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TOPICAL REVIEW

The development of fluorous photolithographic materials and their applications to achieve flexible organic electronic devices

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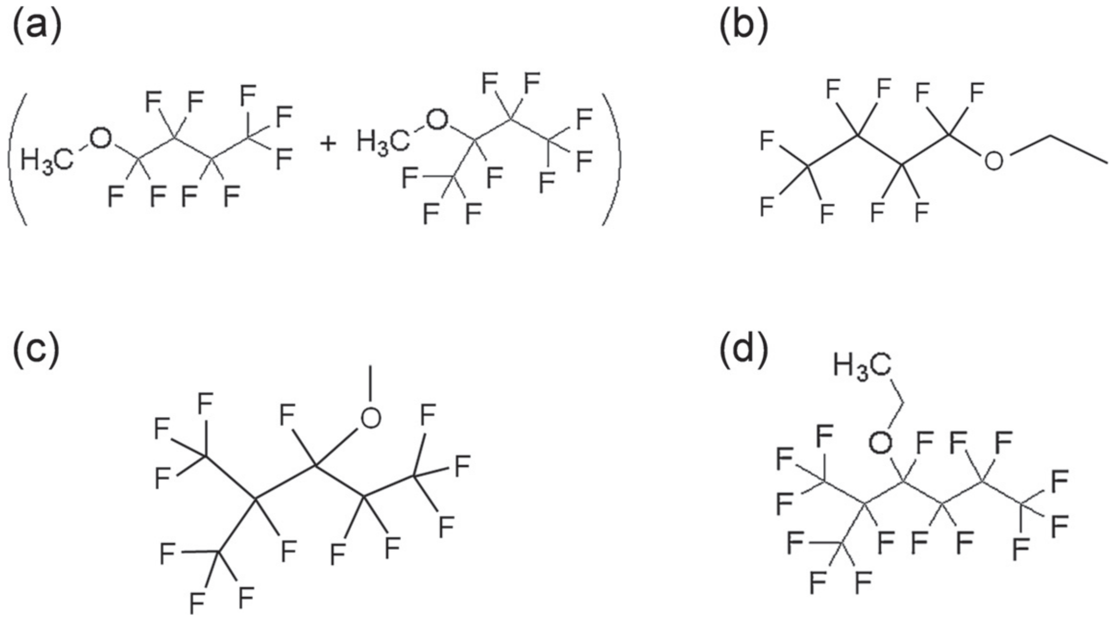
Abstract

Fluorous materials are receiving significant attention as photolithographic materials that can be used in photolithographic fabrication processes, in particular in organic electronic devices, due to their material advantages such as orthogonality to most organic materials, non-flammability and low toxicity. Compared with conventional photolithographic materials, which generally cause chemical damage to organic materials in devices, fluorous materials can be used to construct micro-scale patterned device architecture on organic electronic devices without physical and electrical damage due to their advantageous properties. Fluorous material developments have improved fluorous solvents and imaging materials for successful photolithographic processes to achieve micro-scale resolution in organic device production. Recent studies have demonstrated the application of orthogonal photolithography by using fluorous photolithographic materials in the fields of organic transistors, circuits, memories and light-emitting diodes. This article reviews the development of fluorous photolithographic materials and their application to organic electronic devices. The material properties and device architecture characteristics that require further improvement are also discussed.

1. Introduction

In recent years, numerous studies have focused on organic-based electronics, including organic thin-film transistors (OTFTs) [1–3], photovoltaic cells [4–8], organic light-emitting diode (OLED) displays [9, 10], sensors [11, 12] and memory devices [13–15]. These technologies possess numerous advantages such as low fabrication costs, simple device structures, large-area processing capabilities, mechanical flexibility and limitless material diversity [16–26]. Among these merits, material diversity has particularly enabled the fabrication of organic electronic devices using various manufacturing methods such as spin-coating [27], vacuum-evaporation [28], inkjet printing [29–32], roll-to-roll printing [33] and nano-imprint lithography [34]. However, numerous issues must be overcome before organic electronic devices become core electronic devices in the future, particularly compared with Si-based inorganic devices. Organic-based device shortcomings include unstable degradation [35–37], relatively low performance [38, 39], low device cell density [40, 41] and high operating voltage [42, 43]. Of these, device cell density issues are related to the device fabrication resolution accuracy, which is important because it means that a higher density of devices can be achieved within a fixed device area as the device cell size is reduced. Thus, higher densities increase performance and decrease fabrication costs of the devices. Furthermore, the device cell density also affects the device parameter because cell size reductions generally decrease the operating voltage and power dissipation of electronic devices [44–46]. For the device fabrication of organic electronics with high density and large-area processing, the best way is to apply the photolithographic technique, as in Si-based inorganic electronic products commercially used at present, because of the photolithographic merits of manufacturing electronic devices such as fast production speed, large-area patterning and high resolution [47, 48]. However, photolithographic techniques remain difficult to apply to organic devices because current photolithographic solvents generally cause damage to the organic devices by dissolving not only the part of



Scheme 1. Chemical structures of HFE solvents: (a) HFE 7100, (b) HFE 7200, (c) HFE 7300 and (d) HFE 7500.

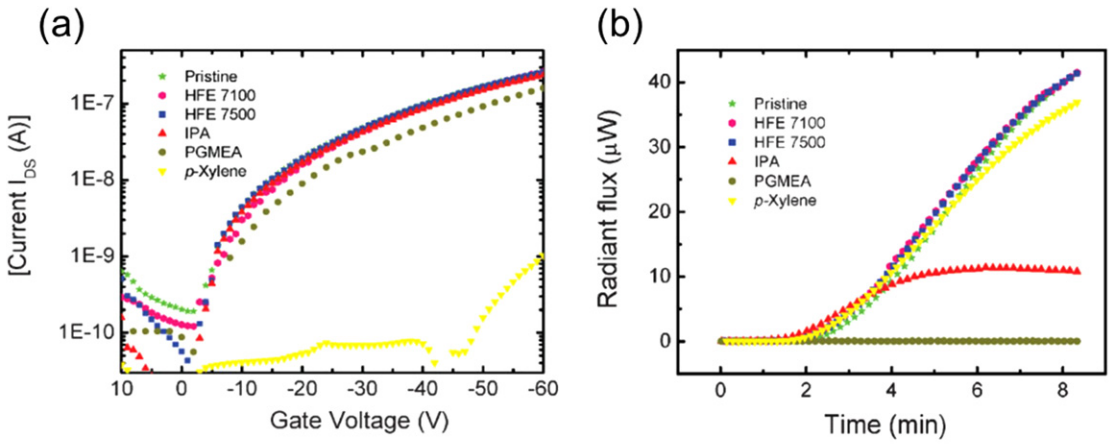
photoresist layer to be removed but also the predeposited organic layer to be preserved [49, 50]. This chemical incompatibility between organic electronic materials and organic photolithographic solvents has resulted in difficulties in developing photolithographic techniques for micro-scale fabrication of organic electronic devices [50–52]. Alternative photolithographic materials and processes have been investigated to overcome these issues so that photolithographic techniques can be directly applied to organic devices without the need for additional protection steps. Fluorous materials represent promising candidates for photolithographic material because their material properties are compatible with photolithographic process properties, such as miscibility and orthogonality [51–53]. Miscibility means the removal of unnecessary layers via dissolution, and the application of this notion can be found in the wet-etching process, where the unnecessary target layer is dissolved and washed away using solvent etchant during wet-etching. By contrast, orthogonality is needed to protect the underlying layers from chemical damage caused by dissolution when additional layers are deposited via a solution coating process. These two properties are essential requirements for photolithography on organic devices because the photolithographic process involves the deposition and removal of a photoresist layer, and because they should not affect the underlying organic layers [53–55]. Unlike inorganic materials, which are intrinsically insoluble to photolithographic solvents, the orthogonality between the organic layer and photolithographic solvents has not been well established. Thus, the fabrication of micro-scale patterned device architecture on organic electronic devices has been hindered using photolithographic processes [55]. However, because most of the fluorous materials are orthogonal to organic materials regardless of their polarity, it is possible to apply the photolithographic process directly to organic devices if it is feasible to construct fluorinated photolithographic materials such as photoresist, photoacid generator and developing solvents. For this purpose, fluorous materials have been explored as photolithographic materials and utilized in various fields of organic electronic devices [50–55].

This review surveys the development of fluorous photolithographic materials and their application to organic electronic devices such as field effect transistors, circuits, memories and light-emitting diodes. Continuous fluorous photographic material development has increased micro-scale organic electronic device production without physical and electrical damage. We also discuss the material properties and device architecture characteristics that require further improvement.

