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Hybrid transparent conductive electrodes with copper nanowires embedded in a zinc oxide matrix and protected by reduced graphene oxide platelets

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Transparent conductive electrodes (TCE) were fabricated by combining three emerging nanomaterials: copper nanowires (CuNWs), zinc oxide (ZnO) nano-particulate thin films, and reduced graphene oxide (rGO) platelets. Whereas CuNWs are responsible for essentially all of the electrical conductivity of our thin-film TCEs, the ZnO matrix embeds and strengthens the CuNW network in its adhesion to the substrate, while the rGO platelets provide a protective overcoat for the composite electrode, thereby improving its stability in hot and humid environments. Our CuNW/ZnO/rGO hybrid electrodes deposited on glass substrates have low sheet resistance ($R_s \sim 20 \ \Omega/sq$) and fairly high optical transmittance ($T_{550} \sim 79\%$). In addition, our hybrid TCEs are mechanically strong and able to withstand multiple scotch-tape peel tests. Finally, these TCEs can be fabricated on rigid glass as well as flexible plastic substrates. © 2016 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4942213]

I. INTRODUCTION

Transparent conductive electrodes (TCEs) usually come in the form of thin films and have both high optical transparency (in a desired range of wavelengths) and high electrical conductivity.¹ Although they are rarely seen as independent devices in their own right, TCEs have been integrated into the fabric of a vast array of common opto-electronic devices and systems. For instance, liquid crystal displays (LCDs) currently provide the largest single market for TCE products.^{2–5} As an example, recall that a sheet of TCE resides beneath the touch-screen display of every iPhone in use today. Another example is provided by the large number of installed photovoltaic modules, each of which requires a TCE as a window to transmit visible and near infrared sunlight to the solar-active material, and then to collect and conduct the photoelectric current that is generated within the cell.^{6–10}

In the aforementioned applications, indium tin oxide (ITO) has always been favored as the TCE material due to its superior optical transmittance and excellent electrical conductivity.^{11,12} In addition, the physical and chemical stability of ITO and its endurance in the face of environmental adversity have been decisive factors in its widespread commercial success. However, ITO has its own drawbacks, the most prominent of which being the fact that indium is a scarce element whose worldwide supply is not expected to meet the rapidly growing market demands. According to a report from the U.S. Geological Survey's Mineral Resources Program, the annual average price of indium form U.S. producers has risen from \$565 to \$735 per kilogram over the past 5 years. Another shortcoming of ITO is its mechanical inflexibility, considering that a number of new technologies such as wearable electronics require the transparent electrodes to be flexible or even deformable.^{13,14} Although ITO can be deposited on flexible substrates such as polyethylene terephthalate (PET), its electrical conductivity rapidly degrades and eventually disappears after multiple bending cycles, especially for small bending radii. The bottom line is that, while ITO has successfully met the stringent requirements of existing applications, finding suitable substitutes for ITO will be crucial for the continued growth and expansion of the opto-electronics industry.

Several materials have been developed and studied in the past decade as candidates to replace ITO: metal mesh,¹⁵ metallic nanowires such as silver nanowires (AgNWs)¹³ or copper nanowires (CuNWs),¹⁴ conductive metal oxides such as fluorine tin oxide (FTO),¹⁶ zinc oxide (ZnO),¹⁷ and doped zinc oxide,² and carbonous materials such as carbon nanotubes⁵ and graphene.⁶ Each of these emerging materials has its own advantages and disadvantages. For example, CuNWs can be synthesized fairly easily and inexpensively in large quantities, but they lack long-term stability; both zinc oxide and graphene can be highly transparent in the visible wavelength range, but their sheet resistance is inferior to that of ITO.

Next generation opto-electronic devices require TCEs to not only have good optical transmittance and sheet resistance but also possess properties such as flexibility, stability in harsh environments, and longevity. Hybridization can help overcome the shortcomings of the new classes of TCE materials by combining their strengths. In the present work, we synthesized CuNWs via a one-pot solution method and used a traditional sol-gel deposited ZnO thin film to embed and anchor the CuNWs onto the substrate. These transparent conductive electrodes, having sheet resistances in the range of 10 to 50 Ω /sq, exhibit excellent electrical conductivity, while their optical transmittance across the visible spectrum exceeds 75%. In order to improve the long-term stability of

119, 085303-1

our TCEs in harsh environments, we applied a reduced graphene oxide (rGO) cover layer via spin-coating followed by annealing in a forming gas atmosphere. Our rGO-coated samples exhibit significant improvement over unprotected samples as demonstrated by their stable sheet resistance in a harsh environment (85% relative humidity at 85°C) during several days of testing.

II. METHODS

A. Fabrication of CuNW TCE

Details of the synthesis of CuNWs have been described in our previous publication.¹⁷ CuNW-based TCEs can be fabricated on rigid glass as well as flexible polyethylene naphthalate (PEN) substrates. Before deposition, the glass substrates were cleaned with piranha solution and stored in Deionized (DI) water. PEN substrates were cleaned using an organic solvent (Isopropyl alcohol, IPA) and DI water.

To fabricate the CuNW TCEs, clean substrates were affixed to a hot-plate maintained at $60 \,^{\circ}$ C. An airbrush was used for spray-coating the desired volume of CuNW solution onto the substrate. Subsequent to the deposition of nanowires, the samples were placed in a plasma-cleaner and exposed to air plasma for 100 s to weld the nanowires at their crossing points in order to bring about electrical conductivity across the sample.

