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Photolithographic patterning of PEDOT:PSS with a silver interlayer and its application in organic light emitting diodes

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ABSTRACT

A patterning scheme for poly(3,4-ethylenedioxythio-phene):poly(styrenesulfonate) (PEDOT:PSS) is reported. With a silver interlayer, the conductive PEDOT:PSS film can be patterned down to micrometer scales by traditional photolithography, and this patterning scheme can be applied on large-area flexible substrates. Through systematical investigations, the patterning processes have no obvious influence on both the bulk and surface properties of PEDOT:PSS films. Efficient organic light emitting diodes (OLEDs) are realized based on this patterned PEDOT:PSS anode, and they show comparable performance to those devices with an indium tin oxide (ITO) anode. High-resolution OLED pixel arrays are also demonstrated. Our interlayer approach here has an advantage of patterning PEDOT:PSS with high resolution and large scale, and it is also compatible with traditional photolithographic processes which substantially save the capital cost. Results indicate that the photographically patterned conductive PEDOT:PSS film becomes a promising candidate for eletrical eletrode material in organic electronic applications.

1. Introduction

Flexible electronics is an emerging technology for many applications such as flexible displays [1]. Sensors array on flexible substrates can be used to detect signals from curved surface [2]. Flexible electronic devices can also be applied to bio applications, such as artificial skin [3]. One key issue for flexible electronics is subject to the choice of flexible electrodes, and these conductive materials should maintain conductivity while bending [4]. Metal is commonly used as a conductive material due to its high conductivity. However, for light-emitting applications such as organic light emitting diodes (OLEDs), metal is not suitable because of its poor transparency, even with a very thin film thickness. Indium tin oxide (ITO) is transparent and conductive. However, it is also brittle and will loss its conductivity while bending. Moreover, ITO is becoming expensive since indium is a kind of rare metals with limited resource. Many other transparent and conductive materials were previously proposed, such as carbon nanotubes [5], graphene [6], silver nanowires [7] and conductive polymers [8].

Poly(3,4-ethylenedioxythio-phene):poly(styrenesulfonate) (PEDOT:PSS) is an intrinsic conductive polymer. It is flexible, low-cost, and can be easily deposited on various substrates such as spin-coating of aqueous solutions [9]. PEDOT:PSS can reach a high conductivity beyond 3000 S/cm [10,11], and also exhibit high transparency in the visual spectrum [12]. For its high work function, PEDOT:PSS can also be used to facilitate hole injection into devices [9]. PEDOT:PSS has already been used in many applications, such as OLEDs [12], organic thin film transistors (OTFT) [13] and bio-electronics [14].

To use PEDOT:PSS in different electronic devices, patterning of PEDOT:PSS films into desired shapes is always essential. However, as a polymer, PEDOT:PSS cannot be patterned using conventional schemes which are designed for

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inorganic materials. Many methods are proposed, such as contact transfer [15], laser cutting [16], ink-jet printing [17] and photolithography [18–23]. Contact transfer can realize nanometer-scale PEDOT:PSS patterns using a nanostructured mold, while the transferring processes are not suitable for the large-area patterning. Laser cutting and ink-jet printing are directly-writing methods without molds or masks, and the materials utilization is very high. However, the patterning resolution is limited to tens of micrometers. Photolithography is a reliable patterning method and is a mature technique employed in silicon-based semiconductor industry. For large-area and high-resolution patterning, photolithography is yet the most favorable approach. However, traditional photolithographic schemes for inorganic materials are not suitable for PEDOT:PSS. Aqueous solutions involved in traditional photolithographic processes will severely destroy acidic PEDOT:PSS films, for example the widely used alkaline developer 2.38% tetramethylammonium hydroxide (TMAH). In the case of the positive-tone photoresist, it is just impossible to form fine patterns, as the acid PEDOT:PSS will decompose the positive-tone photoresist. For the negative-tone photoresist, the acidic component in the PEDOT:PSS will crosslink the resist, and the resist residual will be left on the unexposed areas. Huang et al. and Leem et al. have used the commercially available photoresist SU8 to pattern PEDOT:PSS. PEDOT:PSS is stable in its developer of propylene glycol monomethyl ether acetate (PGMEA) [8,20]. However, SU8 can hardly be removed after its cross-linking which limits its application. Moreover, PEDOT:PSS will lose about 15% of its conductivity after the patterning processes. Ober et al. used highly fluorinated photoresist and solvents to pattern PEDOT:PSS. They achieved nano-scale resolutions [18] although the influence due to fluorianted materials onto PEDOT:PSS films is not fully investigated. By using parylene to protect PEDOT:PSS surface, DeFranco et al. achieved micrometer-scale patterns through conventional photolithographic processes. However, the parylene films need to be peeled off from the PEDOT:PSS surface which is inconvenient for large-scale fabrication, and residuals might exist on the PEDOT:PSS surface after peel-off process [19]. All the approaches described above have their own advantages and disadvantages, and it will be desirable if conventional photolithographic materials and processes can be adopted for PEDOT:PSS patterning. As traditional photolithography is widely used in industry, it will be cost effective to pattern PEDOT:PSS by adopting traditional facilities and materials.