2. Fluorous materials

2.1. Hydrofluoroether

To utilize fluorous materials in the photolithographic fabrication process with their material merits, it is first necessary to find a fluorous photolithographic solvent for the developing process because most of the damage in the photolithographic process occurs in the solvent dipping steps for removing the unnecessary parts of the photoresist layer. Segregated hydrofluoroethers (HFEs) have received significant attention as solvents due to their material advantages, which include nonfluorinated organic material orthogonality, nonflammability, zero ozone-depletion potential and low



(c)

	Polar		Non-polar	Fluorous	
	Protic IPA	Aprotic PGMEA	*p*-Xylene	HFE 7100	HFE 7500
P3HT	95%	90%	0%	100%	100%
$Ru(bpy)_3(PF_6)_2$	45%	0%	85%	100%	100%

Figure 1. (a) Transfer characteristics of the P3HT OTFT devices before and after solvent treatment. (b) Temporal response of $\{[Ru(bpy)_3]^{2+}(PF_6^-)_2\}$ electroluminescent device emissions before and after solvent treatment. (c) The results of solvent treatment on P3HT OTFT and $\{[Ru(bpy)_3]^{2+}(PF_6^-)_2\}$ electroluminescent devices. Reproduced with permission from [50], Copyright 2008 Wiley-VCH.

toxicity level [50–53]. Because of the environmentally friendly properties of HFEs, they were originally used as eco-friendly refrigerants and cleaning solvents [56, 57]. In addition to being utilized as photolithographic solvents, HFEs are also being used in light-emitting fluoropolymer solutions and encapsulation media in OLED displays [58–62]. Scheme 1 illustrates several representative HFE solvents (HFE 7100, 7200, 7300 and 7500) that are commercially available and have been widely applied in academic research fields. Each of these fluorous solvents is orthogonal and immiscible to non-fluorinated organic materials, but their material properties are slightly different to each other, so their ranges of use are also different such as development and lift-off processes. The organic material orthogonality was determined by evaluating the electrical performances of the organic electronic devices before and after dipping using HFE solvents [50]. Figure 1(a) shows the transfer characteristics of OTFT devices with poly(3-hexylthiophene) (P3HT) active layers before and after dipping in a beaker filled with various solvents for 5 min at room temperature. The P3HT, a prototypical conjugated polymer, is a well-known p-type organic semiconductor material that is soluble in common non-polar organic solvents such as chlorobenzene [2, 55, 63]. As expected, a remarkable degradation of transfer characteristics occurred for the devices in the p-xylene solvent (yellow line) unlike other solvents including HFEs because non-polar p-xylene dissolved the P3HT film and caused damage on the devices. The effects of various solvents on electroluminescent devices were observed using ruthenium(II) tris(bipyridine) organic material with hexafluorophosphate counter ions $\{[Ru(bpy)_3]^{2+}(PF_6^-)_2\}$, which represents an ionic metal complex that is soluble in typical polar solvents such as acetonitrile [64]. Figure 1(b) illustrates the emission characteristics of the $\{[Ru(bpy)_3]^{2+}(PF_6^-)_2\}$ devices before and after the solvent treatments as above. The radiant flux degradation was small in the p-xylene solvent, but significantly higher in the isopropyl alcohol (IPA, red line) and propylene glycol methyl ether acetate (PGMEA, khaki line) solvents because those polar solvents dissolved and affected the $\{[Ru(bpy)_3]^{2+}(PF_6^-)_2\}$ electroluminescent devices. Immersion in the HFE solvents did not cause degradation. Figure 1(c) summarizes the effect of various solvents on the organic electronic device performance. The data represent the changes in field effect mobility for the P3HT OTFT devices and quantum efficiency for the $\{[Ru(bpy)_3]^{2+}(PF_6^-)_2\}$ electroluminescent devices. As discussed in figures 1(a) and (b), the non-polar p-xylene solvent mainly affected the P3HT OTFT devices, while the polar IPA and PGMEA solvents affected the $\{[Ru(bpy)_3]^{2+}(PF_6^-)_2\}$ electroluminescent devices. Here also, immersion in HFE solvents did not affect the device performance in both cases, exhibiting orthogonality of fluorous solvents to organic materials with different polarities.

2.2. Photoresist and photoacidgenerator

The standard organic electronic device photolithographic process using fluorous HFE solvents requires compatible fluorous photoresist. The material properties of fluorous photoresist should include organic material immiscibility, which allows the photoresist to be coated onto organic films, and selectivity, which allows the photoresist to be washed with fluorous developing solvents depending on whether the photoresist film was exposed to UV light or not. For this purpose, a number of researches have been conducted for the synthesis and development of a semiperfluoroalkyl resorcinarene photoresist material that can be processed using HFE solvents [49–51, 55]. The motivation has come from a calixarene material, which is a cyclic oligomer that can be easily obtained via the hydroxyalkylation of a phenol and an aldehyde [65]. Because calixarene derivatives possess desirable photoresist properties under conventional photolithographic conditions, including high enough glass transition temperatures to maintain the integrity of developed micro-patterns, resorcinarene, which is one of the calixarene derivatives, was specifically considered as a construction material for the fluorination to be used as fluorinated photoresist material, and is processable with HFE solvents and accessible to the photolithography for the organic electronic devices [51, 66, 67]. Figure 2(a) shows the synthesis and acid-catalyzed deprotection reaction of the resorcinarene photoresist [51]. The synthesis of resorcinarene (6) began with the alkylation of 4-hydroxybenzaldehyde (1) using a semiperfluoroalkyl iodide (2). The recrystallized product (3) then reacted with an equimolar amount of resorcinol (4) under acidic conditions [68]. The resorcinarene (5) was recovered as a fine, pale-yellow powder in high yield. The precipitated powder was filtered and dried at a low pressure to append eight acid-cleavable tert-butoxycarbonyl groups, producing an off-white resorcinarene powder (6), which is normally soluble in HFE 7200 (see scheme 1(b)), but can be converted to be insoluble form using UV light exposure by an acid-catalyzed deprotection reaction where H^+ is liberated from the photoacid generator (figure 2(b)), exhibiting negative tone photographic properties of the semiperfluoroalkyl resorcinarene photoresist material. A photographic evaluation was conducted using these fluorous materials by starting with spin-coating process using a resorcinarene (6) and photoacid generator mixed solution in HFE 7500 (see scheme 1(d)) with a small amount of PGMEA. After the annealing process (at 70 °C), the coated photoresist film was exposed to UV light ($\lambda = 365$ nm), followed by additional annealing (at 70 °C) and development processes in HFE 7200. Figure 2(c) shows scanning electron microscopy (SEM) and optical microscopic (inset) images of the developed resorcinarene (6) on a glass substrate (scale bar represents 10 μm). The intended development structure was precisely obtained without structural discrepancies and the resolution reached approximately 600 nm, demonstrating the applicability of fluorous photolithographic materials for micro-scale device fabrication on non-fluorinated surfaces.

3. Applications for organic electronic devices

3.1. Organic field effect transistors

3.1.1. Photolithography

The OTFT devices are basic and fundamental electronic devices in the field of device area, and they have required a smaller device channel size using the patterning process in order to reduce power dissipation, leakage currents, crosstalk between individual device cells and unnecessary parasitic capacitance to stabilize the device performance [44–46, 69]. To achieve micro-patterned OTFT devices, photolithography is highly appropriate because the technique ensures proper scale resolution and material stability with fluorinated photoresist and solvents. Taylor *et al* [52] reported that sub-micrometer photolithographic patterning of organic electronic materials had been achieved as bottom contact OTFTs with a micro-patterned active layer of pentacene and source-drain electrode of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) materials. In particular, PEDOT:PSS is a mechanically flexible, transparent and highly conductive polymer that is widely used as an electrode material in flexible substrates and a charge injection/extraction layer in photovoltaic cells and OLED displays [5–7, 16, 70–72]. The application of orthogonal photolithography is highly recommended for PEDOT:PSS patterning because PEDOT:PSS films are damaged by not only standard photolithographic solvents but also acid-sensitive photoresists. However, this does not apply to fluorous photolithographic materials, so the sub-micrometer patterning of acidic PEDOT:PSS films was realized for the fabrication of the OTFTs where an organic semiconductor material of pentacene was patterned by the same protocol. Figure 3(a) shows the OTFT fabrication processes using fluorous photoresist and solvents. First of all, a thin PEDOT:PSS film was spin-coated onto a SiO_2/Si wafer and baked at 180 °C, followed by fluorous photoresist spin-coating onto the PEDOT:PSS film. The photoresist film was then patterned by UV exposure using a photomask and developed with an HFE 7200 solvent. The uncovered part of the PEDOT:PSS film was removed via O_2 plasma etching. The remaining photoresist film was then washed away in the IPA/HFE 7100 mixed solvent, resulting in a micro-patterned PEDOT:PSS electrode. To deposit the patterned pentacene film onto the electrode, another layer of fluorous photoresist was spin-coated onto the patterned PEDOT:PSS film, followed by an additional patterning process and pentacene film deposition via thermal evaporation

