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Cite as: AIP Advances 8, 105116 (2018); https://doi.org/10.1063/1.5052221
Submitted: 15 August 2018. Accepted: 03 October 2018. Published Online: 15 October 2018

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Micropatterning of organic electronic materials using a facile aqueous photolithographic process

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(Received 15 August 2018; accepted 3 October 2018; published online 15 October 2018)

Patterning organic semiconductors via traditional solution-based microfabrication techniques is precluded by undesired interactions between processing solvents and the organic material. Herein we show how to avoid these problems easily and introduce a simple lift-off method to pattern organic semiconductors. Positive tone resist is deposited on the substrate, followed by conventional exposure and development. After deposition of the organic semiconductor layer, the remaining photoresist is subjected to a flood exposure, rendering it developable. Lift-off is then performed using the same aqueous developer as before. We find that the aqueous developers do not compromise the integrity of the organic layer or alter its electronic performance. We utilize this technique to pattern four different organic electronic materials: epindolidione (EPI), a luminescent semiconductor, p-n photovoltaic bilayers of metal-free phthalocyanine and N,N’-dimethyltetracarboxylic diimide, and finally the archetypical conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT). The result of our efforts is a facile method making use of well-established techniques that can be added to the toolbox of research and industrial scientists developing organic electronics technology. © 2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

I. INTRODUCTION

Photolithography is a highly-developed field in industrial microfabrication, and a key processing technology enabling electronics production on a massive scale. Organic semiconductor-based devices, however, are not straightforward to process using these photolithographic methods since the organic solvents used for photoresist deposition and stripping/lift-off lead to damage and often delamination of the organic electronic layer. This restriction has led to the adaptation of alternative patterning techniques, including printing,1 shadow masking,2,3 microcontact printing,4 or various methods of soft lithography and self-assembly.5–7 Despite these alternatives, demand exists to adapt photolithography to organic electronics. For photolithographical patterning of organic semiconductors the majority of work has focused on utilizing the combination of fluorinated resists and fluorinated solvents which enable orthogonal processing with traditional organic semiconductors,8–11 or using insoluble protective buffer layers,12 frozen CO2 as a resist,13 or photoinduced destructive patterning of the organic layer.14 The fluorinated resist process is commercially available for organic electronics technology. All these organic electronics photolithography procedures introduce additional costs and their own set of limitations, such as the difficulties in handling and waste management of fluorinated solvents and resists, the need for performing the lithography steps under cryogenic temperatures or the necessity of additional steps involving plasma reactive ion etching. Here, we...
describe a more straightforward method relying on conventional microfabrication materials and processes. This method utilizes the aqueous developer as the only wet-process which interacts with the organic electronic layer, and the novolac/DNQ resist system. Novolac resin with diazonaphthoquinone, DNQ, as a positive-tone photoresist, is the lowest-cost and most common type of photoresist available.\(^{15}\)

Lift-off processes with novolac-based positive-tone photoresists are a classic photolithographic method for patterning metals and inorganic dielectric layers.\(^{15}\) The method cannot be used for most organic semiconductors since the lift-off solvents (like acetone or NMP, 1-methyl-2-pyrrolidone) cause chemical damage or delamination. To overcome this problem, we perform the process flow schematized in Fig. 1a. Following conventional exposure and development of the photoresist, the organic electronic material is deposited (from vapor or aqueous solution), followed with a UV flood exposure step, which renders all remaining photoresist developable in aqueous base. We have tested and applied this process flow to the three organic electronic materials shown in Fig. 1b. The critical steps are the flood exposure (FE) and aqueous lift-off (ALO), thus we will use the abbreviations FE and ALO throughout this paper. In short, the FE step is done by exposing the substrate with the photoresist and organic material stack in a mask aligner’s flood exposure mode without using any mask. The UV exposure dose and thus the exposure time depends on the UV light transmittance through the organic layer on top of the remaining photoresist, and has to be optimized for each material. Following the FE, the ALO step is done in the same aqueous developer, typically NaOH or KOH based, as used in the initial photoresist patterning. The sample is left in the developer until the exposed photoresist with the organic material on top starts flaking off, and is assisted by gentle agitation and rinsing in DI water.

