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Enhanced outcoupling in flexible organic light-emitting diodes on scattering polyimide substrates

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ABSTRACT

We demonstrate an upscalable approach to increase outcoupling in organic light-emitting diodes (OLEDs) fabricated on flexible substrates. The outcoupling enhancement is enabled by introducing a thin film of microporous polyimide on the backside of silver nanowire (AgNW) electrodes embedded in neat colorless polyimide. This porous polyimide film, prepared by immersion precipitation, utilizes a large index contrast between the polyimide host and randomly distributed air voids, resulting in broadband haze (> 75%). In addition, the composite polyimide/AgNW scattering substrate inherits the high thermal (> 360 °C), chemical, and mechanical stability of polyimides. The outcoupling efficiency of the composite scattering substrate is studied via optical characterization of the composite substrate and electron microscopy of the scattering film. The flexible scattering substrates compared to glass/indium tin oxide (ITO) allows for a 74% enhancement in external quantum efficiency (EQE) for a phosphorescent green OLED, and 68% EQE enhancement for a phosphorescent white OLED. The outcoupling enhancement remains unharmed after 5000 bending cycles at a 2 mm bending radius. Moreover, the color uniformity over viewing angles is improved, an important feature for lighting applications.

1. Introduction

White organic light-emitting diodes (OLEDs) are emerging solid-state lighting elements, offering unique advantages of high internal quantum efficiency [1–4] and facile large-area production on flexible substrates [5]. The challenges in producing practical flexible white OLEDs are twofold. First, transparent conducting electrodes (TCEs) must be realized on plastic substrates while simultaneously optimizing their optical, electrical, chemical, and mechanical properties. New classes of TCEs such as metallic nanowires [6–9], graphene [10,11], and carbon nanotubes [12,13] have been incorporated into flexible plastics to replace ITO, whose brittleness and high-temperature processing are generally incompatible with plastics. Second, effective light outcoupling structures should be introduced to these flexible OLEDs since only 20–30% of generated photons can escape an unmodified planar device, owing to surface plasmon polaritons at the metal-organic interface, waveguiding in the high-index organic stack, and internally reflected light at the substrate-air interface [14–16]. These challenges are exacerbated for white OLEDs as they also need to be addressed over the full visible spectrum. In addition, white OLEDs for general lighting are expected to meet an additional set of performance metrics such as a high color rendering index (CRI) and color uniformity across a large-area panel and between panels, as well as color uniformity over large viewing angles [17,18].

Various strategies have tackled these challenges and reported flexible monochromatic and/or white OLEDs with improved performance through the use of nanostructured metal grid-electrodes [19,20], nanotextured plastic substrates [21], microlens arrays combined with scattering nanoparticles [22], and planar substrates embedded with high-index scattering particles [23]. However, many of these outcoupling structures are realized by lithography and are difficult or too costly to upscale. A more scalable approach to extract both waveguiding and substrate losses was introduced in which simple oxygen plasma treatment was used to obtain micropatterned plastic substrates [24]. However, the application was limited to monochromatic OLEDs. We recently introduced a scalable and broadband alternative whereby porous polymer films are used on the substrate backside to outcouple substrate loss in both monochromatic and white OLEDs without costly lithography. The porous polymer film takes advantage of a large index contrast between itself (in that case, Kapton with $n > 1.7$) and non-absorbing air pockets, showing the ability to outcouple as much as 44% of substrate-trapped photons in a rigid glass/ITO structure [25]. The

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porous polyimide films are produced via immersion precipitation in which a film cast from the polyimide precursor (polymer and solvent) is introduced to a coagulation bath containing a nonsolvent. Nonsolvent-induced phase inversion and solvent-nonsolvent exchange take place, and the polymer solidifies to a porous film [26]. The air voids formed spontaneously in this way are randomly distributed within the polyimide host, giving rise to broadband haze. In addition, Go et al. has shown that the choice of nonsolvent has a significant impact on the morphology and thickness of the resulting porous polymer film, and hence its outcoupling efficiency [27]. In this work, we use deionized water as our nonsolvent which is both scalable and highly miscible with our choice of solvent (N-methyl-2-pyrrolidone, NMP), thus accelerating the immersion precipitation process.

Here, we adopt the precipitation immersion principle to obtain microporous polyimide scattering films from colorless polyimide (CPI). Colorless polyimide is an optically transparent material that inherits the excellent thermal, mechanical, and chemical stability of aromatic polyimides. Unlike conventional polyimides such as Kapton that absorb strongly in the short visible wavelengths, CPIs have improved visible transmission by introducing alicyclic [28] or semialicyclic [29] substituents or highly electronegative substituents [30] in the synthesis. These substituents shift the absorption band edge of polyimides by inhibiting the formation of charge transfer complexes between the diamine (donor) and the dianhydride (acceptor) moieties [31]. In particular, CPI has proven to be an excellent host material for AgNWs, and composite CPI/AgNW substrates have a high electrical to optical conductivity ratio comparable to that of glass/ITO [7,32]. Moreover, thermal imidization of CPI with embedded AgNWs resulted in an exceptionally robust TCE resistant to scratching and tensile stress, as well as an ultra-smooth (< 1 nm root mean square roughness) active area, which is critical for preventing a common electrical failure mode (shorting) in large area thin-film devices [33]. As such, we use CPI/AgNW substrates as a platform to integrate the porous polyimide scattering film (pCPI) for outcoupling. By using CPI as both the substrate and the scattering film, we minimize reflection loss from any inherent index contrast as well as parasitic absorption loss in the short wavelengths, an aspect that is particularly important for white OLEDs.