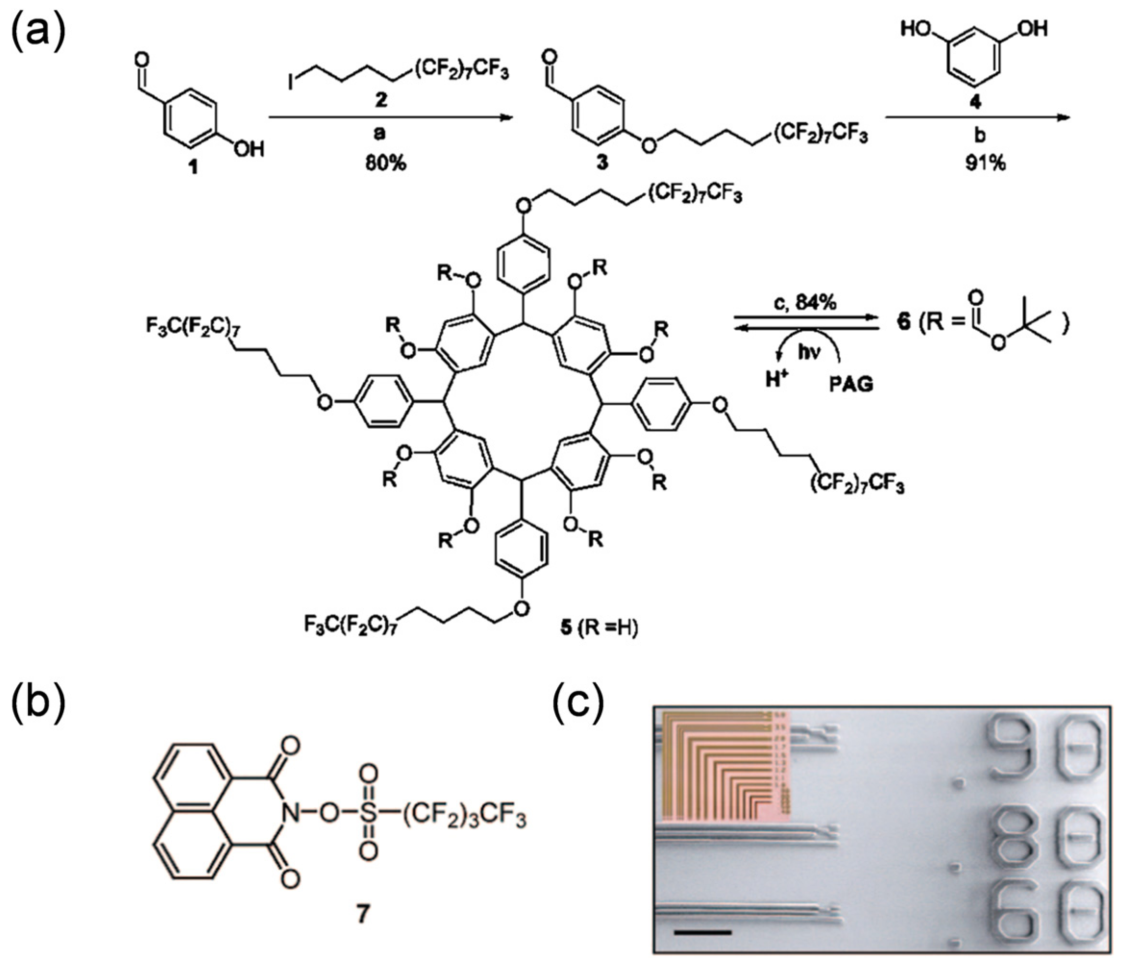


Figure 2. (a) Synthesis and acid-catalyzed deprotection reaction of the resorcinarene photoresist. (b) The chemical structure of a fluorous photoacid generator via photolithographic evaluations. (c) SEM and optical microscopic (inset) images of the developed resorcinarene photoresist on a glass substrate (scale bar represents 10 μm). Reproduced with permission from [51], Copyright 2008 American Chemical Society.

onto the patterned photoresist film, which adhered the patterned pentacene film to the electrode. The photoresist film was lifted off in the IPA/HFE 7100 mixed solvent, leaving a patterned pentacene film on the PEDOT:PSS electrode. Figures 3(b) and (c) illustrate the atomic force microscopy (AFM) images of the 5 μm channel length OTFT devices, and figure 3(d) shows the optical microscopic image of the devices, which indicates that the pentacene fully covered the channel region and PEDOT:PSS electrode contacts without a delamination effect after the fluorous solvent process. Figures 3(e) and (f) illustrate the transfer and output characteristics of the OTFTs with 5 μm channel length, respectively. The obtained electrical performance of field effect mobility (0.03 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$) was higher or comparable to previously reported values, and so this suggested a novel and stable fabrication method for patterning organic material electrode of OTFTs [73].

In addition to the OTFTs on the hard substrate, the application of orthogonal photolithography to the device on a flexible plastic substrate was achieved in the same manner. Figure 4(a) shows the device fabrication process for flexible pentacene OTFTs on a poly(ethylene terephthalate) (PET) substrate using HFE solvents and the above mentioned semiperfluoroalkyl resorcinarene photoresist [53]. HFE 7200 was used for development and an HFE 7200/ethanol mixed solvent was used during the lift-off process. By applying fluorous developing solvents and its compatible fluorous photoresist, the bottom contact OTFTs with channel lengths of up to 3 μm were stably constructed without damaging the underlying polymer layers. The flexible pentacene OTFTs on the PET substrate exhibited stable electrical characteristics of the transfer curves (figure 4(b)) and the field effect mobility values (0.04 ~ 0.1 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$) under bent configurations, with bent radius values of up to 10 mm (figure 4(c)). The results indicated that the fabrication of a micro-scale channel length of OTFTs by orthogonal photolithography can be gently achieved using fluorous photoresist and solvents on a non-fluorinated surface of flexible substrate. In addition, the material stability of the fabricated OTFTs after the photolithographic process was confirmed based on electrical properties in flat and bent configurations.

