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Extremely flexible, transparent, and strain-sensitive electroluminescent device based on ZnS:Cu-polyvinyl butyral composite and silver nanowires

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ABSTRACT

A multifunctional alternate current electroluminescent device (ACEL) was achieved by compositing ZnS:Cu particles in polyvinyl butyral (PVB) with two layers of percolated silver nanowire (AgNW) electrodes. The strong hydrogen bonding interactions and entanglement of PVB chains considerably strengthened the PVB, and thus, the cured mixture of ZnS:Cu particles and freestanding PVB required no additional support. The device was fabricated by embedding AgNWs on both sides of the ZnS:Cu-PVB composite film using an inverted layer process and intense-pulsed-light treatment. The strong affinity of PVB to the polyvinyl pyrrolidone (PVP) layer, which capped the AgNWs, mechanically stabilized the device to such an extent that it could resist 10,000 bending cycles under a curvature radius of 500 μm. Using AgNW networks in both the top and bottom electrodes made a double-sided light-emitting device that could be applied to wearable lightings or flexible digital signage. The capacitance formed in the device sensitively varied with the applied bending and unfolding, thus demonstrating that the device can also be used as a deformation sensor.

1. Introduction

The integration of electronic displays directly into or onto malleable materials such as biological tissues, textiles or elastic polymers is of increasing interest since such technology provides new opportunities in the field of display applications [1–3], such as wearable displays conformable to the complex surface of human skin. Two important emerging features of wearable displays for use on the skin are (1) the ability to provide soft, conformable contact with the epidermis in a manner that does not constrain the natural movement of the human body [4] and (2) high transparency that can make the devices invisible, thus protecting the privacy of the user. One of the most intuitive approaches to obtaining conformable devices is to use an ultrathin polymer substrate for the deposition of various organic and inorganic materials to construct ultrathin, flexible organic light-emitting diodes (OLEDs) [1]. In that case, the thinness of the device makes it not considered as a foreign substance by the user. Employing optically transparent materials for both the electrodes and emitting layers ensures the high transparency of the entire device.

Two inherent drawbacks of this approach, however, hinder its wide application in the fabrication of transparent conformable displays: the opaqueness of the metallic top electrodes [5–7] and the high sensitivity of organic materials to oxygen and water [8–11]. In order to resolve the first drawback, optically clear electrodes such as indium tin oxide (ITO), silver nanowires (AgNWs) or conductive polymers could be considered, but there are many parameters to simultaneously consider such as the work function or energy level, transmittance, and carrier transport or blocking efficiency of the materials. Regarding the poor tolerance of organic materials to oxygen and water, these materials could be encapsulated by thin films [12] or lamination with protective sheets [13]. However, issues remain with both of these approaches, namely, the costly process of atomic layer deposition (ALD) for the thin film approach and the increase in thickness that accompanies the lamination approach. Furthermore, current methods to fabricate highly efficient OLEDs based on small molecule materials generally require fully dry-processed apparatuses, leading to very high manufactur-

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ing costs and limiting their fabrication to a few large companies [14].

For the practical application of conformable displays, the fabrication scheme should be much simpler than the current industrial methods and based on solution processing. This would significantly lower the fabrication costs and facilitate practical conformable display applications with smaller markets, such as bio-medical and military devices [14]. Recent studies have reported that using inorganic light-emitting diodes (LEDs) can be a solution to this challenge due to its more moderate sensitivity to oxygen and water than that of organic materials [15–19]. However, the complicated procedure for attaining LEDs on flexible substrates hinders its practical use in fabricating flexible displays. Quantum dot (QD) LEDs are considered another possible candidate, but their fabrication procedure and most of their constituent materials are nearly identical to those of OLEDs, except for the QD-based emitting layers, implying that they are also costly and require the tuning of many experimental parameters [20–22]. Meanwhile, alternating-current-driven electroluminescent (ACEL) phosphors such as doped ZnS particles sandwiched between two electrodes have drawn considerable attention, since with these phosphors, light-emitting devices can be fabricated in a simpler manner and are less vulnerable to oxygen and water [23–25]. However, ACEL devices are typically composed of two electrodes, a substrate, a dielectric layer, and an emitting layer, and thus, the total thickness of the device is much thicker than that of OLEDs.

Herein, we introduce a novel concept that can eliminate the substrate and dielectric layer required to fabricate phosphor-based ACEL devices, thus achieving a thickness of only 25 μm. For this purpose, a composite material composed of ZnS:Cu particles and a freestanding polymer was fabricated, and inverted layer processing was employed to embed a percolated network of AgNWs in the surface of the composite. A counterpart electrode was formed by spin-coating AgNWs onto the opposite side of the composite, followed by irradiation with intense pulsed light (IPL). Some excellent results were achieved by this approach: the device was highly flexible and could withstand bending to a radius of 100 μm without the visible deterioration of the emitting performance, double-sided emission, or transparency (transmittance higher than 60% at 550 nm). Interestingly, the capacitance formed at the emitting layer was sensitive to the bending of the device, which demonstrates that the device could also be used to measure the mechanical strain induced in it.

