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Microcontact printing and selective surface dewetting for large area electronic applications

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Abstract

A universal microstructuring approach was developed, which facilitates the patterning of surfaces by a combination of microcontact printing (mCP) and selective surface dewetting/wetting. Self-assembled monolayers (SAMs) were patterned on glass or silicon substrates by μCP. The regions coated by the SAMs turn hydrophobic, whereas the uncoated regions stay hydrophilic. Such functionalized surfaces facilitate selective deposition of polymers or resists. Polymethyl methacrylate and prepolymer polyurethane were selectively deposited on the hydrophilic regions of the substrate. The hydrophobic regions of the substrate stay uncoated. Subsequently, the resist was used to lift-off metallic microstructures in order to realize micro coils and electrodes for radio frequency information tags. The printed electrodes were used to define drain and source contacts of organic thin film transistors. The device characteristic of the organic transistors will be presented.

Keywords: Microcontact printing; Self-assembled monolayers; Selective dewetting

1. Introduction

Micro and nanostructuring is central to modern science and technology. The advancement of microelectronics in terms of cost and performance would be impossible without the development of lithographic methods. Optical lithography is the standard technique used in microelectronics industry. However, optical lithography is an expensive technology, which is not necessarily the most suitable technique for all electronic and photonic applications, where micro and nanostructuring is required. Furthermore, optical lithography is not applicable to curved or flexible substrates.

The limitations of classical optical lithography have motivated research on alternative or non-conventional patterning techniques, like microcontact printing (μCP), nanoimprint lithography (NIL) or inkjet printing. These techniques have gained considerable attention in recent years due to their interest to a variety of different applications. All these techniques offer novel and inexpensive routes towards patterning of microstructures.

In the case of μCP, a self-assembled monolayer (SAM) is used to selectively functionalize surfaces or substrates. Patterned SAMs can be used as etch masks to pattern gold [1,2], silver [3], and copper [4] by wet etching. Besides that SAMs can be applied as template to control the selective dewetting/wetting of polymers on different substrates [5]. In this study μCP is combined with selective dewetting/wetting to pattern polymers or resists on glass or silicon substrates. The resist structures were used to pattern metal structures by a lift-off process. Drain and source electrodes of organic field effect transistors (OFETs) and radio frequency (RF) coils were realized by this approach. The combination of μCP and selective dewetting/wetting is of particular interest to applications like radio frequency information tags (RFID tags) as the electrodes of the organic transistors and the RF micro coils can be fabricated at the same time.

2. Experimental results

2.1. Microcontact printing

An elastomeric stamp is used to print SAMs on flat or curved substrates. The stamps were prepared by casting an elastomeric material, polydimethylsiloxane (PDMS), against a relief structure

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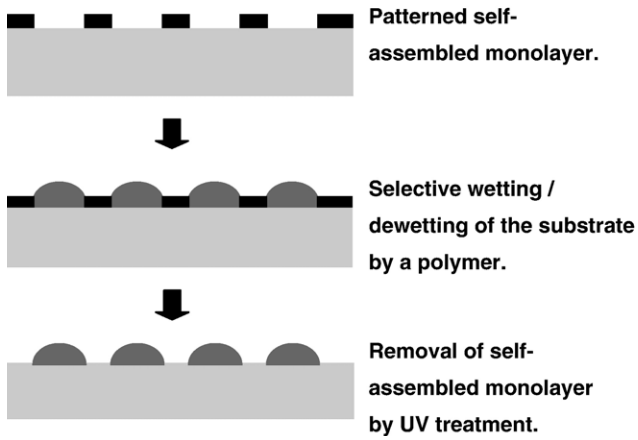

Fig. 1. Patterning of polymers by selective dewetting/wetting.

(master). Afterwards the elastomer was cured at 70 °C for 2 h and removed from the master. A detailed description of the fabrication process of the master and the elastomeric stamp is given in Ref. [6].

Before printing the SAMs on the substrate, the glass or silicon wafers were hydroxylated (−OH terminated) by using a mixture of H_2O_2 and H_2SO_4. The resulting substrates are hydrophilic. A solution of OTS (octadecyltrichlorosilane, $CH_3(CH_2)_{17}SiCl_3$) in hexane was used as "ink" for the printing process. A "fresh" solution was prepared prior to each printing. The "ink" was spin coated on the PDMS stamp before transferring the SAMs to the substrate. The printing of the SAMs was carried under ambient conditions in a clean room.