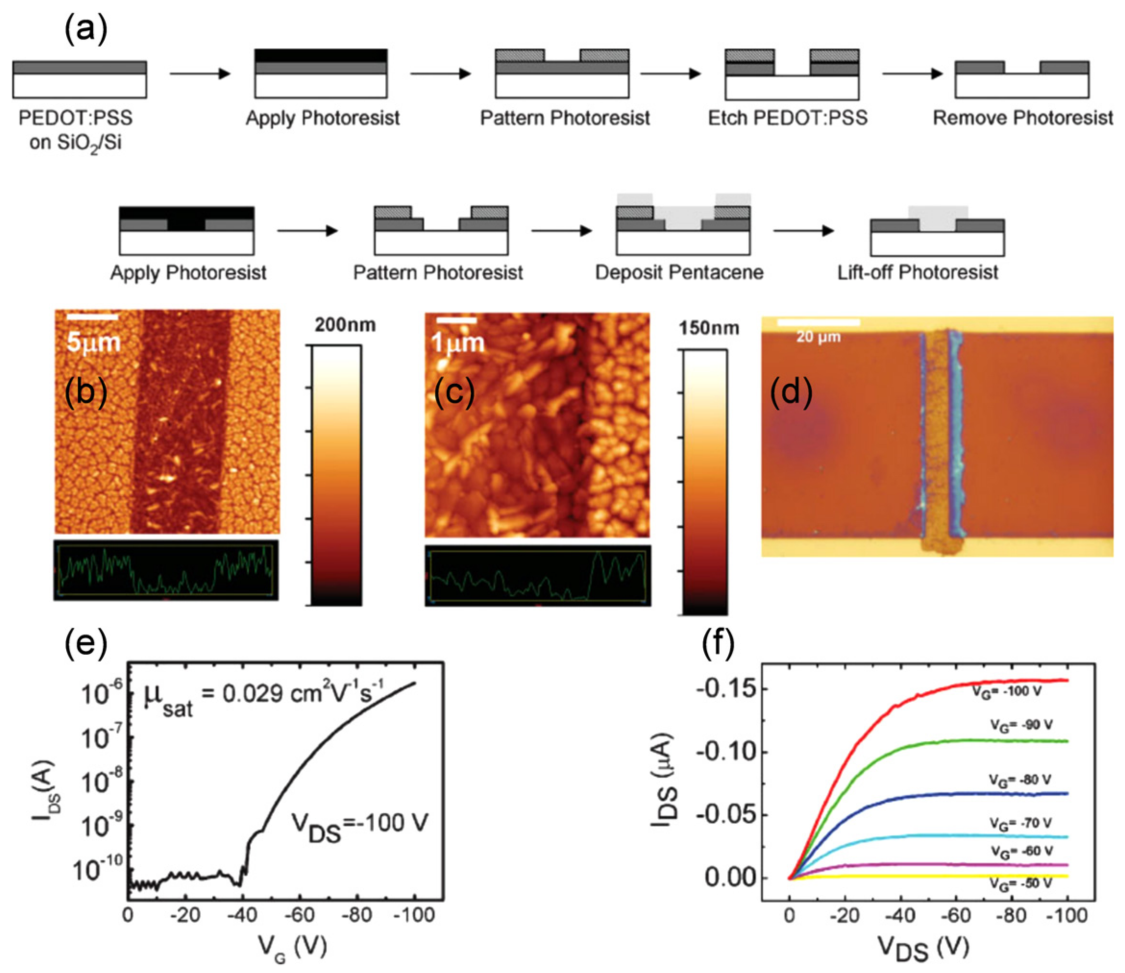


Figure 3. (a) The fabrication process, (b) and (c) AFM images, (d) optical microscopic image, (e) transfer and (f) output characteristics of 5 μm channel length OTFTs composed of a patterned pentacene active layer and PEDOT:PSS electrode using orthogonal photolithography with fluorous photoresists and solvents. Reproduced with permission from [52], Copyright 2009 Wiley-VCH.

3.1.2. Electron-beam lithography

Although photolithographic patterning techniques can be applied to organic electronic devices using fluorous photolithographic materials, the method is subject to resolution limitations of several hundred nanometers. Thus, an alternative patterning method is needed to minimize the channel length of OTFTs less than the length scale of photolithography. In that sense, electron-beam lithography for OTFTs has been investigated to produce nanoscale devices. For patterning of organic layers and depositing top contact nanoscale electrodes directly on the organic layers, a fluoropolymer was used as a protective interlayer e-beam resist deposited on the active organic semiconducting layer, and nanoscale channel resolution was achieved during the electron-beam lithographic process [54]. Figure 5(a) shows the pentacene electronic device fabrication procedure for top nanoscale electrode configuration using fluoropolymer and solvents. To satisfy the requirements of orthogonality to non-fluorous organic materials and eliminability with fluorous developing solvents after patterning, a fluoropolymer CYTOP (Asahi Glass Co.) was selected, which has been used as a low-*k* dielectric and interlayer material for organic electronic devices due to its remarkable protective properties [74–76]. A 100 nm scale lithographic pattern was obtained without degrading the organic semiconducting layer surface when using commercially available ZEP520 (ZEON Co.) e-beam resist to construct a ZEP/CYTOP double layer. The development processes of each ZEP/CYTOP double layer (developing solvents of hexyl acetate for ZEP and FC-40 (3M Co.) for CYTOP) and lift-off of resist (PF-5060, 3M Co.) were cleanly carried out without damaging the underlying nanoscale device structure (figure 5(b)). The electrical properties of the devices of current–voltage characteristics and mobility plots are presented in figures 5(c) and (d) at various nanoscale channel lengths and for multiple device types. Here, the devices with top contact (TC) and bottom contact (BC) configurations were prepared on SiO$_2$ surfaces and modified via hexamethyldisilazane (HMDS) or octadecyltrichlorosilane (OTS) treatments. The results suggest that most of the TC devices exhibited space-charge-limited current (SCLC) behaviors ($I \sim V^2$), and the SCLC mobility

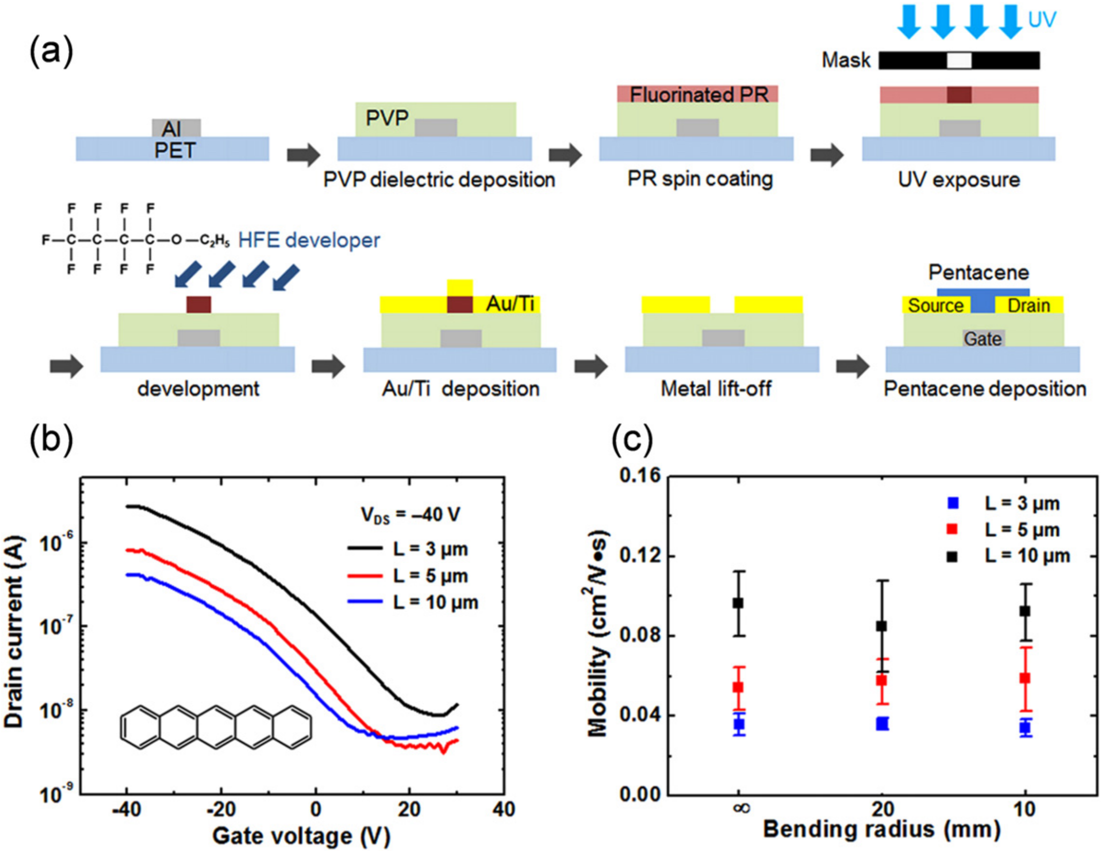


Figure 4. (a) The fabrication process of pentacene OTFTs on a PET substrate using orthogonal photolithography. (b) The transfer curves and (c) mobility versus bent radius plots of the devices. Reproduced with permission from [53], Copyright 2014 American Institute of Physics.

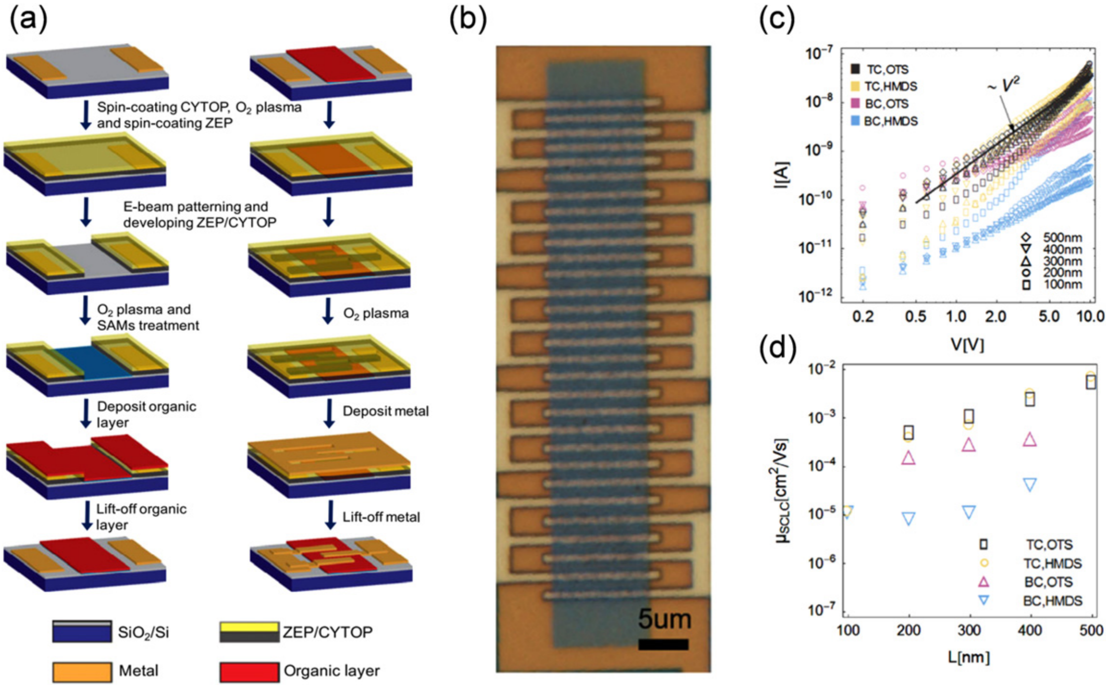


Figure 5. (a) The device fabrication procedure for the nanoscale electrode configuration of pentacene OTFTs with fluoropolymer and solvents. (b) The optical microscopic image of the devices with an array of TC nanoscale patterned Au electrodes on the pentacene active layer. (c) The current–voltage characteristics and (d) mobility versus channel length of the devices. Reproduced with permission from [54], Copyright 2012 Springer-Verlag Berlin Heidelberg.

