

Vacuum-free photolithographic patterning of conducting polymer film

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Published in *Micro & Nano Letters*; Received on 20th July 2016; Revised on 18th August 2016; Accepted on 24th August 2016

Understanding the relationship between a certain organic material and the corresponding orthogonal solvent improves the realistic possibility of photolithographic patterning during the fabrication of organic devices. However, an all-solution-based patterning process has not been established because the dry-etching process used for micropatterning must be performed in a vacuum chamber, which is not appropriate for a printing process and results in a low throughput of products at the industrial level. Here, we demonstrate a vacuum-free patterning method using conventional photolithography. It is a main breakthrough in that it washes away the etchant by blowing with air in a very short time. This short-term air-blowing process dramatically reduces the undercut below the photoresist. As a result, mask patterns of nearly the same size could be transferred onto an organic object. Compared with ordinary wet etching process, the undercut is reduced to the 1-micrometer scale, allowing the realisation of a fine pattern size. The process developed here will enhance the throughput of manufacturing systems using an all-solution-based process.

1. Introduction: Over the past few decades, organic-based electrical and optical devices have been studied extensively for emerging applications due to the pristine, extraordinary properties of organic materials, such as their visible-range transparency, mechanical flexibility and elasticity [1–6]. These material properties enable solution-based processes to be adapted for large-area printing-process manufacturing, which offers a pathway to a cost-effective optoelectronic system in the form of radio frequency identification tags [7, 8]. If these inexpensive and disposable applications are realised, a great ripple effect will arise in all types of industries and in everyday life. For such an innovative breakthrough, organic optoelectronic systems must be capable of performance levels which are compatible with Si-based integrated circuits at the very least. Among several processes which can be used to fabricate these systems, basically, a micropatterning process is crucial for abovementioned high-performance operations. First, fine patterning technology allows the realisation of a smaller electronic device. Therefore, large-scale electronic components can be integrated in a limited space, resulting in greatly enhanced functionality. Second, the patterning process enables individual devices to be fabricated at identical size: thus, all components operate almost identically for reliable and uniform systems. With the shrinkage of the channel length and the minimisation of the parasitic capacitance, the transistor can be switched in a higher frequency range. For field-effect transistors, the leakage current can be reduced significantly [9]. On a large-area organic light-emitting diode display, the image quality of moving pictures depends on the pixel uniformity. Thus, reliable micropatterning technologies must be used in organic electronic/optic systems for more advanced performance. Thus far, many soft lithographic methodologies have been demonstrated [10–15], especially over the past few; however, there is no certain technology capable of replacing conventional photolithography due to reliability, mass-productivity and cost-effectiveness [16]. Thus, at this moment in time, the best way is to adapt conventional lithography for the fabrication of organic systems.

In general, the procedures associated with photolithography include photoresist deposition, UV exposure, developing, etching, and photoresist removal. During the etching step, there are two types of etching methods, wet etching and dry etching [17].

When the wet-etching method is used to etch away specific organic layers, the solvent used for the etching must not dissolve or deteriorate other organic layers. This can be prevented with an orthogonal solvent. Another severe problem which has been reported is that the length of the under-cut region is out of proportion to the thickness of the etched organic film [9], which limits the integrated density. In contrast, the dry-etching method suppresses this severe under-cut length, and the validity of this method is maximised by adapting a reactive ion etching technique (Fig. 1). However, with an organic multi-layered structure, there is no distinct material to serve as an etch-stop. Therefore, the organic substrate can be seriously affected by radicals. Moreover, dry etching should be performed in a high vacuum chamber to generate plasma, which is not appropriate for large-area flexible substrate.

In summary, a new and/or improved etching method which combines the advantages of the two etching methods is crucial for the fabrication of organic electronic devices. In this Letter, a photolithographic patterning method which minimises the under-cut length will be demonstrated. It utilises the conducting polymer, poly (3-hexyl thiophene) (P3HT). P3HT was chosen because it is a widely used conducting polymer for such devices as field-effect transistors, and solar cells [18–22]. Thus, a micropatterning method for P3HT can make a strong impact in various electronic and optics fields. The method demonstrated here does not require a vacuum process as a dry-etching method, instead utilising a simple modification of the conventional wet-etching method. However, severe under-cut was prevented. This improved result will attribute to high throughput in the industry level.

