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The effect of helium plasma etching on polymer-based optoelectronic devices

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ABSTRACT

In this paper the optoelectronic performance of selectively patterned conjugated polymers in light emitting diodes (LEDs) and photodetectors was examined. Polymers were patterned via a dry, non-reactive ion etching process using helium plasma. The polymers studied were the light-emitting poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and poly[9,9-di-(2′-ethylhexyl)fluorenyl-2,7-diyl], and the conducting poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate). The electroluminescent spectra of etched and unetched LEDs are almost identical. There is no correlation between He-ion etching times and LED emission spectra changes. The MEH-PPV-based photodetectors show no decrease in external quantum efficiencies due to increased etch times. Results show that using helium plasma is effective at etching these polymers at predictable rates from selected areas without damaging the working device.

1. Introduction

Polymer optoelectronics hold enormous potential because of their relative inexpense and ease of processing compared to silicon and GaAs-based technologies. While advances in organic/inorganic thin film materials will continue, complementary improvements in processing tools and techniques are also needed for these devices to realize their promise.

Most processing techniques used for inorganic (e.g. silicon) device fabrication do not port well for use in organic device fabrication. A major obstacle to the use of optoelectronic polymer nanofilms is the accurate patterning of these soft and easily degraded materials. This investigation was started because of our need to accurately pattern polymer photodiodes, without damaging device performance. The diversity of materials (metals, ceramics and organics), the difficulties in finding appropriate etchants, the introduction of water, the stringent controls needed for precise wet etching and its inherent variability, and the similarities of the polymers being studied to those in photoresist, make traditional wet etching techniques incompatible with this type of fabrication.

The use of reactive ion etching (RIE) has become commonplace in the traditional microfabrication industry [1,2], but its efficacy in patterning semiconducting polymers, and effect on polymer optoelectronic device performance has not been studied. Oxygen O_2 and tetrafluoromethane CF_4 have been used for etching photoresist [3] or dielectric polyimide [4]. Oxygen is one of the major causes of semiconductive polymer degradation [5–9], thus oxygen RIE must be avoided to mitigate oxidative degradation. Dry etching with physical mechanism only, typically utilizes a nonreacting gas such as argon [10]. Instead of RIE, we proposed that a helium plasma excited inside an RIE chamber might be used to pattern semiconductor polymers [11]. The main physical mechanism is bombarding the surface with inert helium ions and sputter etching [12].

We selected helium ion etching because it is an inert gas that will not react with the polymer or other material and since it has low atomic weight, it loses its kinetic energy quickly and thus is a gently etchant suitable for low modulus materials such as polymer films. To our best knowledge inert helium in RIE chamber was never used alone by other researchers to pattern the semiconducting polymers. However, helium together with reactive gases such as oxygen (He–O_2) [13,14], carbon dioxide (He–CO_2) [13], or He–CF_3Br:Ti [12] were used in the past by other researchers. Mixing inert gas (He or Ar) with reactive gas stabilizes plasma, dilutes etchant, and improves heat transfer [12]. In this paper we use only helium plasma to pattern semiconducting polymers.

In this paper, the effects of ion etching on the optoelectronic performance of these polymers, namely poly [2-methoxy-5-(2′-ethylhexyloxy)-1, 4-phenylenevinylene] (MEH-PPV), poly [9,9-di-(2′-ethylhexyl) fluorenyl-2,7-diyl] (polyfluorene) and the conducting polymer poly (3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), chemical structures of which are given in Fig. 1, are investigated. There was concern that such a high powered technique, especially using reactive species, would damage the performance of these devices. Using O_2 for patterning would likely leave residual oxides or other sources of oxygen that would be available as a degradative species to MEH-PPV, and a detrimental layer of aluminum oxide might be formed in our cathode. To avoid these concerns, helium plasma was used. This showed very good results in the etching of both polymers,

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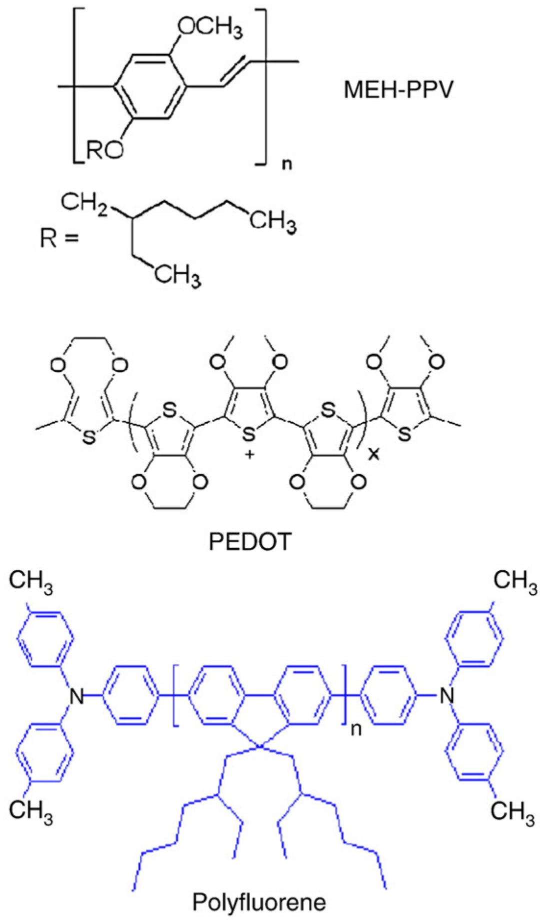

Fig. 1. The chemical structures of the MEH-PPV, polyfluorene and PEDOT:PSS polymers.

and no effect or apparent damage was seen on the aluminum layer. Several experiments were performed that demonstrate, firstly, that ion etching is an effective method for the removal of the polymer(s) from the substrate in the selected etch areas, and secondly, that ion etching is not contraindicated because of adverse effects on the active properties of these polymers. It is amenable to application in polymer optoelectronic fabrication such as patterning photonic crystalline structures, complex multi-layer devices and to facilitate packaging.

