Nondestructive photolithography of conducting polymer structures

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We have demonstrated a nondestructive method using ultraviolet (UV) photolithography to fabricate micrometer-sized conducting polymer structures. By coating a polymer film on patterned photoresist and then performing liftoff, UV exposure to the conducting polymer film was prevented throughout the lithography processes. We created features down to 1 μm with high yield. Such complementary metal-oxide-semiconductor-compatible microfabrication can be applied generally to various organic films, and may allow the speed of organic electronics to be improved. Organic thin-film transistors (OTFTs) were fabricated using poly(3-hexylthiophene) as the active material, and typical OTFT characteristics were obtained. © 2006 American Institute of Physics. [DOI: 10.1063/1.2159073]

I. INTRODUCTION

The interest in organic thin-film transistors (OTFTs) and organic light-emitting diodes has grown very rapidly in recent years because of the unique combination of electronic and mechanical properties of organic (semi)conductors.1 For practical applications, it is essential to tailor transistor channels and reduce gate dimensions to increase the much needed speed of OTFTs (currently only around or below KHz), isolate individual devices to avoid crosstalk, and improve on/off ratios.2 To meet these requirements, several approaches to pattern organic materials have been developed, including screen printing,3 ink-jet printing,4,5 soft lithographic stamping,6 and photochemical crosslinking.7 Despite these methods, conducting polymers in OTFTs reported to date are often not patterned, largely because of the lack of nonstandard equipment and methods available. Even though jet printing is one of the most promising choices for future organic electronics, achievable feature dimensions are limited by the size of the droplets, which is typically around tens of μm.8

Ultraviolet (UV) photolithography is a well-established complementary metal-oxide-semiconductor (CMOS) technology and has been used to manufacture billions of transistors operating at clock speeds in the GHz range on a modern silicon chip. To date, little has been reported to take advantage of this high-throughput technology in patterning conjugated polymers such as the well-studied poly(3-hexyl thiophene) (P3HT).9,10 and it was considered either incompatible or quite difficult.19,20 Due to the weak bonds in conjugated polymers, UV light exposure could seriously degrade the electronic properties of the materials.12 Chemical reactions between conducting polymers and the solvents and other chemicals used in photolithography might also arise.2,11,13 Recently, Austin and Chou developed an indirect way to pattern a P3HT film. A layer of SiO2 was evaporated directly on the P3HT film and photolithography was carried out to pattern the SiO2 to form an etch mask. The pattern transfer was finished by a CHF3 reactive etching to remove SiO2 and P3HT in the desired areas.14

We demonstrate a direct method to pattern P3HT film by the standard photolithography. Feature sizes down to 1 μm were realized with high yield. To demonstrate this technique, P3HT-based OTFTs were fabricated. Since photolithography is also widely available in university laboratories, such a method can provide predefined and well-controlled structures for material and device research.

II. EXPERIMENTAL RESULTS AND DISCUSSIONS

In general, either etching or liftoff may be used to pattern a conducting polymer film during photolithography. The etching method requires the photore sist to be coated on top of the conducting polymer. After UV exposure and development of the photore sist, P3HT in areas where there is no photore sist coverage is removed by a chemical etch. In this approach, the UV exposure may affect the electronic properties of the conducting polymer. For micrometer-sized organic devices, UV exposure at the edges of the structures could seriously degrade the device performance. We hence focused on the liftoff method, in which the conducting polymer is applied after the spin coating, UV exposure, and development of the photore sist. Compared to the etching method, UV exposure to the conducting polymer is completely avoided and the time for the conducting polymer to react with oxygen and moisture in ambient air is shortened, which is important for most types of conjugated polymers.15-20 This approach can also be applied to pattern small molecules, such as soluble pentacene.21

A. Patterning method

We fabricated P3HT-based OTFTs using the following steps. Standard photolithography was performed to make Ti-Au source and drain ohmic contacts and then Ti-Au bond pads on a 200-nm-thick SiO2 layer that was thermally grown on an n+ silicon substrate. Photore sist was then spin coated and patterned using photolithography, followed by spin coating or drop casting of P3HT. Finally, the liftoff of P3HT was performed by immersing the sample in a photore sist solvent,
causing the semiconducting polymer on top of the patterned photoresist to be lifted off, resulting in a desired P3HT pattern.

Although these processing steps resemble those used to pattern thin metal films, such as the Ti-Au ohmic contacts and bond pads, a number of changes have to be made in order to pattern P3HT films. This is due to the very different physical and chemical properties of conducting polymers. First, the most common solvent of P3HT, chloroform, was found to react rapidly with the standard positive photoresist Shipley S1813. After spin coating or drop casting P3HT on S1813, the reaction caused the surface of the P3HT film to be visibly rough and also distorted the edges of the photoresist pattern, as shown in Fig. 1(a). The desirable undercut profile of S1813, created by chlorobenzene curing, was also destroyed, causing the subsequent liftoff to be unsatisfactory. Our experiments also showed that the edges of the resulted P3HT patterns were badly defined, even if the liftoff process was carried out immediately after the P3HT film had been dried. To solve the problem, a different solvent, xylene, was used, which showed no visible reaction with S1813. The edges of the obtained P3HT patterns were very well defined, as shown by the optical microscope image in Fig. 1(b).