2. Experimental details: A SiO₂/Si wafer was prepared by cleaning with a mixture of hydrogen peroxide (H₂O₂) and sulphuric acid (H₂SO₄), and 50-nm-thick aluminium was thermally evaporated in a chamber at a pressure of 1×10^{-6} Torr. Regioregular poly (3-hexylthiophene), P3HT, was purchased from Solaris Chem Inc. To remove metal catalysts from the pristine P3HT, Soxhlet extraction was performed following a previous published method [23]. In this method, 0.01 g of P3HT was dissolved in 1 ml of mono-chlorobenzene by stirring for 24 h, after which the solution was filtered. The thickness of the P3HT was 50 nm when the spin coating speed and time conditions were 1500 rpm and 10 s, respectively. For solubility tests, the P3HT films were dipped into

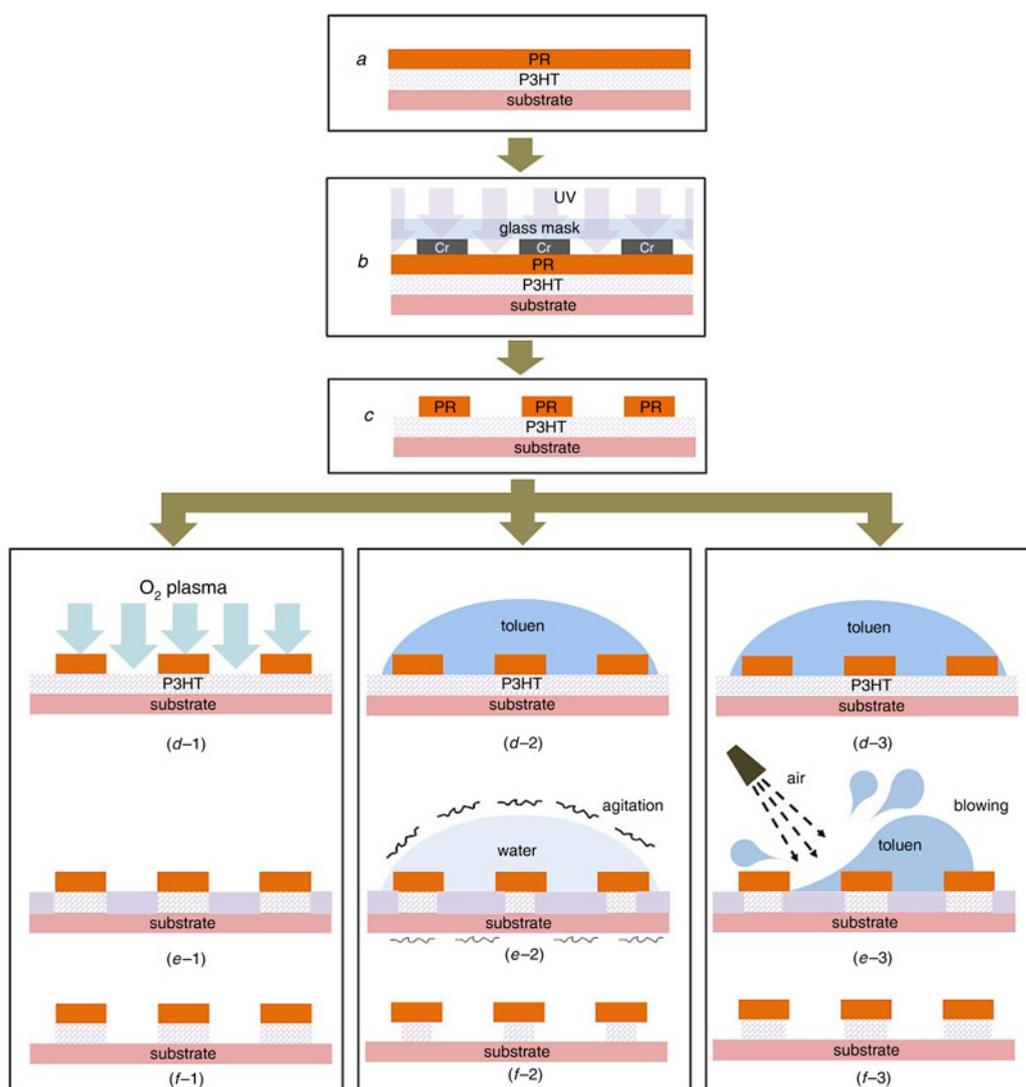


Fig. 1 Schematic of the patterning method

a PR deposition

b UV exposure

c PR development,

(d-1) dry-etching with oxygen plasma, (e-1) P3HT etching by dry-etching, (f-1) P3HT patterning by dry-etching, (d-2) toluene dropping, (e-2) P3HT washing with agitation in water, (f-2) P3HT patterning by conventional wet-etching, (d-3) toluene dropping, (e-3) P3HT removal with air blowing, and (f-3) P3HT patterning by vacuum-free wet-etching