2. Experimental procedures

2.1. Materials

Polyvinyl butyral (PVB, Butvar B-98, Mn = ~36,000 g/mol) whose hydroxyl content in polyvinyl alcohol was about 18%, was purchased from Victorchem, Korea. Hexamethylene diisocyanate (HDI) and N,N'-dimethylformamide (DMF) were obtained from Tokyo Chemical Industry, Japan. All chemicals were used as received without purification. A 0.5 wt% AgNW solution dispersed in isopropanol (IPA) was purchased from Dittotechnology Ltd., Korea. The average diameter and length of the nanowires were 35 nm and 20 μm, respectively. The AgNW dispersion was used as received without removing the polyvinyl pyrrolidone (PVP) that capped the nanowires.

2.2. Fabrication of ACEL devices

The fabrication procedure is schematically described in Fig. 1. A glass substrate was first cleaned sequentially with detergent, de-ionized water, IPA, and acetone. The dispersion of AgNWs was spin-coated onto the glass and heated on a hot plate at 80 °C for 10 min to remove any remaining organic solvent from the coated layer. To prepare the polymer, 2 g of PVB was dissolved in DMF (20 mL) by sonication for 5 min, and 0.3 g of HDI was added to the solution. Then, ZnS:Cu microparticles (National EL Technology, Korea) mixed into the prepared PVB solution (in a weight ratio of 1:1) were spin-coated (spin velocity: 800 rpm, duration time: 60 s, temperature: 25 °C) onto the AgNW-coated glass, followed by curing at 80 °C overnight to cross-link the polymer; this procedure resulted in a film with a thickness of 25 μm. Another layer of AgNWs was spin-coated onto the cured ZnS:Cu-PVB film and dried at 80 °C for 10 min. The samples were exposed to 500 μs pulses of intense light using a photonic sintering system (Sinteron 2000, Polytec Ltd., USA) operating at an input voltage of 1.9 kV to enhance the adhesion between the AgNWs and PVB. The samples were soaked in water at 25 °C for 10 min to induce the hygroscopic swelling of the PVB film, which enabled safely peeling the film from the preliminary substrate (glass).

2.3. Evaluation of the devices

A field-emission scanning electron microscope (FESEM; JSM6700F, JEOL Ltd., Japan) was used to investigate the microstructure of the AgNW networks. The optical transmission was measured using a UV–vis spectrophotometer (V-560, Jasco, Japan), while the sheet resistance (R_s) was measured using a non-contact measurement system (EC-80P, Napson Corporation, Japan). The surface morphology was investigated by an atomic force microscope (AFM; XE-100TM, Park Systems, USA). An automatic bend-testing machine (Bending Tester, Jaeil Optical System, Korea) was used to measure the long-term reliability of the devices under repeated bending cycles at a rate of 1.2 cycles/min. An AC power source (6600 series, Extech Electronics, Taiwan) was used to power the emitting devices, and the luminance was measured by a luminance meter (LS-100, Konica Minolta, Japan). The dynamic capacitance of the devices was measured using an oscilloscope (ZM2353, NF, Japan). Most of the parameters were measured on more than 10 replicate samples.

3. Results and discussion

Revisiting the typical fabrication scheme for flexible ACEL devices, four essential layers must be sequentially deposited on the freestanding polymer: an electrode, a dielectric layer, a phosphor layer, and a counterpart electrode [26]. However, the size of the phosphor particles employed in typical ACEL devices ranges from 10 to 30 μm, and the thickness of the commercially available and mechanically reliable polymer films is thicker than 25 μm, the total thickness of the devices can be ~100 μm, which is not appropriate for a highly flexible device. If we consider that the strain formed on the surface of a film is equal to its thickness divided by twice the bending radius, the thickness must be significantly reduced to enable highly flexible devices. In order to reduce the device thickness, we designed a new structure of ACEL devices comprising a composite film of ZnS:Cu particles dispersed in a freestanding polymer and two transparent AgNW electrodes, thus eliminating substrate and dielectric layers from the device structure. Therefore, we first synthesized a polymer that could be used as a binding material for ZnS:Cu particles. This polymer should be solution-processible, optically transparent, mechanically stable, and freestanding, thereby eliminating the need for a separate substrate for the structure. Colorless polyimide (cPI) varnish was a potential candidate for this purpose because of its high transparency, high modulus of elasticity, and mechanical stability [27,28]. However, the high light absorption of cPI caused by aro-

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