The success of the patterning method also strongly depends on how the liftoff process is carried out. It is different from fabricating ohmic contacts or bond pads, in which a metal film is evaporated or sputtered onto the prepatterned photoresist from the normal direction. If the edges of the patterned photoresist have an undercut profile, the metal film will discontinue at the photoresist edges (unless the metal film is too thick), which results in successful liftoff in a photoresist solvent and formation of a metal pattern. This is also the case for vacuum-evaporated organic materials. For a spin-coated or drop-cast polymer such as P3HT, however, the film is generally continuous across the edges of the predefined photoresist pattern. This, on the one hand, requires a certain force, which might be provided when the patterned photoresist is dissolved beneath the polymer film, to break the polymer film at the photoresist edges. On the other hand, the force has to be within some limit because a polymer film is often very thin, typically only tens of nm, causing the liftoff process to be more delicate than conventional liftoff of metal films. Acetone is a common solvent used in liftoff processes to strip positive photoresists. If pure acetone was used, however, we observed that it often led to the liftoff of the whole P3HT film. Acetone was therefore diluted at different ratios to reduce the strength of the liftoff. The best results were achieved when one part of the acetone was diluted with four parts of methanol.

Figure 2(a) is an optical microscope image of an array of 1-μm-wide gate patterns, which are the smallest features that we have attempted to create with this method. The well-defined pattern is better viewed in the zoomed image in Fig. 2(b). Apart from P3HT films, we have also performed successful photolithography of other soluble conducting polymer materials, such as poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS).

**B. OTFT fabrication**

With prepatterned ohmic contacts and bond pads, OTFTs of different dimensions were fabricated. The n+ silicon substrate acted as a back gate. Regioregular P3HT (more than 98.5% head to tail coupling) was obtained from Aldrich and used without further purification. A P3HT solution of 0.8% weight in xylene was filtered through a 0.2 μm PTFE syringe filter, to remove insoluble particles and impurities. Before coating P3HT, a layer of hexamethyldisilasane (HMDS) was deposited by spin coating to improve the interface be-
 tween the SiO₂ surface and P3HT. Atomic force micro-
graphs not shown here have been taken of the surfaces of
the P3HT pattern after the liftoff, and the morphology was
found similar to that reported. Furthermore, acetone did not
seem to cause an obvious decrease in the mobility of P3HT.
Actually, we expect that the technology should also allow
acetone-sensitive polymers to be patterned by encapsulation
and then liftoff of both the polymer and encapsulation layers
simultaneously.

Figure 3 shows an optical microscope images of two
of the patterned P3HT transistors. The rectangular P3HT pat-
ttern covers the source and drain ohmic contacts, which are
connected to the big bond pads. Yields well above 90% were
achieved. Figure 3(b) shows a typical source-drain current,
Iₜₜ, versus source-drain voltage, Vₛdue, characteristic of an
OTFT with a 9 μm long and 40 μm wide P3HT channel.
Since the lithography processes were carried out in ambient
air, the semiconducting polymer was slightly doped by
oxygen. The field effect mobility was around 5 × 10⁻⁴ cm²/V s, which is in agreement with typical values
reported previously when xylene rather than chloroform was
used as the solvent of P3HT. Experiments were also per-
formed to heat up P3HT OTFTs to 140 °C in vacuum for
about 1 h to de-dope the semiconducting polymer, and on/off
ratios over 10³ were achieved.

OTFTs often suffer from a large contact resistance at
source and drain electrodes, which could be much larger than
the organic channel resistance. In general, bottom-
contact (BC) OTFTs are easier to apply to denser electrical
circuits than top-contact (TC) OTFTs, but usually show a
higher contact resistance. To examine whether the contacts
between the P3HT film and metal pads were weakened by
the force that broke the P3HT film at the edges of the pho-
toresist pattern during the liftoff process, we fabricated BC
OTFTs with different channel lengths simultaneously. The
contact resistance was determined by plotting the total
source-drain (SD) resistance as a functional of the channel
length shown in Fig. 4. The extrapolation of the linear fit
dashed line passes the origin, indicating that the contact
resistance of our devices is substantially smaller than the
channel resistance, even for the 3 μm long OTFTs.

III. SUMMARY

In summary, a direct method to pattern P3HT has been
demonstrated using standard high-throughput photolithogra-
phy technique with high yield. The method can be applied
generally to both small molecules and conducting polymer
materials. This technique can be extended to using optical
phase-shifting masks to manufacture structures down to
~100 nm dimensions, which may significantly increase the
speed of plastic electronic devices and circuits into the MHz
range, which is crucial in practical applications.

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