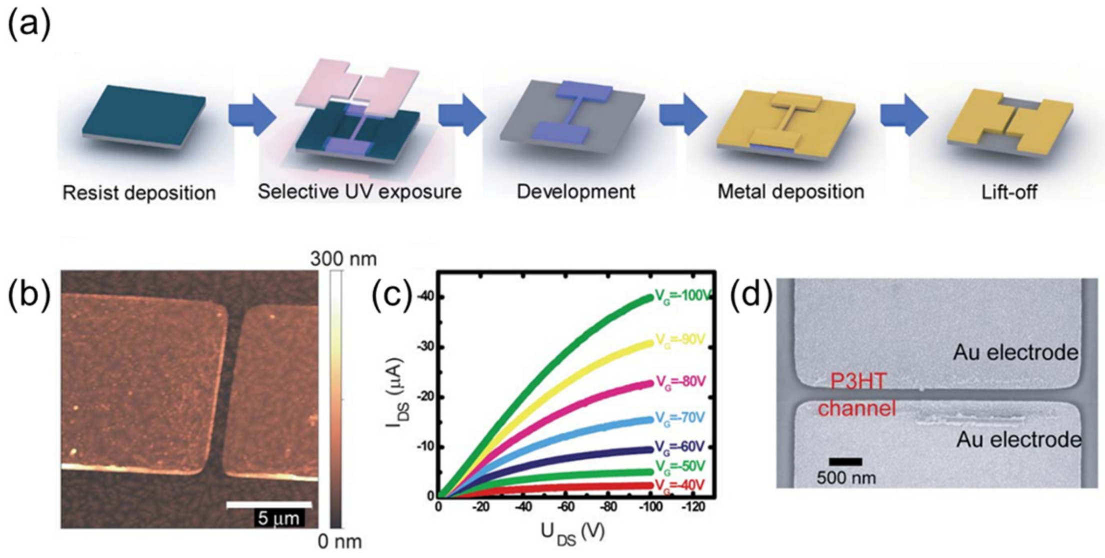


Figure 6. (a) The standard photolithographic process with semiperfluoroalkyl resorcinarene material and HFE solvents for OTFT fabrication. (b) The AFM image and (c) output curves of the TC OTFTs with a 1 μm channel length using a pentacene active layer. (d) The SEM image of the TC P3HT OTFTs with a channel length of 200 nm fabricated by an e-beam lithographic process using semiperfluoroalkyl resorcinarene e-beam resist. Reproduced with permission from [55], Copyright 2011 The Royal Society of Chemistry.

($10^{-4} \sim 10^{-2}$ $\mathrm{cm^2\,V^{-1}\,s^{-1}}$) was found to be in the range of previously reported mobility values of polycrystalline pentacene, except in the case of extremely low channel length regions, where the importance of the contact effect can be dominant [77–79]. Also, the fluoropolymer CYTOP exhibited potential applicability as the constituent of fluorous e-beam resist for organic nanoscale patterning.

The double layer structure combined with fluoropolymer and non-fluorous e-beam resist, of course, is useful to perform e-beam lithography for patterning organic electronic devices, but it is not an efficient method for that because each patterning step, including the development process, should be carried out individually for each resist layer. The simplest way may be to construct a single fluorous e-beam resist layer that has both orthogonality to organic materials and lithographic properties in e-beam patterning. The above mentioned semiperfluoroalkyl resorcinarene material possesses such properties and can be used in photo- and e-beam lithography [55]. By using a standard photolithographic process with semiperfluoroalkyl resorcinarene resist material and HFE solvents (developing solvent of HFE 7200, lift-off mixed solvent of HFE 7100/ethanol) as shown in figure 6(a), the TC OTFTs with 1 μm channel length using pentacene active layer were fabricated (figure 6(b)). The electrical characteristics were stably obtained and presented as output curves in figure 6(c)) with the field effect mobility found to be 0.45 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$. To reduce the channel length scale by up to several hundred nanometers, the semiperfluoroalkyl resorcinarene resist itself was used as e-beam resist material with the same lithographic fluorous solvents as above. This material was then used to fabricate TC P3HT OTFTs with 200 nm channel lengths (figure 6(d)). Thus, it has become possible to fabricate nanoscale channel OTFTs by using an orthogonal e-beam lithographic process with a semiperfluoroalkyl resorcinarene material based single layer e-beam resist and HFE solvents, providing a positive outlook for the progress of nanoscale organic electronic devices.

3.2. Organic light-emitting diodes

Recently, the field of OLED displays has received significant attention as highly efficient large-area light sources due to their polymeric material advantages and a wide range of display applications [9, 35, 80, 81]. Full color OLED displays using vacuum processable light-emitting organic small molecules can be straightforwardly fabricated by a commonly used shadow mask deposition method, but it is challenging to achieve solution-processed light-emitting polymer (LEP) based full color displays because of chemical incompatibility among each active LEP component and other lithographic materials for the patterning process. For the stable fabrication of full color OLED displays with solution type LEP materials dissolved in organic solvents, the chemical compatibility issues need to be resolved in respect of miscibility between not only active LEP layers and lithographic organic solvents but also each LEP layer deposition. To solve this problem, the simplest method may be to give immiscible material properties to the current LEP materials by adding fluorinated molecular end groups into the LEP backbone, resulting in a highly fluorinated LEP (R_F-LEP) that contains semiperfluoroalkyl side chains [58, 80]. The R_F-LEP materials were

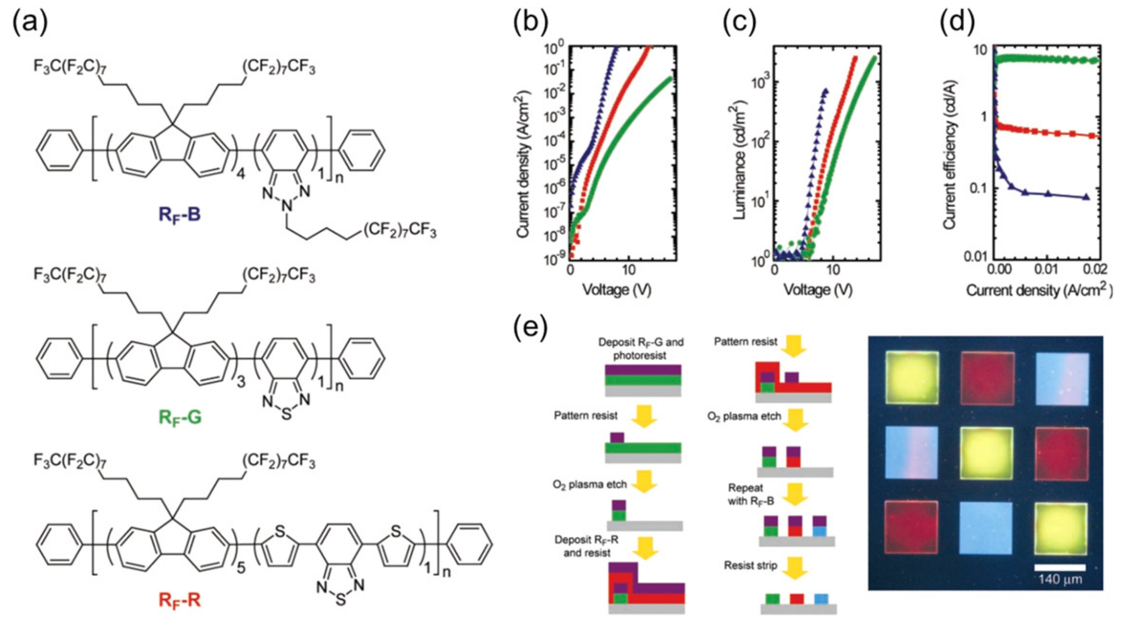


Figure 7. (a) The molecular structure of designed R_F-LEP materials. (b) The current–voltage characteristics, (c) luminance–voltage characteristics and (d) current efficiency of the OLED devices. (e) A schematic diagram of the patterning process (left) and photoluminescence image under 365 nm of UV light of RGB individual 3 × 3 pixel array (right). Reproduced with permission from [80], Copyright 2011 Wiley-VCH.