Herein we demonstrate this patterning technique using three different vacuum-evaporated small molecules (both single and double layers) and the conducting polymer poly(3,4-ethylenedioxythiophene), PEDOT. The desire to form pixelated arrays of organic electrolytic photocapacitors (OEPCs)\(^{16}\) for artificial retina applications was a major motivation behind the present

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FIG. 1. (a) Process flowchart for the all-aqueous development and lift-off procedure for patterning organic electronic materials. The procedure starts with a substrate coated with positive-tone novolac/DNQ photoresist (PR). Following conventional exposure and development (1), the organic electronic material is deposited (2). Next, flood exposure (3, FE) of the whole wafer is performed, to render the remaining resist developable. Finally, the aqueous lift-off (4, ALO) is performed by placing the sample into basic pH aqueous developer solution. (b) The organic electronic materials patterned using the FE-ALO process: EPI, a luminescent ambipolar semiconductor; H\(_2\)Pc/PTCDI, a typical donor/acceptor photovoltaic pair; and PEDOT:PSS, an aqueous-based conducting polymer.
work. The OEPC is a recently-introduced device which, when illuminated in physiological conditions, generates photovoltage and displacement currents which stimulate adjacent cells, generating action potentials.

II. EXPERIMENTAL METHODS

General lithography methods. Soda lime glass wafers were used as substrates throughout this study (University Wafer, 100 mm diameter, 550 μm thick). These substrates were cleaned by soaking in the circulating solution of 2% Hellmanex III detergent solution heated to 50°C for two hours, followed by UV/ozone treatment for 15 minutes before use. Two types of positive tone novolac/DNQ photoresists were used – Dow S1818 G2 (S1818) for thin films and Shipley SJR 5740 (SJR5740) for thicker films of photoresist. Both photoresists were spin cast by ramping from 500 rpm to 4000 rpm for 5 seconds and continuing at 4000 rpm for 45 seconds, followed by a soft-bake at 95°C for 90 s, typically giving a photoresist thickness of 1.7 μm for S1818 and 7 μm for SJR5740 films. Plastic film photolithography masks were prepared in-house using a Bungard Filmstar photoplotter at a resolution of 8192 dpi. Developed films were then taped to 5” glass mask plates for usage in the mask aligner. Photoresists were exposed by a Karl Süss MA6/BA6 mask aligner using a 350W mercury vapor lamp calibrated to the power of 15 mW/cm² at a wavelength of 405 nm. The S1818 photoresist films were exposed for 20 seconds, while thicker SJR5740 films were exposed for 40 seconds. The same mask aligner was used for UV flood exposure (FE), in the aligner's flood exposure mode without a mask. S1818 films were developed using the Microposit MF-319 TMAH developer, while SJR5740 films were developed in a 1:4 solution of Microposit 2401 KOH-based developer, while SJR5740 films were developed in a 1:4 solution of Microposit 2401 KOH-based developer and DI water.

Evaporated small molecules and devices. Organic small molecule semiconductors used were EPI, epindolidione (synthesized and purified as described in the literature\(^\text{17}\)), H\(_2\)Pc, metal-free phthalocyanine (Alfa Aesar), and PTCDI, N,N'-dimethyl perylene tetracarboxylicdiimide (BASF). All three materials were purified three times by temperature gradient sublimation. EPI films were prepared by sublimation from a resistively-heated carbon crucible in a vacuum of 1×10\(^{-6}\) mbar at a rate of 2-4 Å/s to a thickness of 80 nm. Following evaporation, the substrate was exposed to FE from the top (irradiating through the organic layer) for 3 minutes. Lift-off was conducted using a Shipley Microposit 2401 KOH-based developer diluted 1:4 with DI water without agitation for 5 minutes.

H\(_2\)Pc/PTCDI devices were prepared on indium tin oxide (ITO) glass (Kintec, 10 Ohm/square, 0.7 mm thick), or on glass wafers with evaporated Cr/Au electrodes (2 nm Cr used as a sticking layer with 9 nm of Au for transparent electrodes). Cr/Au was patterned using etching in I\(_2\)/KI solution, with SJR 5740 as an etch mask. SiN was used as a passivation layer. SiN was deposited by plasma-enhanced chemical vapor deposition device (Advanced Materials) using SiH\(_4\), NH\(_3\), N\(_2\) and He as the working gasses in a capacitive coupled parallel plate reactor. Deposition of SiN was conducted in a reactor heated to 300°C, while plasma was excited by a 35W RF source operating at 13.56 MHz and coupled with the reactor using an impedance matching network. After 20 minutes of deposition, samples were conformally coated by a SiN layer 400 nm thick. H\(_2\)Pc thin films were evaporated from resistively-heated carbon crucibles in a vacuum of 1×10\(^{-6}\) mbar at a rate of 1-2 Å/s to a thickness of 30 nm, followed by PTCDI at a rate of 2-4 Å/s (30 nm for OEPCs, 80 nm for photodiodes). Following evaporation, the substrate was exposed to FE from the top (irradiating through the organic layer) for 3 minutes. Lift-off was conducted using a Shipley Microposit 2401 KOH-based developer diluted 1:4 with DI water without agitation for 30-90 minutes.