2.2. Formation of self-assembled monolayers

During the printing process the stamp is brought in conformal contact with the substrate, so that the OTS molecules are transferred from the stamp to the substrate in the regions of contact. The OTS consists of an alkyl ($C_{18}H_{37}$) group and polar ($SiCl_3$) head group. The OTS head bonds to the surface by forming Si–O–Si bonds to the −OH terminated substrate. As a result the regions covered by OTS are hydrophobic, whereas the unexposed regions stay hydrophilic. The surface wetting behaviors of the two regions were characterized by water contact angle measurements. Complete wetting is observed in the hydrophilic areas, whereas the hydrophobic regions exhibit contact angles in the range of 90° to 113°.

2.3. Selective surface wetting

After functionalizing the surface with SAMs the substrates were coated with a polymer. The polymers were either dip or spin coated. The polymers form a film in the hydrophilic region of the substrate, whereas the hydrophobic regions stay uncoated. The selective dewetting/wetting process is illustrated in Fig. 1. Resists like polymethyl methacrylate (PMMA) and polymers like prepolymer polyurethane, and PEDOT-PSS (poly (3,4-ethylenedioxythiophene)-polystyrenesulfonate) were selectively deposited on the substrate. The resolution of the selective wetting process is determined by the viscosity of the polymer, the surface tension of the substrate and the spinning or dipping conditions. A typical example of a selectively dewetted/wetted substrate is shown in Fig. 2. Fig. 2 exhibits the micrograph of a PMMA resist pattern (Fig. 2a) and a prepolymer polyurethane (Fig. 2b and c) on a silicon substrate. Conductive polymers like PEDOT-PSS were patterned by the same procedure. The best resolution was achieved for the prepolymer polyurethane. Features down to 1 μm could be patterned by using this material combination.

2.4. Patterning of metal structures

The resist or polymer pattern can be used as masking layer to carry out further processing steps like dry or wet etching or lift-off processes. In this study the resist patterns were used to lift-off metal films from the substrate. Prior to the deposition of the metal the OTS monolayer was removed by a UV treatment. The process

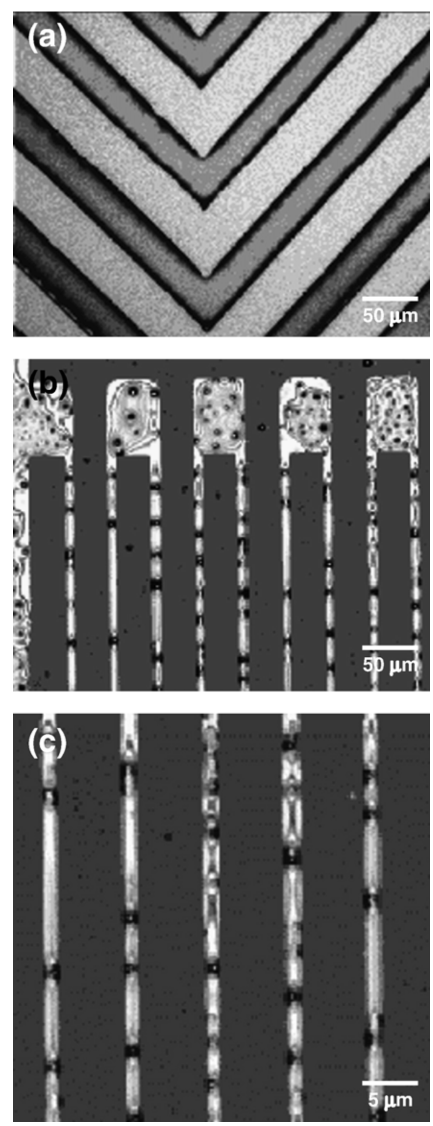

Fig. 2. Patterned polymer (white region) on silicon substrate: (a) PMMA resist. (b) and (c) prepolymer polyurethane.