2. Experimental details

Thin films of 150 nm of MEH-PPV were prepared by spin coating in air. Powdered MEH-PPV (Sigma Aldrich™) from a single batch with molecular weight 86,000 g/mol was dissolved in chlorobenzene. These solutions were heated to 80 °C and stirred for 8 h, then filtered and spincast onto indium tin oxide (ITO) coated substrates (Colorado Concepts). The MEH-PPV film thickness was measured to be 150 nm with good uniformity (±10%). PEDOT:PSS was purchased in a prepared aqueous solution (Sigma Aldrich™) and spincast onto ITO substrates in the same manner as MEH-PPV. These films were also measured to be 150 nm with good uniformity (±5%). Polyfluorene (American Dye Source™) was dissolved in chlorobenzene in a manner similar to that of MEH-PPV. Spincast polyfluorene films with thicknesses of 120 nm were measured with uniformity of ±15%; i.e. the MEH-PPV films were generally smoother than the polyfluorene films. All of these samples were then dried *in vacuo* for 8 h at room temperature.

Table 1
Summary of helium ion etch rates for various polymers.

Polymer	Power (W)	Etch rate (nm/min)
Polyfluorene	25	~12
PEDOT:PSS	25	~15
MEH-PPV	25	~22
MEH-PPV	100	~35

These films were then partially covered with stainless steel shadow masks, and etched in a helium plasma for various times in a PlasmaTherm SLR 720/740 RIE chamber with the following settings: power 25–100 W, pressure 26.66 Pa, and helium gas flow rate of 50 standard cm^3/min. The He ion energy is about 3–12 eV. The resulting profiles were measured KLA Tencor™ profilometer with 1 nm resolution. Low power and short etch times allowed partial etches, which allowed us to measure and compare the profiles of unetched regions with partially etched ones. Scratches were made in the films to expose regions of glass for reference points used to calculate the etch rates that are summarized in Table 1. These data were used in the next fabrication for calculating minimum etch times to fully remove films from unwanted areas of functioning devices.

The fabrication procedure was the same for the light emitting diodes (LEDs) and the photodiodes. The ITO coated glass substrates with a surface resistance of 40 Ω/□ were cleaned and etched using diluted HCl. Pattern transfer defining the anode was achieved with standard photolithography. PEDOT:PSS, polyfluorene, and MEH-PPV

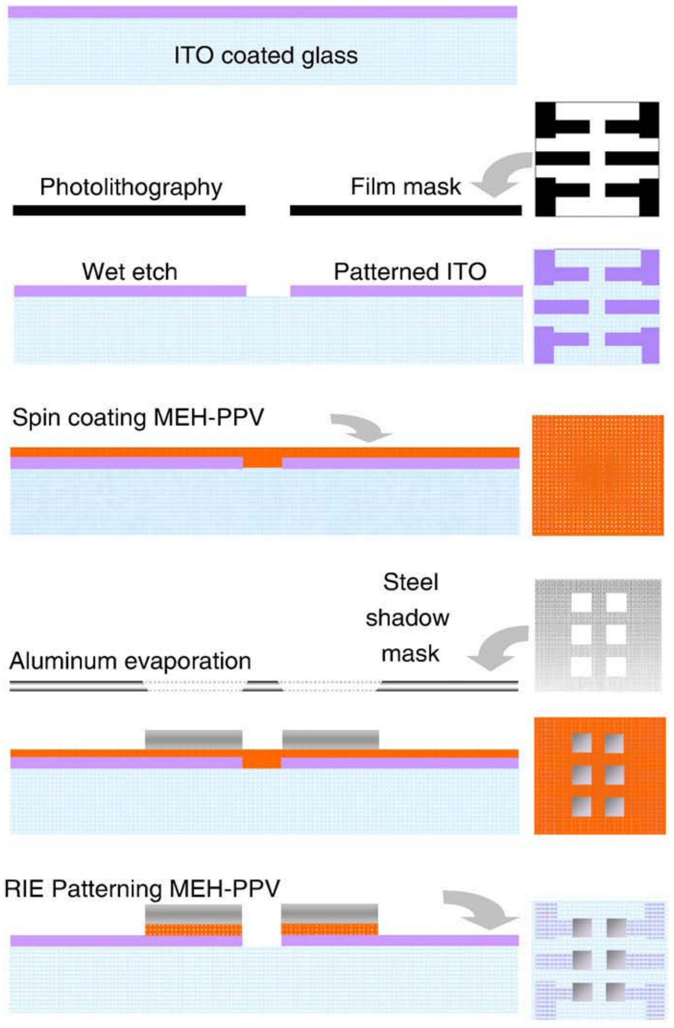

Fig. 2. Overview of fabrication procedure of MEH-PPV based photodiode.