several solvents used as part of the photolithographic patterning process and inspected with optical microscopy. The solvents used for the solubility tests were acetone, n-methyl pyrrolidone (NMP), tetra-methyl ammonium hydroxide (TMAH), and propylene glycol mono-methyl ether acetate (PGMEA). Acetone is widely used for photoresist removal, NMP is an ingredient in a commercialised photoresist stripper (AZ 400T, AZ Materials), TMAH is included in a commercialised developer (AZ340, AZ Materials). PGMEA is the main solvent of commercialised photoresists (positive: AZ 1512, AZ Materials). To etch away the P3HT film which is revealed after the developing step, mono-chlorobenzene and toluene were used in different conditions, such as different dipping times, and temperatures. During all patterning processes, the following conditions are maintained in common. The photoresist (PR), AZ 1512, was spin-coated and soft-baked at 95°C for 90 s. The thickness of PR after soft-baking was about 1.6 µm. After then, g-line UV (wavelength = 436 nm) was exposed for 20 s. With the pristine developer (AZ 300 MIF, AZ Materials), the developing was performed for 40 s. After P3HT etching, the remained PR was removed with the pristine stripper (AZ 400 T, AZ Materials) for 60 s.

3. Results and discussion: Our patterning studies focus on photolithographic patterning using a positive photoresist. Fig. 2 shows many of the experimental results of patterning. To compare the under-cut lengths, photoresist residues after a wet etching process was left for optical microscopy images. Fig. 2a is a sample for reference, which was prepared by dry-etching process as described in Fig. 1(d-1). Fig. 2b shows the result of the wet-etching process with chlorobenzene as an etchant for 10 s followed by washing with deionised water. Semi-transparent rectangular patterns remain on the photoresist, showing that nearly all of the patterns are detached from the substrate because the under-layered film of P3HT was nearly completely dissolved. This dissolution was expected to be avoided by reducing the wet-etching time. Fig. 2c shows the result of the wet-etching process with chlorobenzene as an etchant for 1 s followed by washing with deionised water. From this test, a wet-etching time of only 1 s is enough to etch away the P3HT as the P3HT is only a few tens of nanometers thick. However, the magnified optical image in Fig. 2d shows a dim edge around the patterned rectangles. From comparison with the colour in Fig. 2a, this dim