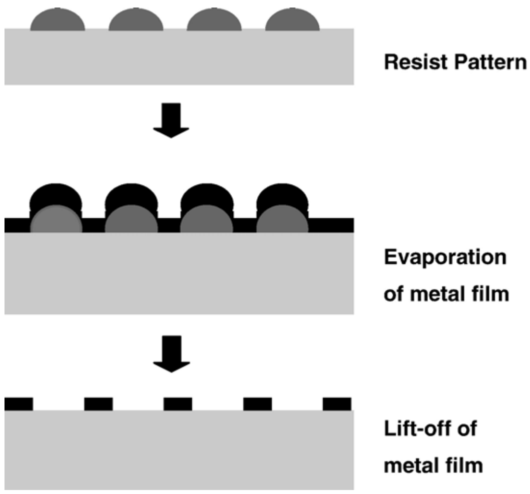

Fig. 3. Patterning of films by a lift-off process.

flow is schematically illustrated in Fig. 3. Gold films were electron beam evaporated on the pre-patterned substrates. In order to improve the adhesion of the gold film a very thin titanium layer was deposited prior to the evaporation of the gold film.

2.5. Radio frequency coils

To demonstrate the applicability of the process, various metal structures including planar RF coils and electrodes were realized. All structures were prepared without using optical lithography. Planar coils with dimensions ranging from 20 µm to 200 µm were fabricated by lifting-off gold films from the substrate. A micrograph of a planar micro coil is shown in Fig. 4b. A micrograph of the elastomeric stamp used for printing of the self-assembled monolayer is shown in Fig. 4a. The windings of the coil have a width and a spacing of 50 µm. The

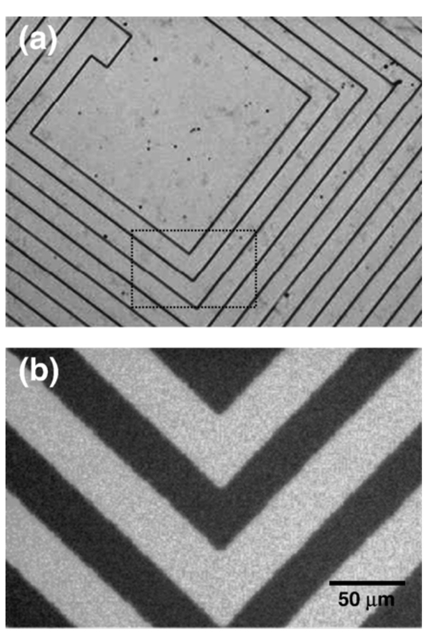

Fig. 4. Micrographs of an elastomeric stamp used for printing SAMs (a). Micrograph of a part of RF coil (b). The coil was patterned on a silicon substrate.

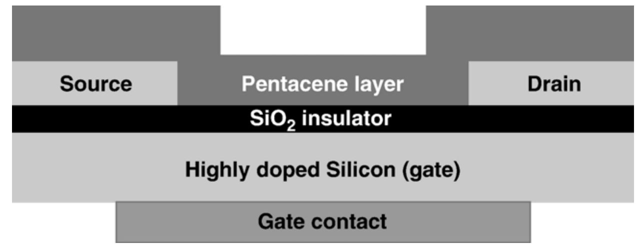

Fig. 5. A schematic cross section of a pentacene TFTs. The source and drain electrodes were patterned by selective dewetting and µCP.

RF coils prepared on glass and silicon substrates exhibit an inductance of approximately 1 µH. The measured inductance is comparable to the inductance of standard RFID tags that operate at 13.56 MHz [7].

2.6. Organic field effect transistors

In the next step gold (Au/Ti) electrodes for organic transistors were fabricated. In this case two parallel electrodes are used as source and drain electrodes of an organic thin film transistor. The spacing between the two parallel electrodes defines the channel length of the bottom gate organic thin film transistors (TFTs).

A cross section of the transistor structures is shown in Fig. 5. Only a single patterning step is required to define the transistor. The OFETs were fabricated on highly doped silicon wafers. The insulator of the transistors consists of 100 nm thermal oxide. Before depositing the organic semiconductor, pentacene, the thermal oxide was treated by hexadimethylsilazane (HMDS). The pentacene molecules were deposited by Organic Molecular Beam Deposition (OMBD). A detailed description of the deposition conditions is given in Ref. [8].

