Silver nanowire transparent electrodes for liquid crystal-based smart windows

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A B S T R A C T

A significant manufacturing cost of polymer-dispersed liquid crystal (PDLC) smart windows results from the use of indium tin oxide (ITO) as the transparent electrode. In this work, films of silver nanowires are proposed as an alternative electrode and are integrated into PDLC smart windows. Both the materials and fabrication costs of the nanowire electrodes are significantly less than that of ITO electrodes. Additionally, nanowire electrodes are shown to exhibit superior electro-optical characteristics. The transmittance of a nanowire electrode-based PDLC smart window is both higher in the on-state and lower in the off-state compared to an equivalent device fabricated using ITO. Furthermore, it is found that a lower external field strength (voltage) is required to actuate the nanowire-based smart window.

1. Introduction

Electronically switchable windows, or “smart windows”, enable alteration of their optical properties (transparency, translucency) with an applied electric field. There are currently three different technologies used to fabricate optoelectronically active components for smart window technology: chromic materials, suspended-particles, and polymer dispersed liquid crystals (PDLC) [1]. PDLC smart windows are used in the architectural and automotive industries due to their relatively simple fabrication process, durability, fast switching speed, and low transmittance in the “off” or translucent state [2]. These windows can be used as switchable privacy glass or as energy saving windows through the modulation of solar heat gain [1,3,4].

The operating principle behind PDLC-based smart windows involves the use of an electric field to actuate an optoelectronically active PDLC film sandwiched between two parallel transparent electrodes. An alternating voltage potential is applied across the two electrodes to “switch” the film between a translucent “off” state and a transparent “on” state. The cost of these transparent electrodes is a significant issue for increased adoption of PDLC smart windows [1]. Candidate transparent electrodes require a balance of high transparency, low sheet resistance, and low-cost. While the benefits of increased transparency and low-cost are obvious, low sheet resistance is beneficial in minimizing the voltage drop across the electrode [5,6] and to ensure fast switching times [7,8]. Most commonly, the transparent electrode type used in the manufacture of PDLC smart windows and other optoelectronic devices is indium tin oxide (ITO). These ITO transparent electrodes are relatively high-cost due the cost of indium metal and its processing into ITO. This cost is exacerbated by the fact that PDLC-based smart window deployments involve large surface areas on the order of ~1 m² compared to other applications of ITO electrodes such as LCDs where surface areas are on the order of ~0.1 m². Furthermore, the fabrication of smart windows on plastic substrates instead of glass is often desired because plastic substrates are lightweight, flexible, and can be laminated onto existing windows. However, the temperatures typically used for ITO deposition are not compatible with plastic substrates, so lower than ideal deposition temperatures must be used which results in higher sheet resistances.

There are several candidate materials for manufacturing alternatives to ITO-based transparent electrodes. They include conductive polymers [9], graphene [10], carbon nanotubes [11,12], metallic grids [13], and copper [14,15] or silver nanowires [16–18]. The first two options have been successfully integrated into PDLC smart windows [19,20]. In the case of conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) was used. Its performance in the on-state; however, results in lower transmittance than the traditional ITO electrodes [20]. Additionally, such conductive polymers are known to be unstable in air [21]. In the case of graphene-based...
electrodes, quantitative results have yet to be published. However, graphene electrodes are known to provide lower transmittance than ITO at a given sheet resistance and their fabrication process is typically complex [22].

This study presents the first results using silver nanowire electrodes integrated into PDLC-based smart windows. These electrodes provide significant promise compared to other ITO alternatives due to their low cost, high conductivity, and high transmittance [22–26]. They are more mechanically flexible than ITO and can be deposited at room temperature with roll-to-roll fabrication processes [27]. Furthermore, unlike ITO electrodes, silver nanowire electrodes maintain a high transparency at infrared wavelengths [17] which is useful in applications where solar gain is regulated.

In this letter, a PDLC smart window using silver nanowire electrodes is demonstrated for the first time. The electro-optical characteristics of the device are measured and compared to an equivalent ITO device. It is shown that the nanowire electrodes have superior performance characteristics compared to traditional ITO electrodes while being lower in cost.

2. Concept and methods

2.1. Silver nanowire electrode

Silver nanowire transparent electrodes have received much attention in the past five years. These electrodes consist of a film of randomly-oriented silver nanowires (see Fig. 2b). When the density of nanowires is high enough, there is a conductive path for electrical current to flow from one end of the film to the other. Silver nanowires can be synthesized in solution by the well-known polyl process, where silver nitride is reduced in ethylene glycol in the presence of poly(vinyl pyrrolidone) (PVP) [28,29]. In this work, silver nanowires dispersed in ethanol with an average diameter of 35 nm and an average length of 15 μm were supplied by Blue Nano Inc. Using the Mayer rod coating method [18], films of nanowires were uniformly deposited on 5 × 5 cm polyethylene terephthalate (PET) substrates of 125 μm thickness. The nanowire density was selected so that a sheet resistance of 50 Ω/sq was obtained. The films were dried in air for 5 minutes and then rinsed with acetone to remove any remaining polyvinylpyrrolidone (PVP) left as a result of nanowire synthesis. The nanowires were then embedded in the surface of the PET substrate using a rolling press (MSK-HRP-01, MTI Corporation). Rolling serves several purposes [30]: (i) reduction of the sheet resistance of the film by mechanical welding of overlapping nanowire junctions, (ii) reduction of the surface roughness of the film to prevent electrical shorts between the two electrodes at final device assembly, and (iii) to promote adhesion of the nanowires to the substrate. By avoiding the annealing step typically used in the preparation of nanowire electrodes [17,24], this simple room temperature process avoids deformation of the plastic substrates resulting from elevated temperatures.

