A Simple Method for Fabricating Polymeric Light-Emitting Diodes

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A simple, inexpensive method involving chemical deposition of silver metal onto a polymer layer by noncatalytic chemical reduction from silver nitrate solution is used in the fabrication of polymeric light-emitting diodes (LEDs). The method yielded silver films with good polymer/metal interfaces and the resulting LEDs emitted light uniformly over the entire device area, but the emission efficiencies were lower by an order of magnitude compared to LEDs with vacuum-deposited metal electrodes. The chemical deposition of the metal film was carried out on a lab bench in open air without any special precautions. In addition to its cost advantage over vacuum deposition methods, the chemical process may also allow fabrication of polymer LEDs on nonflat and/or large area substrates.

Reported light emission from radiative recombination of injected charge carriers in a conjugated polymeric light-emitting diode (LED) expanded the scope of conductive polymers as potential candidate materials for light-emitting displays.[1] Advantages of conductive polymers over conventional materials include ease of synthesis, chemically tunable color of emission over the entire visible range, high emission efficiency, and ease of casting into large area films. These features, in addition to low processing costs associated with polymer synthesis, provided the driving force for rapid exploration of existing conjugated polymers along with the development of numerous luminescent homopolymers and blends for use in display applications. A polymer LED is typically a three-layer device in which a luminescent conjugated polymer is sandwiched between a high workfunction indium−tin oxide (ITO) (a transparent conductive oxide electrode serving the purpose of hole injection into the valence band of polymer) and a low work function metal electrode (acts as a source for electron injection into the conduction band of polymer). Typical metal electrodes used in the fabrication of polymer LEDs are aluminum, calcium, silver, gold, and Ag−Mg alloy. Metal electrodes are commonly deposited onto cast films of conjugated polymer by thermal evaporation in a high vacuum on the order of 10^{-6} Torr under clean room conditions. Occasional reports have also appeared on the use of cathodic sputtering as another method for metal deposition.[2]

Soon after the discovery of conjugated polymer electroluminescence (EL), the possibility of using polymers in flexible/nonflat displays was demonstrated by fabricating a MEH−PPV polymer LED on a flexible poly(methyl methacrylate) substrate with polyaniline and vacuum-deposited calcium as positive and negative electrodes, respectively.[3] In such LEDs fabricated on flexible substrates with vacuum-deposited metal electrodes, bending is likely to introduce stresses at the metal/polymer interface and in the metal film, causing interface failure. In view of the solution processibility of polymers, it should be possible to cast films on curved substrates by techniques such as dip coating for fabrication of nonflat displays. There is, however, a limitation on the shape/size of substrates that can be used for metal deposition by physical vapor deposition methods. More importantly, both vacuum evaporation and sputtering are cost intensive processes requiring high-cost capital equipment along with substantial operational expenses. This necessitates the need to explore other low-cost metal deposition processes for the fabrication of polymer LEDs.

Wet metal deposition processes such as electrolytic, electroless, and chemical methods have an edge over physical deposition processes in this regard and can be used to plate any size/shape of substrate. Among the chemical deposition processes, a chemical reduction method has no limit on the thickness of the film obtained and deposition continues as long as there is a supply of metal ions and reductant.[4] In this paper, we will report a very simple, inexpensive noncatalytic chemical reduction method as a process for the deposition of silver films useful in the fabrication of polymer LEDs.

Experimental Section

The xanthate precursor of poly(phenylene vinylene) (PPV) was synthesized according to the published procedure[5] and

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purified by repeated precipitation from methanol/acetone mixtures to remove unreacted monomer and base. The polymer was redissolved in THF at a concentration of 5 mg/mL and the polymer solution was filtered prior to spin-casting using a 5 μm syringe filter. ITO-coated glass plates (Photran Corp.) were thoroughly cleaned in an ultrasonic bath using trichloroethylene, acetone, 2-propanol, and deionized water. Simple photolithography and etching were performed to pattern substrates with a 4 mm wide ITO strip. Polymer films were coated on patterned ITO-coated glass substrates by spin-casting inside an argon-filled glovebox. The thermal elimination of the precursor PPV polymer films was carried out by heating at 170 °C for 2 h under high vacuum.[5] This was followed by deposition of a metallic silver layer onto polymer film using Brashear's process for silvering mirrors.[6] This involves the chemical deposition of a silver mirror by using a two-part solution. In this process, it is necessary to age the reducing solution for at least 1 week prior to its use. The $AgNO_3$ solution is generally prepared when used.

Reducing Solution (Aged). An 80 g portion of pure sugar was dissolved in 700 mL of distilled water. To this solution were added 175 mL of ethanol and 3 mL of concentrated HNO_3. Water was added to make up a solution of 1 L. This solution was then stored for at least 1 week at room temperature.