Here, we propose a method using a silver interlayer to protect PEDOT:PSS during photolithography, and therefore conventional photoresist and solvents can be used. As previously mentioned, proper treatments can enhance the conductivity of PEDOT:PSS films, for example acid treatments [10]. Since PEDOT:PSS is stable in acid, the silver interlayer, acts as an etch mask, on PEDOT:PSS can be removed using an acidic etchant. The influence to PEDOT:PSS during patterning processes are systematically investigated, including both the bulk and surface properties. Using this proposed method, ITO-free OLEDs and OLED pixel arrays were demonstrated. These results here will be beneficial to future flexible electronics.

2. Experimental details

PEDOT:PSS aqueous solution (Clevios PH1000) was purchased from Starck and it was filtered with 0.45 μm PVDF syringe filters before coating. The substrates were 1 inch square TN glasses and were pre-cleaned by detergent, acetone, IPA, de-ionized water and oxygen plasma. PEDOT:PSS films were deposited on glasses using spin-coating, and different thicknesses were obtained by tuning the spin coating conditions. After the spin-coating of pristine PEDOT:PSS, 10-min baking at 180 °C, 10-min ethylene glycol (EG) immersion and 10-min post-baking at 180 °C were used to enhance the conductivity of PEDOT:PSS. The sheet resistance and thickness of the films were measured respectively by four-point probes through a Keithley SMU 2400 and a surface profilometer (Alpha-Step D-120 from KLA-Tencor Technology, Inc.). The optical transmittance of films was measured by a spectrophotometer. Multimode Nanoscope from Digital Instruments, Inc. was used for surface morphology studies via atomic force microscope (AFM) mode.

Aluminum was first used as an etch mask to protect PEDOT:PSS films. However, the alkaline TMAH solution will react with aluminum. Silver was finally chosen as interlayer here due to high chemical stability. The etchant for silver consists of several components including nitric acid (65 wt%), phosphoric acid (85 wt%), acetic acid (99.5 wt%) and de-ionized water with the volume ratio of 1:16:16:2. Silver film of about 100 nm was first deposited on PEDOT:PSS using thermal evaporation to protect its surface. A commercial available negative-tone photoresist AZ2020 purchased from AZ Electronic Materials was used for photolithography, and used as received. Its developer was the 2.38% TMAH solution. N-methyl-2-pyrrolidone (NMP) was used as a stripper to remove the photoresist.

For OLED fabrications, 1 inch square pre-patterned ITO glasses (Kintec Company) were used and pre-cleaned by detergent, acetone, IPA, de-ionized water and oxygen plasma. Before the fabrication of OLEDs, the conductive PEDOT:PSS films were baked at 180 °C for half an hour in a nitrogen-filed glove box to remove moisture. Then, it was directly transferred into the chamber for the deposition of organic materials and metal cathodes. The evaporation for organic materials was controlled to about 1 Å/s under an operating pressure of 5×10^{-6} Torr. The devices were then encapsulated with a glass cap using an UV epoxy under nitrogen so as to protect the devices from oxygen and moisture during measurements. The current–voltage characteristic was measured by Keithley 2400, and the luminance was measured by a luminance colorimeter (BM7A from Topcon Inc.).

3. Results and discussion

Here, a facile patterning method was proposed, and the processes were illustrated in Fig. 1. Before patterning the conductive PEDOT:PSS films, a silver thin film of about 100 nm was deposited onto PEDOT:PSS to protect the surface. Then, a commercial available photoresist (AZ2020) was spun-coated on it (shown in Fig. 1(a)). After UV expo-