PEDOT devices. Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) samples were prepared from an aqueous formulation (PH1000, Heraeus GmbH). Organic electrochemical transistors (OECTs)\(^\text{18}\) were chosen as a canonical PEDOT:PSS-based device for a demonstration. For OECT fabrication, the PH1000 mixture was modified by adding 5% by volume of dimethylsulfoxide (DMSO), 2.5 v% (3-glycidyloxypropyl)trimethoxysilane (GOPS), and 0.1% of ZONYL-FSO fluorosurfactant. GOPS is added to provide good adhesion to the glass substrates, while DMSO is an additive which increases the PEDOT:PSS conductivity. The modified PH1000 mixture was spin coated on photoresist-patterned substrates from freshly-made solutions at 1000 rpm for 30 seconds, preceded by a spreading step of 5 seconds at 500 rpm. Coated samples were baked on a vacuum hotplate at 100°C for 10 minutes. Following the coating, the substrate was exposed to FE from the
top (irradiating through the PEDOT:PSS layer) for 3 minutes. Lift-off was conducted using a Shipley Microposit 2401 KOH-based developer diluted 1:4 with DI water with slight agitation for 5 minutes, followed by a DI rinse and a post-bake at 120°C for 10 minutes. Electrochemical transistor devices (ECTs) were fabricated using Cr/Au contacts (2 nm of Cr used as a sticking layer for Au, with 70 nm of Au for the contacts) and SiN passivation layers prepared as described in the previous section. ECTs were measured using an HP 4145B semiconductor parameter analyzer, with 0.1M Na$_2$SO$_4$ electrolyte.

### III. RESULTS AND DISCUSSION

The patterning process was first carried out using the organic semiconducting small molecule EPI on soda-lime glass wafers. EPI is processed by vacuum sublimation and is a fluorescent molecule. The intensity of fluorescence can be used as an indicator for the integrity of the semiconducting film. Films of 80 nm thickness with lateral dimensions down to 10 µm are shown in Fig. 2a (fluorescent microscopy images). The fluorescence intensity registered for films processed by photolithography versus reference samples patterned with shadow masking during evaporation was found to be identical (Fig. 2b). As a resolution test, we applied the method to reproduce a fluorescent microfabricated replica of a historical lithograph (Fig. 2c).

We next applied the FE-ALO method to photovoltaic bilayers of H$_2$Pc and PTCDI. These bilayers were tested in two devices: patterned photodiodes and organic electrolytic photocapacitors (OEPCs). Photodiode and OEPC arrays were fabricated identically by starting with a patterned bottom electrode of ITO or semi-transparent layer of Cr/Au (1/9 nm) to give back-electrode pixels (0.1 – 1.6 mm in diameter) and contact pads. SiN was then deposited and patterned by photolithography and SF$_6$/O$_2$ reactive ion etching (RIE) process step to provide passivation of the bottom electrodes and contact pads. The passivation step was followed by photoresist deposition, exposure, vapor deposition of H$_2$Pc/PTCDI (30/30 nm for OEPCs, 30/80 nm for photodiodes), and FE-ALO, producing differently-sized islands of H$_2$Pc/PTCDI on the bottom contacts surrounded by SiN passivation. Finally, the top electrode was deposited by thermal evaporation of Ti (100 nm). The general device structure is presented in Fig. 3a. First, to check if the FE-ALO process impairs the H$_2$Pc/PTCDI layers, large pixels on ITO glass were fabricated by the photolithography process versus shadow masking. Photovoltages and photocapacitive charging currents were measured using the electrical photoresponse measurement (EPR) method described previously, and sketched in Fig. 3b. OEPCs were compared upon illumination (630 nm, 5 ms) in 0.1M KCl. It is known that delamination or pinholes in the layers would cause a dramatic decrease in the measured photovoltage of OEPCs, and also the photovoltage and its transient behavior is highly sensitive to chemical changes and defects in the H$_2$Pc/PTCDI layers. Photovoltage was found to be identical for reference layers of H$_2$Pc/PTCDI prepared by conventional stencil masking, compared with layers which had been prepared by the FE-ALO process and kept in the developer solution for 30 minutes during the lift-off process (Fig. 3c). Photocapacitive current density was found to be independent of pixel size (Fig. 3d, red squares), indicating that the FE-ALO process allows fabrication of smaller devices without a decline in performance. The same device arrays with additional Ti top contacts were characterized as photodiodes (Fig. 3e). With the same illumination conditions as used for the OEPCs, the photocurrent density was also size-independent in the diodes (Fig. 3d, black circles). The photodiodes were found to have good rectification and dark/light ratio of at least 10$^4$ - 10$^5$ in the blocking direction (Fig. 3e). Based on the performance of the devices, it can be said that the flood exposure does not lead to photochemical damage of the semiconducting layers. A potential limitation of the FE-ALO process is that certain semiconductors may indeed be sensitive to the UV light wavelengths used in typical mask aligners. These unwanted effects can likely be mitigated by exposure not from the top of the organic film, but through the back of the substrate.