Silver Nitrate Solution (Fresh). A 2 g sample of $AgNO_3$ was dissolved in 5 mL of water. A potassium hydroxide solution was prepared separately by dissolving 1 g of KOH in 5 mL of water. Dilute aqueous ammonia was added dropwise to the $AgNO_3$ solution and the solution turned dark brown. Ammonia was continually added slowly until the precipitate was nearly but not quite all redissolved. At this stage, the KOH solution was poured into the $AgNO_3$ solution. Again ammonia was added little by little to redissolve the precipitate that formed upon adding KOH. It is necessary to make sure that excess ammonia is not added to completely redissolve the precipitate, as it influences the quality of silver films deposited. The solution was filtered to remove particles of undissolved precipitate and the filtered solution exhibited a brown tint.

Deposition Method. A quantity of reducing solution equal to about one-fourth of the fresh silver nitrate solution prepared was measured out. The polymer sample was masked with a film of Teflon to allow silver deposition only in a specified region. Samples were then laid out "face up" at the bottom of a glass beaker and a quantity of the fresh siver nitrate solution was poured into the beaker to cover the polymer sample. The measured amount of reducing solution was added to it and the mixture was stirred with a glass rod taking care not to scratch the sample surface. The solution turned black to brown and finally a light gray, indicating completion of the deposition. The sample was taken out, washed in water followed by a rinse in 2-propanol, and dried by blowing with compressed nitrogen. The silver metal film surface was gently wiped with a tuft of cotton to remove sediment; and the rinse and drying steps were repeated to obtain a shiny silver surface. Samples were then dried under high vacuum for at least 8 h to remove all moisture. Electrical contacts to the ITO strip and the deposited silver film were made using 36-gauge platinum wire and conductive silver paint.

Typical polymer and metal film thicknesses were found to be 35 and 80 nm, respectively, using a profilometer. The resulting devices had an active area of 4 mm × 4 mm. Current−voltage characteristics were measured under ambient conditions using a Kiethley 236 Source-Measure unit, while light intensity measurements were made with a calibrated Silicon photodiode attached to a Newport 1830-C Power meter. EL spectra were acquired with a Tracor-Northern 1710A diode array spectrometer. A Cambridge Stereoscan 120 scanning electron microscope was used to check the quality/continuity of the silver films.

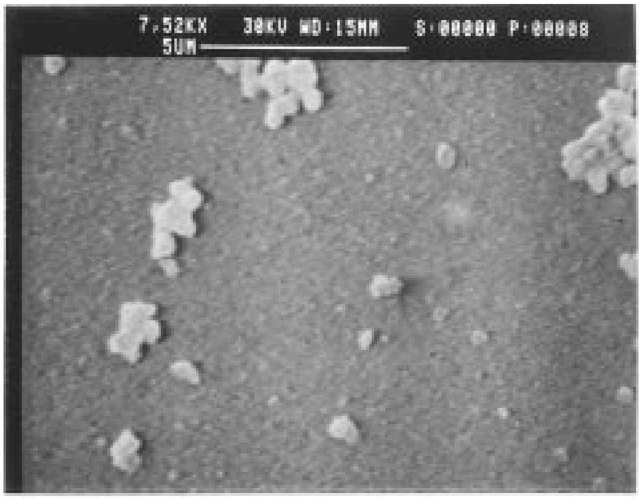

Figure 1. SEM micrograph of a chemically deposited Ag film surface.

Scheme 1

$$AgNO_3 + 3NH_4OH \longrightarrow [Ag(NH_3)_2]OH + NH_4NO_3 + 2H_2O$$

$$2[Ag(NH_3)_2]OH + R\text{-}CHO \longrightarrow 2Ag^0 + RCOONH_4 + H_2O + 3NH_3$$

Results and Discussion

The chemistry involved in the deposition of silver is based upon Tollen's test used for identifying aldehydes. The role of the nitric acid added to the sugar solution is to oxidize the terminal CH_2OH groups in the sugar to form aldehydes. Upon addition of the ammonical silver nitrate solution, the aldehyde groups are oxidized to carboxylic acids while the Ag^+ is reduced to give a deposit of silver metal. Reaction continues until all the Ag^+ is consumed and colloidal silver is deposited on all surfaces that were in contact with the reaction mixture. Scheme 1 shows the pertinent reactions.

Reaction conditions were observed to exert a great influence on the quality of films deposited. Strong reduction conditions which gave fast reaction rates resulted in gray or brown spongy films of poor quality, while slower reaction rates under mild reduction conditions yielded consistent films of good quality. Under the optical microscope, the polymer side of the silver film appeared very smooth and as shiny and reflecting as vacuum-deposited silver films. Figure 1 shows an SEM micrograph of a chemically deposited silver film. The films were observed to be continuous and contain agglomerations of silver grains, which is a characteristic of chemically deposited films from colloidal solutions. Figure 2 shows an EL spectrum of a ITO/PPV/silver (chemically deposited) device wherein the emitted light was yellowish green in color. EL spectra of devices prepared by vacuum evaporation of silver and chemical deposition of silver were found to be identical, confirming that it is a property of conjugated polymer and independent of the injection electrode deposition method, even though the emission efficiencies were observed to depend upon the fabrication method.