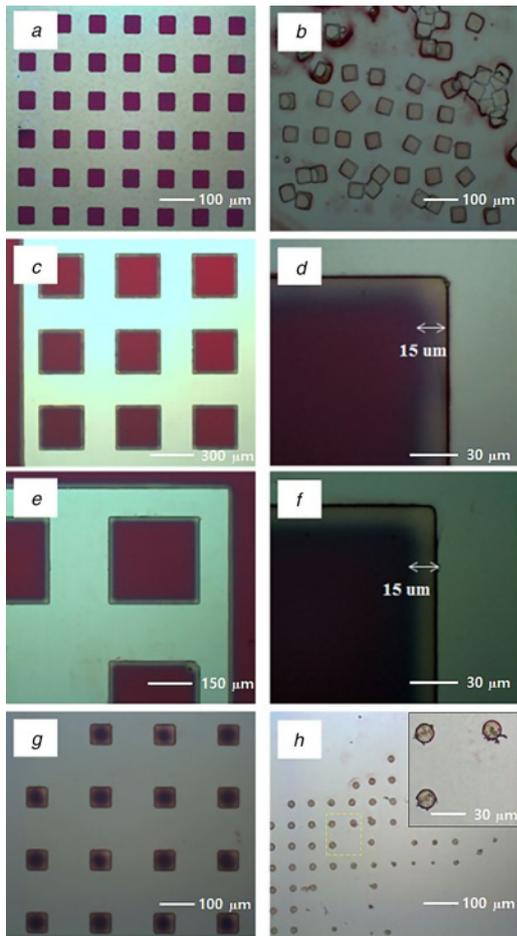


Fig. 2 Optical microscopy images of step (b-2) in Fig. 1
a Reference sample after fabrication with the dry-etching method, sample results after fabrication with wet-etching methods
b With mono-chlorobenzene for 10 s
c With mono-chlorobenzene for 1 s
d A magnified image of (c)
e With toluene for 1 s
f A magnified image of (e)
g With 0°C toluene for 1 s
h With 0°C toluene for 1 s. Pattern sizes are rectangles of 50 × 50 μm for (a), (b), and (g), and 300 × 300 μm for (c), (d), (e), and (f). The circles have diameters of 15 μm in (h). The inset of (h) is a magnified version of the yellow dotted box shown in (h)

area was thought to be an under-cut, the length of which is about 15 μm or more. This under-cut scale represents a severe bottleneck in that no P3HT patterns smaller than 30 μm can be achieved using the wet-etching process in photolithography. To reduce the under-cut length, toluene, less soluble for P3HT than mono-chlorobenzene [24], was also used for wet-etching, but the same scale of under-cut was observed, as shown in Figs. 2*e* and *f*. Dissolution is a thermodynamic phenomenon dependent on the temperature; therefore, the temperature of the toluene was lowered to 0°C by keeping the toluene bottle in ice water for 1 h. However, the cooled toluene did not reduce the length of the under-cut, as shown in Figs. 2*g* and *h*. Though many circles in Fig. 2*h* are positioned at their original position, the remained P3HT layers underneath all patterned photoresist are thought to be dissolved partially, because their magnified images in the inset of Fig. 2*h* show rainbow colours which may be generated by interference of light.

First of all, the adhesion strength was focused to analyse the dissolution of the edge of P3HT. To ensure adhesion, standard test methods for measuring adhesion by tape test was performed [25]. Scotch tape purchased by 3M[®] was stuck on the photoresist-

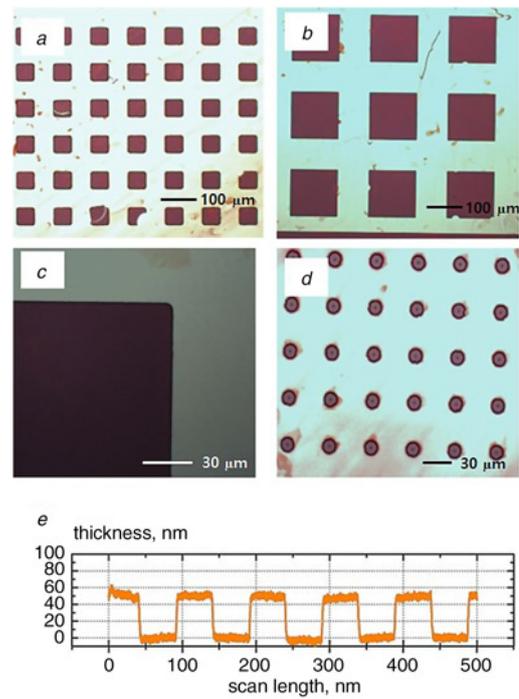


Fig. 3 Optical microscopy images of step (c) in Fig. 4. Rectangles array of *a* 50 × 50 μm
b 300 × 300 μm are shown
c Magnified images of (b)
d Circles with a diameter of 15 μm
e α-step measurement result for the rectangles array of 50 × 50 μm and the 50 nm-thick P3HT

patterned P3HT/wafer sample, and the tape was pressed by hand tightly. Finally, the tape was slowly pulled out of the sample. In spite of repetitive tape testing, we could not observe any P3HT residue or photoresist on scotch tape. Therefore, it is concluded that both of adhesions between P3HT and wafer and between photoresist and P3HT are enough strong.

When the etchant was dropped on samples, optical microscopic observation informed that there was no serious under-cut after dropping the etchant in a few seconds; the dominant factor to generate such a large under-cut was the washing process with deionised water. We assumed that the etchant residue may dissolve more P3HT when the sample was washed with water by stirring under a water flow because agitation generally promotes the dissolution process. In other words, the rapid removal of the etchant may lead to the formation of a fine pattern using a positive photoresist. To fulfil the subduction speed of the etchant and sample fixation specifications, the etching method was simply modified, as described in Fig. 1(e-3). The only difference between the previous wet-etching process and the modified process is the manner in which the etchant was removed after the etching of the organic layer, P3HT. To remove the etchant residue after the etching process, dry air was blown at a high rate from an air gun.