designed to be soluble in fluorinated solvents but insoluble in most organic solvents, including photoresist and developing solvents, with the help of their orthogonal material properties [82]. Based on these advantages, full color OLED displays using active R_F-LEP materials can be directly fabricated by conventional photolithography without changing the lithographic conditions, cross-linking functionalities, protection layers and other special imaging materials. Figure 7(a) shows the molecular structure of designed R_F-LEP materials that exhibit highly efficient illumination quality for full color solution based OLED devices [80]. All these polymers have in common semiperfluoroalkyl side chains to improve solubility in fluorinated solvents, and their light-emitting properties are decided by a functional group for each R_F-LEP material, where comonomer benzotriazole was contained in the blue-emitting polymer (R_F-B), benzothiadiazole in the green-emitting polymer (R_F-G) and thiophene-benzothiadiazole-thiophene in the red-emitting polymer (R_F-R). The OLED devices were fabricated with a conventional OLED structure of ITO/PEDOT:PSS/R_F-LEP/Ca/Al with an optimized thickness, and their performance is exhibited in figures 7(b)–(d). The OLED devices exhibited turn-on voltages (defined by a luminance of 1 cd m^{-2}) of 4 V, 6 V and 4.5 V for R_F-R, R_F-G and R_F-B, respectively. The corresponding current efficiencies were found to be 0.75 cd A^{-1}, 6.8 cd A^{-1} and 0.15 cd A^{-1} at a current density of 1 mA cm^{-2}. In addition to the basic luminescent properties of OLED devices using single R_F-LEP materials, a full color 3 × 3 RGB pixel array was also fabricated by standard photolithography and a dry etch approach with a photoresist solution in PGMEA and aqueous based developing solvent to prove the immiscibility and applicability of R_F-LEP materials to organic photolithographic processes. Figure 7(e) shows a schematic diagram of the patterning process (left) and photoluminescence image under 365 nm of UV light of RGB individual 3 × 3 pixel array (right). In the fabrication steps, photoresist remained after the dry etching procedure was able to protect the underlying polymer during the spin-coating of the subsequent R_F-LEP layer. These patterned RGB pixels (140 μm × 140 μm) indicate the feasibility of R_F-LEP patterning using standard photolithographic processes that employ organic solvents and an aqueous photoresist solution. The fluorinated functional materials exhibited high chemical stability, orthogonality to organic materials and a wide range of applicability by actualizing the photo-patterned array-type device architecture with standard photolithography, providing great flexibility in device structure design and processing in large-area multi-layer organic device integration.

3.3. Organic circuits

In addition to the fabrication of single devices in the organic electronic device field, the orthogonal photolithographic technique can also be applied to integrated organic device groups such as logic circuits, which consist of several OTFTs. In particular for OTFT based ring oscillator (RO) devices, device miniaturization by scaling down of the channel length is important to achieve efficient high oscillating frequency values, and also micro-scale fabrication of

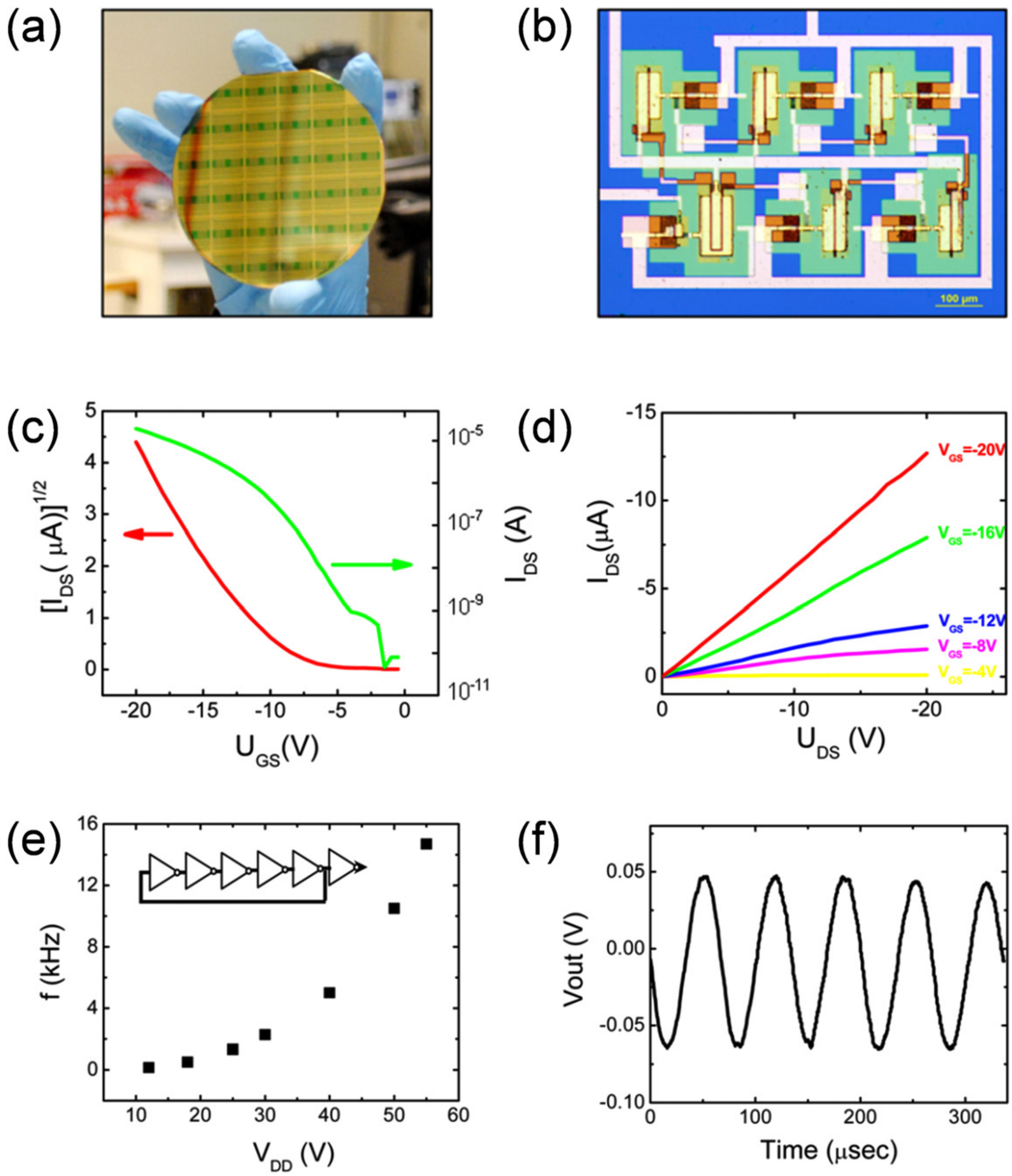


Figure 8. (a) The photographic and (b) optical microscopic images of the five-stage RO devices, which consist of 1 μm channel length TC OTFTs fabricated using orthogonal photolithography. (c) The transfer and (d) output electrical characteristics of the OTFTs. (e) Dependence of oscillation frequency of the RO devices on the applied voltage of V_{DD}. (f) Output characteristics of the RO devices at $V_{\mathrm{DD}} = 55$ V. Reproduced with permission from [83], Copyright 2011 American Institute of Physics.