Figure 3a illustrates a typical forward-biased current−voltage ($I-V$) curve for an LED with a chemically

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(6) Laboratory Arts and Recipes. In *Handbook of Chemistry and Physics*, 38th ed., Hodgman, C. D., Weast, R. C., Selby, S. M., Eds.; Chemical Rubber Publishing Co.: Cleveland, 1956; p 3047. [It should be noted that unfortunately this section on Laboratory Arts and Recipes is not included in more recent editions of the *Handbook of Chemistry and Physics*.]

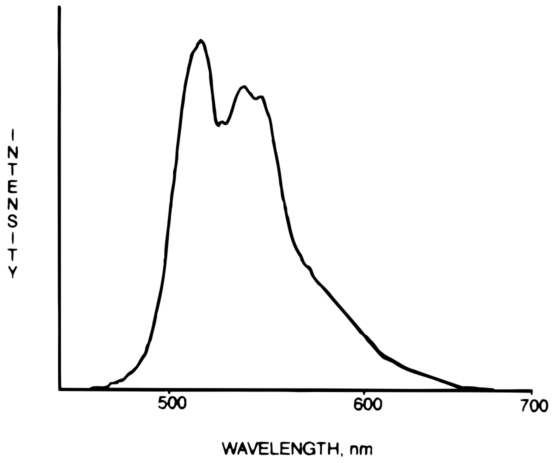

Figure 2. EL spectrum of PPV prepared via the xanthate precursor route.

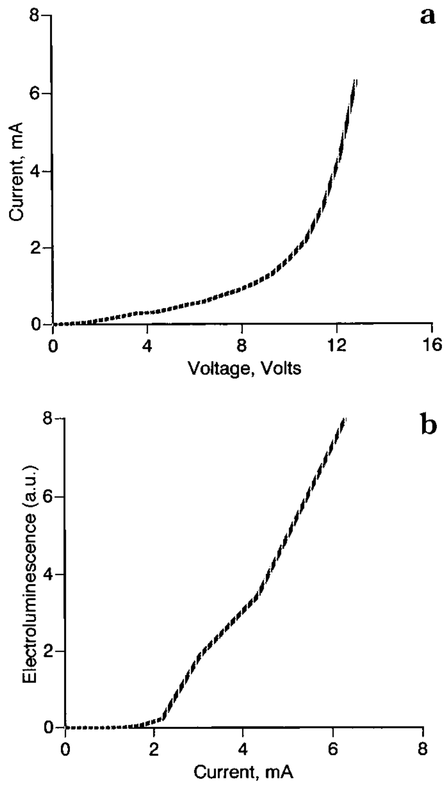

Figure 3. (a) $I-V$ curve for an LED with chemically deposited Ag electrode. (b) Light output vs current for an LED with chemically deposited Ag electrode.

deposited silver electrode. The knee-shaped curve is characteristic of diode operation and is similar to that observed for LEDs with vacuum-deposited metal electrodes. The physics involved in the operation of polymer LEDs is described in the literature.[7] The light onset, for LEDs with chemically deposited silver electrodes, was observed at applied fields of 1.4×10^6 V/cm, which is slightly higher than that reported for LEDs with vacuum-evaporated silver electrodes.[8] At 10 V, the light emitted by the device could easily be seen and devices exhibited lifetimes of approximately 2 h in air. $I-V$ curves of LEDs were found to be dependent on the fabrication conditions and vary from batch to batch, as also reported in the literature for LEDs with vacuum-deposited metal electrodes.[9] Figure 3b illustrates the variation of light emitted with total current passing through the device. Within experimental error, it was observed to follow a linear relationship, as observed in devices prepared by vacuum deposition techniques.

Although the light emission was uniform over the entire device area, LEDs with chemically deposited silver electrodes operated with about an order of magnitude lower efficiency compared to LEDs fabricated in our laboratory with vacuum-deposited silver as negative electrode. Lower efficiencies for these devices were not surprising since the deposition was carried out on a lab bench in open air without any special precautions. It is known that the crystallinity of metallic films can be improved by annealing after the films are deposited. Ample scope exists for further improvement in efficiency by subjecting the devices to annealing under vacuum before operation. Other polymer systems explored using chemical deposition of silver include poly(octyl thiophene-3-carboxylate) (POT-3-C), which emitted orange light with peak wavelength at 615 nm. POT-3-C was observed to show low emission efficiency with both vacuum-deposited and chemically deposited silver electrodes compared to LEDs fabricated with aluminum as negative charge injection electrode. This could be explained by taking the higher workfunction of silver and the resulting larger energy barrier for electron injection at the polymer/metal interface into consideration.

In conclusion, a very simple, inexpensive, noncatalytic chemical reduction method for the deposition of silver films for the fabrication of polymer LEDs has been demonstrated. The method yielded silver films with good polymer/metal interfaces and fairly smooth surfaces. This technique may be useful especially for light-emitting polymers with suitable electronic bandstructures that allow for charge injection with the relatively high workfunction silver electrode. By adopting other wet deposition processes, such as electroless plating developed for use in VLSI technology, it is possible to further improve the performance of LEDs.

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