Fig. 3 shows optical microscopy images of the rapid-etchant-removal method, in which the rectangles show no dim edges, unlike the conventional wet-etching method. From the magnified images shown in Fig. 3*c*, an under-cut of 15 μm is not found at all. Fig. 3*e* shows the α-step measurement result of the 50 μm × 50 μm rectangle array after the photoresist removal step, showing that nearly precise patterns were formed, as designed. Therefore, our assumption and the use of rapidly blown air are shown to be appropriate for the formation of fine patterns of P3HT.

Fig. 4 describes the line patterns in a mask and real patterns in a sample. In our experiment, both of the line (I_{ML}) and the space (I_{MS}) in mask are 2 μm. After vacuum-free wet-etching process, the line

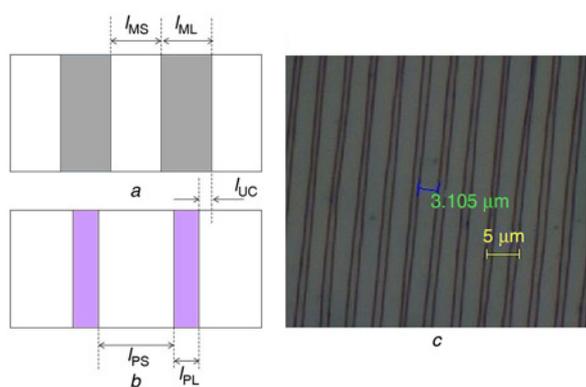


Fig. 4 Fabricated minimum pattern size. Schematic of *a* Line patterns with width (l_{ML}) and space (l_{MS}) in mask *b* P3HT lines with width (l_{ML}) and space (l_{MS}) in sample *c* Optical microscopy image of P3HT lines patterned by vacuum-free wet-etching process. For l_{ML} of 2 μm and space l_{MS} of 2 μm , l_{ML} of 1 μm and l_{MS} of 3 μm were achieved, therefore, the length of undercut (l_{UC}) was 0.5 μm

(l_{PL}) and the space (l_{PS}) were about 1 and 3 μm , respectively. Therefore, the undercut (l_{UC}) was about 0.5 μm . A little non-uniformity in the patterns are shown, which may be caused by the non-uniformity of the direction and intensity of air blowing. Moreover, the dissolving speed may depend on the position. At this moment in time, the solubility of toluene is thought to be large. For further uniform patterning, the solubility of etchant needs to be engineered. Though this under-cut scale is also quite large compared with the P3HT thickness so an optimised process for much shorter under-cut length is required, it can be sure that the fast removal of the etchant is an important factor for micropatterning of organic film.

Thus, it can be sure that the vacuum-free photolithography is distinctly valid to fabricate micropatterning of P3HT, in principle. Only main factor to govern reliability and uniformity of our demonstration is a blowing system. To demonstrate the vacuum-free wet-etching process, we used air blow gun so the quantity of emissive air and the direction of air were operated by hand. If the air blow system is exquisitely automatised and controlled, uniform and reliable patterns will be fabricated in large-area substrate.

4. Conclusion: This work demonstrates a modified patterning method for the conducting polymer, P3HT using conventional photolithography. The current patterning method which uses a wet-etching process causes a severe under-cut length compared with the thickness of the organic film, necessitating a dry-etching process for micropatterning. We introduce a wet-etching-based patterning method for micropatterning, in which under-cut scale could be reduced to about 0.5 μm experimentally. It is important to note that a vacuum chamber and related equipment are not at all needed for patterning when using this method. Because inexpensive and disposable organic optoelectronic devices fabricated by a large-area printing process strongly require a high throughput, the vacuum-free patterning method can capture the two advantages of productivity and high performance. Moreover, there are no radicals which can damage the under-layered organic materials, resulting in reliable operation. Therefore, the etchant removal technique with rapidly sprayed inert gas such as nitrogen is considerably cost-effective and compatible with the conventional printing manufacturing system after simply by grafting a gas spray system.

5. Acknowledgments: This work was supported by a Preparatory Project (grant no. N10110074) at the Korea Advanced Institute of Science and Technology (KAIST).

6 References

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