2.2. Polymer dispersed liquid crystal layer

A cross-sectional schematic of the PDLC smart window fabricated in this work is shown in Fig. 1. A PDLC layer is sandwiched between two transparent electrodes; the PDLC layer is composed of a nematic liquid crystal mixture (E7) guest phase domains dispersed in a polymer matrix (NOA-65) host phase. This film is formed via phase separation above the nematic transition temperature of the LC so that phase separation results in spheroidal nematic domains. In the absence of an electric field (the “off” state), the liquid crystal droplets are randomly oriented. In this state, incident light is scattered due to both the birefringence of the LC domains and a refractive index mismatch of the LC/polymer [31] which results in a translucent film. When a voltage potential is applied across the two electrodes the electric field aligns the liquid crystal droplets parallel to the electric field, correlating the optical axes of each droplet. In this state, incident light is no longer scattered given that the indices of refraction of the guest and host phases are commensurate and results in a transparent state (the “on” state).

The structure and size of the LC droplets dispersed in the polymer matrix phase can be controlled through the conditions of phase separation. The most common methods of PDLC film formation are polymer-, thermal-, and solvent-induced phase separation. In this work polymer-induced phase separation is used since it results in the most durable films [31] and is the method predominantly used in the manufacture of PDLC-based smart glass [31].

2.3. PDLC device fabrication

The PDLC layer in this work used a 1.6:1 weight ratio of E7 to NOA-65 monomer mix [31] and 22–27 μm diameter (Cospheric LLC) silica microsphere spacers to impose a uniform thickness of the PDLC film. Conductive copper tape was first applied to one end of each transparent electrode to act as connector points for later

Fig. 2. (a) Transparency spectra of silver nanowire and ITO films of the same sheet resistance. (b) SEM image of the silver nanowire electrode.
device testing. The E7, NOA-65, and silica were then thoroughly mixed into a transparent solution and spread over one electrode. The second electrode was placed on top with the copper connector facing in the opposite direction of the first (Fig. 1). Two flat sheets of glass were used to sandwich the whole device for several minutes in order to displace excess mixture from the device to achieve a uniform PDLC film thickness.

The PDLC device was then placed into a UV chamber and exposed for 10 min to 365 nm ultraviolet light, curing the NOA-65 matrix. Complete curing of the device is evident when the transparent mixture transitions into a translucent film. A final cleaning of the outer surfaces of the device with methanol completes the fabrication of the PDLC device.

2.4. Characterization

The transparencies of the nanowire and ITO electrodes were measured using a UV–vis spectrophotometer (Shimadzu, UV-2501 PC) with an uncoated PET substrate as a reference. Electrode sheet resistances were measured using a multimeter after affixing copper tape to the ends of each electrode. The nanowire electrodes were imaged in a scanning electron microscope (SEM) after coating the electrode with a 10 nm thick gold layer to prevent electron charging. To characterize the fabricated smart windows, an alternating voltage potential (0–100 V) was applied across the films inline with a spectrophotometer with an integrating sphere for measurements of transparency, haze, and reflected light.

3. Results and discussion

Fig. 2a shows the specular transmittances (unscattered transmitted light) of the silver nanowire and ITO electrodes. The nanowire electrode is slightly more transparent than ITO. At 550 nm, the transparency of the nanowire and ITO electrodes are 92.4% and 89.6%, respectively. An SEM image of the nanowire electrode is shown in Fig. 2b.

The materials used to synthesize silver nanowires cost approximately $32.50/g of nanowires obtained [14]. The material cost of ITO is much less expensive, at $2.40/g [32]. However, due to the small amount of silver nanowires used to achieve an electrode with a sheet resistance of 50 Ω/sq, 0.02 g/m², the material cost for film formation is $0.70/m². The materials cost of a 50 Ω/sq ITO electrode, on the other hand, is approximately $1.60 m² (assuming a required ITO film thickness of 100 nm [33,34] which would require 0.6 g of ITO per square meter [35]). Furthermore, the fabrication cost of ITO (estimated to be 1.10/m² [36]) is higher than that of silver nanowire electrodes, the latter of which does not require vacuum or specialized equipment, and can be deposited in a roll-to-roll process.