OTFTs is particularly significant in terms of reducing parasitic capacitance by lowering the overlapped region between the gate and source/drain electrodes [83]. By using the orthogonal photolithographic process with the above mentioned highly fluorinated photoresist and HFE solvents, five-stage RO devices were fabricated with the conventional conditions of five consequent lithographic steps directly onto a 100 mm sized Si wafer [83, 84]. Figures 8(a) and (b) show the photographic and optical microscopic images, respectively, of a typical five-stage RO device consisting of a single channel enhancement mode inverter based on 1 μm channel length TC OTFTs. The semiconducting active material was chosen as poly(2,5-bis(thiophene-2-yl)-(3,7-ditri-dec-anyltetrathienoacene)), which has exhibited high field effect hole mobility and excellent environmental stability, and the micro-patterning of electrode lines onto the semiconducting layers became possible with the help of orthogonality of highly fluorinated photolithographic materials [85]. Figures 8(c)–(f) show the electrical characteristics of the five-stage RO devices. The individual TC OTFTs exhibited p-type behavior with an ON/OFF current ratio of 10^5 and a linear regime of output curves was consistently maintained with increased voltages of the comparable contact

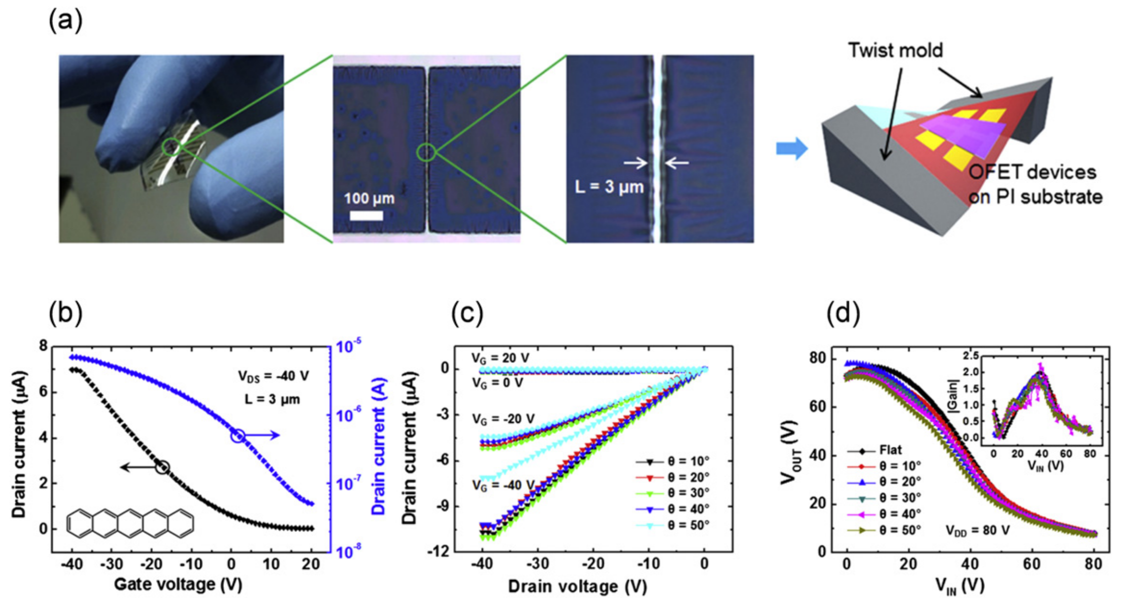


Figure 9. (a) Photographic and optical microscopic images with a schematic illustration of the cleanly micro-patterned twistable pentacene OTFT devices on the polyimide substrate. (b) The transfer curves of OTFT devices of flat configuration with the molecular structure of the pentacene active material. (c) The output curves of the pentacene OTFT devices in the twist configurations. (d) The voltage transfer curves of the complementary inverters in the flat and twist configurations with twist angles ranging from 10° to 50°. The inset figure presents the voltage gains of the devices. Reproduced with permission from [94], Copyright 2014 Elsevier.

resistance effect with that of the channel in geometry of the OTFTs. The RO devices began to oscillate at $V_{DD} \sim 12$ V and reached an oscillation frequency of ~15 kHz at 55 V. This result corresponds to a signal delay of 7 μs per stage, which is comparable to that of OTFT based RO devices fabricated by other methods [86–90].

In addition to micro-patterned organic logic circuit devices on a hard substrate, the fabrication of logic devices on a flexible substrate was also achieved by applying orthogonal photolithographic processes. Because technological development in terms of user-friendly devices will be a major issue in future electronic industries, the flexibility of organic electronic devices has become increasingly important for their application to foldable and wearable devices [91]. To ensure the applicability of flexible organic devices for user-friendly practical usage, flexible devices should work reliably not only in typical bent conditions but also in complex twist configurations that may occur in practical situations [92, 93]. By applying orthogonal photolithography with highly fluorinated photoresist and developing solvents, micro-patterned organic complementary logic inverters consisting of both p- and n-type OTFT devices with channel lengths of 3 μm have been stably fabricated on a flexible and twistable polyimide substrate without damaging the underlying polymer films [94]. Figure 9(a) shows photographic and optical microscopic images with a schematic illustration of cleanly micro-patterned twistable pentacene OTFT devices on a polyimide substrate. As shown in figures 9(b) and (c), the 3 μm channel pentacene OTFT devices exhibited typical p-type transfer characteristics with a field effect mobility of ~0.1 $cm^2 V^{-1}$ s, and the electrical properties of output curves were well maintained in twist configurations with angles ranging from 10° to 50°, represented by different colors for different twist angles. For the complementary logic inverters, an additional deposition process of an n-type $F_{16}CuPc$ layer was performed on the opposite region of the pentacene active film, thereby sharing the output voltage line. Figure 9(d) shows the voltage transfer curves of the complementary inverters in flat and twisted configurations for twist angles ranging from 10° to 50° with the inset figure presenting the voltage gains of the devices. Because of the compatibility between p- and n-type organic semiconductor materials in the electrical and mechanical properties with the stable orthogonal photolithographic micro-patterning process, the micro-scale complementary inverters exhibited reliable logic inverter operations as the voltage transfer characteristics in both flat and twisted configurations. These results ensured that orthogonal photolithographic techniques can be generously applied for micro-patterning of organic integrated functional devices fabricated on a flexible substrate and the electrical performance was well preserved even in complex twist configurations, providing an optimistic prospect of orthogonally photo-patterned micro-scale integrated organic devices for core elements in future electronic devices.

3.4. Organic memory devices

On the basis of the material advantages of organic-based electronics, organic non-volatile memory

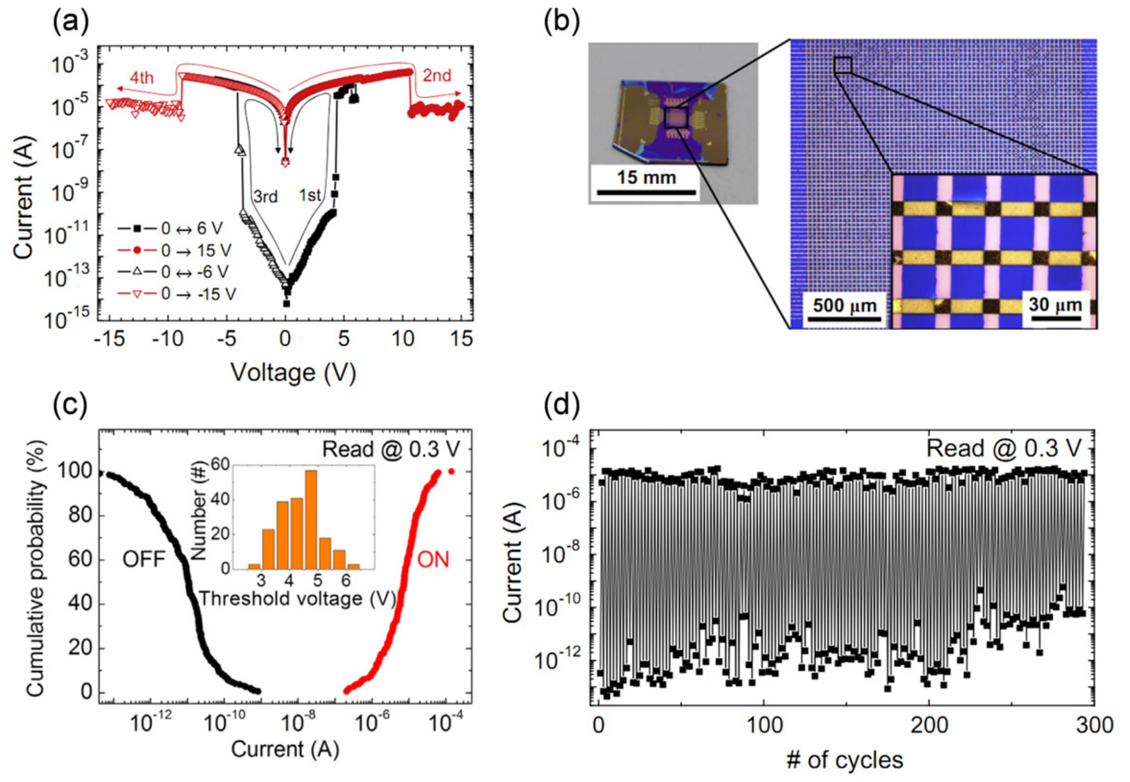


Figure 10. (a) The representative semi-logarithmic current–voltage characteristics of the micro-patterned organic PI:PCBM memory devices. (b) Optical images of the fabricated 4 Kbit memory devices. (c) The cumulative probability of each resistive state current and threshold voltage distribution of 195 selected memory device cells. (d) DC sweep endurance tests of the devices. Reproduced with permission from [97], Copyright 2014 Elsevier.