2. Experimental

The preparation of the conductive and scattering flexible substrates is schematically illustrated in Fig. 1. As a first step, a random network of AgNWs (ACS Material) is deposited on a carrier substrate (Fig. 1a) via spin coating. The AgNWs are then patterned via pulsed UV laser ablation (Fig. S1) to define an active OLED area of 2 × 5 mm^2, and 30 μJ of 22 ns-pulse energy is sufficient to completely eject the AgNWs from the glass substrate. To protect the remaining AgNWs during thermal imidization [34], a titania (TiO_2) sol-gel is synthesized as in Ref. [7] and deposited via spin coating (Fig. 1c). A thin (~2 nm) layer of TiO_2 is sufficient to prevent AgNWs from breaking up into droplets, a process that occurs in nanowires at temperatures much below the melting point of bulk silver due to the Rayleigh-Plateau instability [35,36]. Then, colorless polyimide precursor solution (10 wt%) is blade coated and dried under vacuum for 40 min at 80 °C to remove most of the solvent (Fig. 1d). This CPI precursor is synthesized by polymerization of two equimolar moieties in NMP: 4,4′-oxydiphthalic anhydride (TCI America) and 2,2-bis[4-(4-aminophenoxy)pheny] hexafluoropropane (TCI America). The solution was stirred in a nitrogen-filled chamber for at least 24 h before use. For the outcoupling-enhanced scattering substrate, a freestanding pCPI film is obtained by spin coating the same CPI precursor solution (2 krpm for 90 s) on a glass substrate and immediately submerging the film for 20 min in a deionized water bath for immersion precipitation. The resulting pCPI film is then laminated to the backside of the dried CPI/TiO_2/AgNW (referred to as CPI/AgNW hereafter) stack prior to imidization to promote cross-linking of the CPI and pCPI end units and create a smooth, homogeneous interface (Fig. 1e). The full stack is then imidized (Fig. 1f) in a furnace (20 min at 160 °C followed by 20 min at 360 °C). At this stage, a freestanding pCPI/CPI/AgNW substrate is obtained by delaminating it from the carrier glass substrate (Fig. 1g). The scattering substrate prepared in this way consists of AgNWs embedded in a 50 μm-thick neat CPI film with a 6.3 μm-thick pCPI on the substrate backside, and the control substrate (CPI/AgNW) consists of AgNWs in a 50 μm thick neat CPI film. The optical characterization of the flexible substrates is conducted using an integrating sphere with a 350 W xenon lamp and a monochromator, in accordance with ASTM D1003-13. The sheet resistance of the substrates is measured with a custom four-point probe, and the morphology of the pCPI scattering layer is studied with FEI Helios NanoLab DualBeam (FIB/SEM) after coating the sample with 100 nm aluminum.

The CPI/AgNW substrates with and without the pCPI scattering layer were used to fabricate green and white phosphorescent OLEDs (PHOLEDs), with device structures shown in Fig. 2a and b, respectively. Each device was simultaneously fabricated on glass/ITO, CPI/AgNW, and scattering pCPI/CPI/AgNW substrate for direct comparison. First, a modified PEDOT:PSS (Heraeus) layer was deposited on each substrate via spin coating (2 krpm for 60 s) and annealed on a hot plate for 10 min at 150 °C. This is to achieve not only an efficient hole injection from ITO or AgNW, but a more uniform distribution of current in which sparse AgNWs are filled in with conductive PEDOT:PSS. The

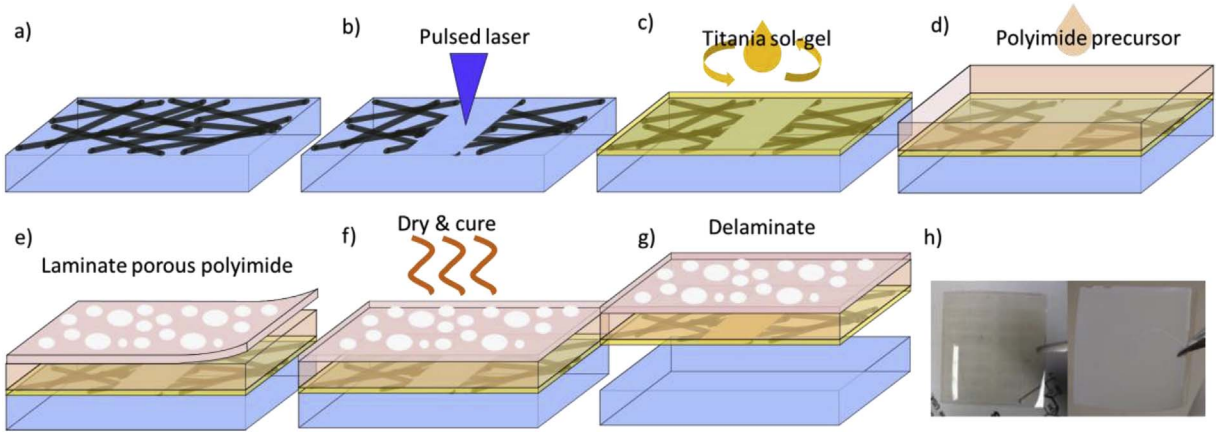

Fig. 1. a) AgNWs are spin coated on a clean glass slide. b) A UV pulsed laser is used to ablate the AgNWs for device integration. c) Titania sol-gel is spin coated. d) Colorless polyimide precursor is blade coated and dried under vacuum. e) Freestanding porous colorless polyimide is prepared and laminated on the polyimide precursor film. Note that this step is omitted for CPI/TiO_2/AgNW control substrates. f) The glass/AgNW/TiO_2/CPI/pCPI stack is imidized. g) The flexible substrate is delaminated from the glass carrier. h) Photographs of 3 × 3 cm^2 substrates of CPI/TiO_2/AgNW (left) and the hazy pCPI/CPI/TiO_2/AgNW (right).