Nanowire electrodes are structured as two-dimensional networks on a micro scale, in contrast to ITO electrodes which are uniform films. For a 50 Ω/square nanowire electrode, the characteristic lengthscale between nanowires is approximately 2 μm (Fig. 2b). Given that the electrooptically active domains in the PDLC film are on the order of 1 μm, there is the possibility of
non-uniform electric field effects in the transparent “on” state. However, from the images in Fig. 3a and b which show the PDLC-based smart window using nanowire electrodes, it can be seen that the window is uniform in both on and off states for the surface coverages used in this work. This indicates that the electric field between the nanowire electrodes is sufficiently uniform.

The variation of specular transmittance (transmitted light through the device without scattering) and haze (transmitted light that is scattered) on the applied voltage for both the nanowire-based and ITO-based window devices is shown in Fig. 3c and d. In the off state (0 V), almost all the incident light in both devices is forward scattered or reflected. As the voltage potential increases, more of the incident light is transmitted through the device without scattering and saturates above a critical voltage. As can be seen in Fig. 3c, the nanowire-based device reaches its maximum specular transmittance of 58.5% at 50 V while the ITO-based device reaches its maximum transmittance of 50.5% at 85 V. Thus, the nanowire-based device is not only more transparent in the on state, but it can also be operated at a lower voltage which results in lower energy consumption. Referring to Fig. 3d, the haze of the nanowire-based device in the on-state is also superior to the ITO-based device, being 8% less.

Fig. 4a shows the specular transmittance versus wavelength for both devices in the on and off states. 85 V was selected as the on state voltage as according to Fig. 3c the transmittance of both devices is saturated at this voltage. The transparency difference at 550 nm between the on and off states for the nanowire-based device, \( \Delta T_{\text{on-off}} \), is 57.3% (58.5% in the on state and 1.2% in the off state). \( \Delta T_{\text{on-off}} \) for the ITO-based device is 46.4% (50.5% in the on state and 4.1% in the off state). The higher transmittance in the on-state and the lower specular transmittance in the off-state of the nanowire-based device are desirable attributes for use as smart windows.

The 8% higher transmittance of the nanowire-based device in the on-state cannot solely be explained by the higher transparency of the two nanowire electrodes alone, as each nanowire electrode has only a 2.8% higher transparency than ITO. The higher transmittance is likely also due to less light being scattered at each nanowire electrode compared to the ITO case. ITO has an index of refraction of 1.9 [22]. Because this is higher than the refractive index of PET \((n=1.6 [37])\) and the PDLC layer \((n=1.5 [38.39])\), some light will reflect at each of the two PET/ITO and ITO/PDLC interfaces. The nanowire film, on the other hand, only covers 10% of the PET surface and thus it is expected that less light would reflect and refract at the PET/nanowire-film and nanowire-film/PDLC layer interface. The slightly higher transmittance of the ITO-based device in the off-state may be because some of the light backscattered by the PDLC is internally reflected at the first ITO/polymer interface and gets transmitted forward.

Fig. 4b shows the light incident on the two types of devices that is reflected backwards toward the light source. The difference of reflectivity in the off and on states for the nanowire-based device is 14.3% (23.6% in the off-state and 9.3% in the on-state), while for the ITO device it is 9% (15.5% in the off-state and 6.5% in the on-state). A higher modulation range is advantageous for solar gain applications. The higher reflection of the nanowire-device is likely because metals are reflective and do not absorb much visible light. ITO on the other hand will absorb up to half of the untransmitted light in the visible range [40].

By decreasing the density of the nanowires on the electrode, a higher transparency is obtained with a trade-off of a higher sheet resistance. PDLC smart windows fabricated using silver nanowire electrodes with sheet resistances of 100 \( \Omega \)/square were also tested. These devices worked successfully with on and off transmittances of 63.5% and 1.1%, respectively \((\Delta T_{\text{on-off}}=62.4\%)).\) If a lower sheet resistance is required to minimize the voltage drop across the electrode, a higher density of nanowires can be used. Table 1 tabulates what transparency and sheet resistances can be obtained through varying the nanowire density.

The PDLC device fabricated using nanowire electrodes operated successfully when the device was bent to a radius of curvature of 20 mm and thus these devices can be formed onto curved geometries. Although the silver nanowire electrodes themselves can be bent to lower radii of curvature without degradation, and maintain their sheet resistances after repeated bends [25], the flexibility of the PDLC device is limited by the PDLC layer. The PDLC layer delaminates from the electrodes at lower bending radii or after repeated bends.

4. Conclusions

Silver nanowire electrodes are a viable alternative to ITO for use in PDLC smart windows. The material and fabrication costs of
silver nanowire films are lower than ITO and enable superior optical transparency performance. The transparency of nanowire PDLC smart windows can be modulated over a larger range, with $\Delta T_{on-off}=57\%$ versus $\Delta T_{on-off}=46\%$ for the ITO-based devices. A lower voltage supply is required to operate the nanowire-based device since its on-state can be reached 15 V lower than the ITO-based device. The presented results support the use of nanowire electrodes to both increase performance and lower the cost of PDLC-based smart windows. Furthermore, these results support the use of nanowire-based electrodes for a range of other liquid crystal and smart window technologies.

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