devices have been considered as an excellent promising candidate for future information storage media because of their potential application to flexible memory devices [13, 22, 41]. Organic memory devices have been mostly fabricated in a simple cross-bar array structure, which can actualize high integration of memory device cells [19, 95, 96]. However, the cell size of the cross-bar structured organic resistive memory devices has generally been limited to be several hundreds of micrometers with limitative fabrication methods such as shadow mask evaporations because of the difficulty of applying the standard photolithographic technique to the organic functional layers of memory devices, which has resulted in a challenging problem for achieving high integration memory arrays [97, 98]. However, with the help of highly fluorinated photoresist and solvents, the application of conventional photolithography for organic electronic devices has become possible with micro-patterned device architecture, and these material concepts can be made available to highly integrated organic non-volatile array-type memory devices. Song *et al* [97] achieved a 4 Kbit (64 × 64) integration of an organic resistive memory array with a micro-scale cell size of 10 μm × 10 μm by applying orthogonal photolithography with semiperfluoroalkyl resorcinarene photoresist material and HFE developing solvents [49–51, 55]. Figure 10(a) shows the representative semi-logarithmic current–voltage characteristics of the micro-patterned organic memory devices using polyimide and 6,6-phenyl-C_{61} butyric acid methyl ester (PI:PCBM) active resistive memory materials. These materials exhibit typical unipolar resistive switching properties, electrical reliability and mechanical durability [22, 41, 93]. As shown in figure 10(b), the 4 K cells of micro-patterned memory devices were highly integrated into a small region of hard substrate (1.9 mm × 1.9 mm) using orthogonal photolithographic processes. A statistical analysis of the devices was conducted in select regions of the devices due to the large number of cells. Figure 10(c) shows the cumulative probability of each resistive state current and threshold voltage distribution of 195 memory cells. The statistical results illustrate a well-defined margin between the ON and OFF current level states (magnitude of 10^2) and a normal threshold voltage distribution with narrow deviation regions. Figure 10(d) shows the DC sweep endurance tests, which were used to investigate the switching performance of the devices. Each state current were well maintained throughout the 300 switching cycles, displaying a high ON/OFF ratio of over 10^4 without significant fluctuations.

To improve the density of the organic memory devices for the purpose of highly integrated device architecture, the horizontal miniaturization of cell size was carried out by applying orthogonal photolithography to the organic memory devices. A high

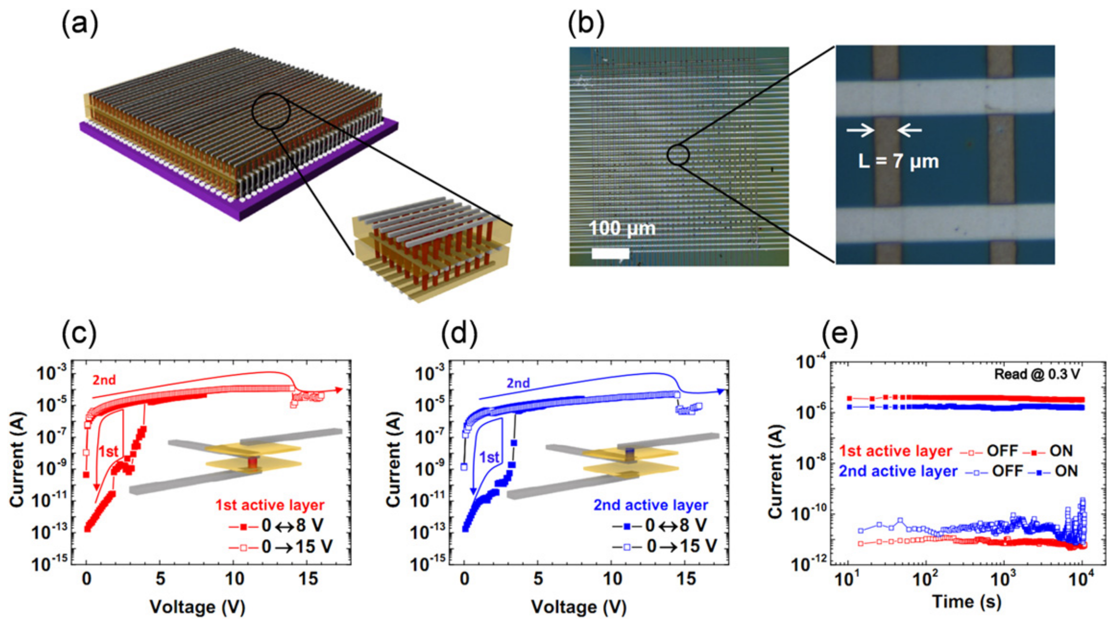


Figure 11. (a) Schematic representation and (b) optical microscopic image of the vertically stacked micro-scale organic memory devices. The current–voltage curves of the memory devices for each (c) first and (d) second layer. (e) The retention time properties of the memory devices. Reproduced with permission from [98], Copyright 2015 Elsevier.

resolution of array structure of organic memory devices was generously achieved with the help of highly fluorinated photolithographic materials. In addition to these efforts, a vertically stacked structure of active memory layers was also investigated because of their usefulness in achieving three-dimensional highly integrated array structures of organic memory devices. The micro-patterned top and bottom electrodes of each resistive memory layer in the array structure were fabricated by using orthogonal photolithography with fluorous photolithographic materials, and the PI:PCBM organic material was used as the active memory layer because of its chemical and thermal robustness to endure dissolving damage from each spin-coating process of the stacked layers [41, 98]. By using the semiperfluoroalkyl resorcinarene photoresist and HFE developing solvents, micro-scale cross-bar organic memory devices were fabricated on a hard substrate with vertically stacked double layer structured PI:PCBM memory cells where the cell size was further reduced by up to 7 μm × 7 μm by optimizing detailed fabrication techniques. Figures 11(a) and (b) show a schematic representation and optical microscopic image of the vertically stacked micro-scale organic memory devices. As shown in figures 11(c)–(e), the electrical characteristics of the memory devices exhibited reliable and stable memory switching performance in both the first and second resistive PI:PCBM memory layers based on the current–voltage curves and retention times. These results provide a positive outlook on three-dimensional highly integrated organic memory devices by achieving both micro-scale electrode patterning and vertical active layer stacking with the help of orthogonal photolithography.

4. Outlook and perspective

In summary, we have reviewed the development of fluorous photolithographic materials and their application to organic electronic devices such as field effect transistors, circuits, memories and light-emitting diodes. Due to the excellently selective material properties of fluorous photoresist and solvents for miscibility and orthogonality, it has become possible to stably actualize the fabrication of a micro-patterned structure of organic electronic devices by applying orthogonal photolithography or e-beam lithography without damaging the underlying polymer layers. In addition to the chemical development of photolithographic materials such as semiperfluoroalkyl resorcinarene photoresist and HFE solvents, highly fluorinated functional materials have also been improved so that they are processable in conventional photolithography such as R_F-LEP materials used in photo-patterned full color displays and designed to be soluble in fluorinated solvents but insoluble in most of organic solvents due to the addition of fluorinated molecular end groups to the LEP backbone. The application of orthogonal photolithography in various organic electronic devices has resulted in diverse advantages for each application as well as micro-scale device miniaturization. For photo-patterned OTFTs and circuits, the device properties have been enhanced and stabilized in terms of decreased operating voltage, power dissipation, leakage currents, crosstalk between the device cells and parasitic capacitance. Moreover, the photolithographic fabrication of full color OLED displays based on solution type R_F-LEP active materials has been enabled by resolving the chemical compatibility issues between not only active LEP layers and lithographic organic solvents but also each LEP layer deposition. The highly integrated cross-bar structure of organic resistive memory devices was fabricated by achieving both horizontal high resolution electrode micro-patterning and vertical active layer stacking. Although there have been a number of advancements of the material properties and applications of fluorinated photolithographic materials, there are also remaining tasks to further improve the application of orthogonal photolithography to more organic electronic devices. Firstly, the solvents for semiperfluoroalkyl resorcinarene photoresist need to be completely fluorinated because current photoresist solvents contain some portion of PGMEA organic solvent. To constitute a fully fluorous photoresist solvent, the material properties of semiperfluoroalkyl resorcinarene should be further optimized. The development of a positive tone single layer e-beam resist is also needed because the current negative tone e-beam resist based on semiperfluoroalkyl resorcinarene material demands too much fabrication time and cost during the e-beam lithographic exposure process. From the point of view of application to organic devices, more research on micro-scale flexible organic devices should be carried out, especially on OLED displays and memory devices. We believe that future studies will contain increasingly improved properties of fluorous lithographic materials and extensive applications for flexible organic electronics including foldable and wearable devices by using orthogonal photolithography.

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