSEM 500 and an FEI Helios Nanolab 660. Atomic force microscope images were obtained by AIST-North CombiScope.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

colloidal lithography, organic-static-induction transistors, small molecules, space-charge-limited current, vertical organic transistors

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