Device structures with channel length down to 5 µm were realized by this approach. The output curves of a pentacene transistor, whose source and drain electrodes were prepared by

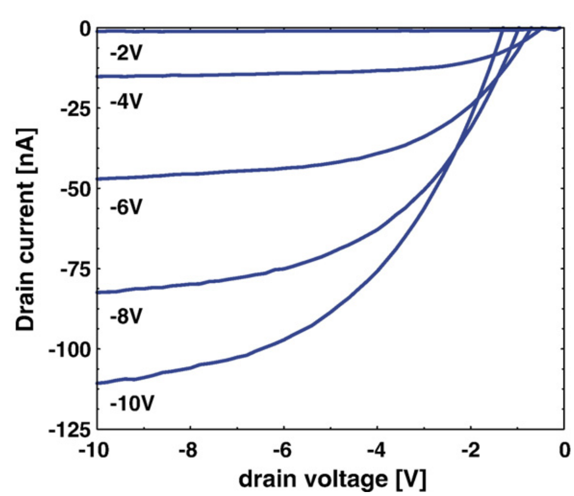

Fig. 6. Output curves of pentacene TFT prepared on a silicon wafer. The drain and source electrodes were defined by µCP in combination with selective surface wetting.

the presented approach, are shown in Fig. 6. The transistor exhibits an effective carrier mobility of 0.3 cm^2/Vs. The length and width of the transistor channel were 100 μm and 4000 μm. The mobility of the transistor with printed drain and source contacts is comparable to transistors patterned by optical lithography [10].

3. Discussion

The combination of μCP and selective surface dewetting/wetting allows for the patterning of resists, conductive polymers and metal films. However, the resolution of the printed electrodes (straight and parallel electrodes) is almost one order of magnitude better than the resolution of the printed coils. The difference in resolution is caused by the different geometry of the device structures. For closed device geometries like coils, spirals or boxes the flow of the excess polymer is inhibited, which limits the resolution of the process. This is not the case for parallel electrodes. In general the resolution of the selective wetting process depends on the surface chemistry, the viscosity of polymers, the device pattern and the preparation conditions of the polymer (spin or dip coating).

If polymers are selectively deposited on heterogeneous or pre-patterned substrates, they tend to form structures with an arc-like cross section. The maximum height of the structure is proportional to the width of the structures. Thus the fabrication of small structures leads to the fabrication of structures with a reduced height [9]. Furthermore, the height of the polymer film depends on the viscosity of the polymer and the surface tension of the substrate. Therefore, reducing the viscosity of the polymer will lead to a reduction of the height of the film. As a consequence small structures can be selectively deposited. Furthermore, the resolution of the selective deposition process depends on the applied materials. In our study PMMA and prepolymer Polyurethane were selectively deposited on glass and silicon substrates. PMMA structures down to 2–5 μm could be realized by this approach. Polyurethane allows for the fabrication of structures down to a minimum feature size of 1 μm. For polyurethane the resolution was limited by the feature size of the elastomeric stamp. However, beading of the stripes is observed for small polyurethane structure. The beading is caused by the non-uniform coverage of the hydrophilic regions by the polyurethane.

4. Conclusion

A universal patterning method was presented, which combines μCP and selective surface dewetting/wetting. The simple and cost effective approach allows for the patterning of resists, conductive polymers and metal films. OTS SAMs were microcontact printed to functionalize silicon or glass substrates. The printed regions are hydrophobic, while the unprinted regions stay hydrophilic. The hydrophilic/hydrophobic patterns were used to selectively deposit polymers and resists on the substrates. The resolution of the selective wetting process depends on the material properties of the polymer and the substrate. Moreover, the resolution is affected by the geometry of the device structures. After forming resist patterns on the substrate the patterns were used to pattern metal films by a lift-off process. RF coils and electrodes for organic TFTs were realized by this approach. The electrical performance of the OFETs is similar to that of pentacene OFETs fabricated by optical lithography. The presented printing approach allows for the low cost fabrication of RFID tags.

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