Finally, we applied the FE-ALO process to the widely-used conducting polymer formulation PEDOT:PSS. PEDOT:PSS was processed from an aqueous dispersion. To provide good adhesion to the glass, we treated the substrate with GOPS, a well-known adhesion promoter for the PEDOT:PSS formulation, by exposing the substrate to GOPS vapor at 70°C for 2 hours, and rinsing in acetone to remove multilayer residues. Following photoresist spin coating, exposure, and development,
FIG. 2. (a) Photomicrograph showing patterned EPI islands (80 nm thickness). (b) Line scans of fluorescence intensity for a large pixel and the smaller pixels shown in panel (a). The intensities are normalized to the luminescence of control films evaporated through a shadow mask, with intensity ratio being roughly equal to 1 across all measurements of pixels patterned by FE-ALO. (c) Fluorescent photomicrograph of a high-resolution EPI pattern over a large area (original lithograph used for mask printing is a public domain image, source: Wikimedia/Pearson Scott Foresman).

PEDOT:PSS mixture was spin coated and baked at 100 °C for 10 minutes, after which the FE-ALO steps were done. PEDOT:PSS structures with resolution down to 4 µm were fabricated (Fig. 4a). We found that the success of the lift-off step was heavily dependent on the use of the GOPS additive.
FIG. 3. (a) Sample pixel used for OEPC characterization and photodiode fabrication. The H$_2$Pc/PTCDI islands are patterned by FE-ALO onto an array of patterned gold or ITO electrodes which are passivated by SiN. For photodiodes, an additional Ti electrode is evaporated on top. (b) Measurement setup for photovoltage and photocurrent characterization of OEPC layers. (c) Comparison of photovoltage for samples patterned with shadow masking versus FE-ALO. (d) Photocurrent as a function of OEPC (red squares) and photodiode (black circles) device active area, showing that smaller pixels do not have inferior photocurrents, but rather that photocurrent is constant with different pixel size. Identical illumination conditions with 630 nm LED were used for both devices. (e) J-V characteristic of a 0.4 mm diameter photodiode pixel patterned with FE-ALO, in the dark and under illumination with 630 nm light. The inset diagram illustrates the diode device cross-section.

No GOPS would lead to rapid lift-off of all PEDOT, while too much would give “dangling” pieces of PEDOT at the edges of the photoresist after lift-off. Optimal results were obtained by limiting the amount of GOPS in the PEDOT spin-coating formulation (2.5 %v) while preceding the deposition of PEDOT with a vapor-phase creation of a GOPS monolayer on the glass. Modification of the surface by GOPS promotes covalent crosslinking of the PSS component in the PEDOT:PSS directly to the substrate, ensuring that it does not delaminate during lift-off. In the case of PEDOT, it is most critical to validate that the developer solution does not lower the conductivity. Four-probe conductivity measurements on PEDOT:PSS reference films versus developer-treated ones revealed no detriment to conductivity – the sheet resistance remained around 20 \( \Omega/\text{sq} \). We next tested the
applicability of this process workflow to PEDOT electrochemical transistors (ECTs). These were fabricated by patterning Cr/Au source, drain, and gate electrodes, passivating the traces with SiN, and opening trenches in the SiN for the PEDOT, the gate electrode and the contact pads (Fig. 4b). PEDOT was patterned via FE-ALO on top of this structure. The characteristics of ECTs fabricated using this method (Fig. 4c) showed characteristic performance for PEDOT-based ECTs, with max
transconductance around 5.5 mS. It can, therefore, be stated that the FE-ALO technique can be a powerful new method for PEDOT patterning. Up to now, the two lithographical methods regularly employed to pattern PEDOT are protection with resist followed by etching (either by plasma, bleach, or electrochemically), or using parylene lift-off lithography. The FE-ALO process may be a simple patterning alternative.

**ACKNOWLEDGMENTS**

The authors gratefully acknowledge financial support from the Swedish Foundation for Strategic Research (SSF) and the Knut and Alice Wallenberg Foundation within the framework of the Wallenberg Centre for Molecular Medicine at Linköping University. We are grateful to Gustav Knutson for support in printing photolithography masks.