B. Sol-gel deposition of zinc oxide thin film

The ZnO precursor is prepared by mixing diethanolamine, zinc acetate, and 2-methoxyethanol. The precursor mixture was vigorously stirred to achieve a homogeneous solution. Before deposition, the solution was aged for at least 24 h. Subsequent to aging, the ZnO precursor solution was pipetted onto the CuNW samples and spun at 1000 rpm for 45 s, followed by another round of spinning at 4000 rpm for 15 s. After the deposition, the CuNW/ZnO thin film was annealed in a forming gas environment (95% $N_2 + 5\%$ H₂) at a moderate temperature for 1 h.

C. Deposition and reduction of GO platelets

GO solution with concentration of 6 mg/ml was purchased from Graphene Supermarket. Before use, it was diluted to 0.2 mg/ml with IPA and sonicated in a water bath. GO was spin-coated on bare CuNW TCEs for purposes of comparing their scotch-tape-resistance and also for passivation of CuNW/ ZnO thin films. The spin-coating parameters were the same as those used for coating ZnO thin films. After the GO deposition, the samples were annealed in a forming gas environment at $250 \,^{\circ}$ C for 1 h, which resulted in partial reduction of the graphene oxide platelets.

D. Characterizations

We measured the sheet resistance of our samples using the 4-probe method with a Keithley 2400 unit. Optical transmittance spectra were measured using a Cary-3000 UV-Vis spectrometer and corrected with blank substrates as baselines. Scanning electron microscope (SEM) images were taken using a Hitachi 4800 SEM. Grazing angle SEM images were taken by mounting the samples vertically and tilting the stage by 5°.

III. RESULTS AND DISCUSSIONS

In our previous work,¹⁷ we demonstrated that the synthesized CuNWs have an average length of $70 \,\mu m$ and an average diameter of 45 nm. Depending on the amount of CuNW solution used during spray-coating, our fabricated TCEs exhibit a range optical transmittance and sheet resistance values, as shown in Fig. 1(a). It is clearly seen that sheet resistance R_s and optical transmittance T have an inverse relationship. Our best CuNW TCE on a glass substrate has $R_s = 22.4 \Omega/sq$ and T = 88% at a wavelength of 550 nm. For a CuNW network deposited on a flexible PEN substrate, the sheet-resistance is seen in Fig. 1(a) to have slightly increased to $R_s = 36 \Omega/sq$, while the optical transmittance remains essentially the same as that for the sample on a glass substrate. To demonstrate the flexibility of the CuNW TCE on a plastic substrate, we bent our samples, including CuNW and CuNW/ZnO, on PEN substrates with a radius of $\sim 5 \text{ mm}$ in multiple cycles of compressing and stretching. As shown in Fig. 1(b), the sheet resistance of the samples did not change much after 1000 bending cycles.

Although our CuNW TCEs have good sheet resistance and high optical transmittance, their adhesion to the substrate is rather weak. Figure 2(a) shows photographs of two CuNW TCEs on glass substrates (one bare sample and one covered with rGO platelets) both before and after a scotch-tape peel



FIG. 1. (a) Optical transmittance (at the wavelength of 550 nm) versus the sheet resistance for CuNW samples fabricated on glass substrates, on PEN substrates, and on glass substrates while embedded in ZnO. (b) Sheet resistance versus number of bending cycles of CuNW and CuNW/ZnO samples on PEN substrates. The inset is a photograph of a flexible sample of a CuNW TCE on PEN held over the OSC logo.

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FIG. 2. (a) Photographs of bare CuNW and CuNW/rGO samples before and after a scotch-tape-peel test; yellow boxes indicate the taped areas. (b) Sheet resistance of CuNW/ZnO samples on rigid glass substrates and also on flexible plastic (PEN) substrates versus the number of scotch-tape-peel tests. The embedding of the nanowire network within the ZnO matrix clearly improves the adhesion of CuNWs to the glass substrate.

test. It is seen that the right-half of the bare sample and the bottom-half of the rGO-coated sample (inside the yellow box, where the scotch tape was applied) are more transparent because the tape has effectively peeled off and removed the copper nanowires from the substrate. A subsequent measurement of sheet resistance also confirmed that the portion of the samples within the yellow boxes of Fig. 2(a) had lost their electrical conductivity after the removal of the scotch tape.

In order to improve the adhesion of our CuNWs to the substrate, we deposited a coating/embedding layer of ZnO via the sol-gel deposition method. After the network of CuNWs on a glass substrate was plasma-treated, the ZnO precursor was cast onto the CuNWs and made to spread evenly using a spin-coater. The hybrid film was then annealed in a forming gas environment at a moderate temperature for 1 h. The CuNW/ZnO film has slightly reduced transmittance compared to the bare CuNW sample, which can be readily inferred from the data plotted in Fig. 1(a). However, the hybrid film now firmly adheres to the substrate, as confirmed by a repeated application of the scotchtape peel test. As shown in Fig. 2(b), the CuNW/ZnO TCE is mechanically strong, without suffering an appreciable loss of conductivity after five consecutive applications of the scotch-tape peel test. This enhancement in adhesion to the substrate was observed for both glass and flexible substrates. For a comparison, we deposited a GO thin film layer on top of the bare CuNW sample on glass and proceeded to reduce the GO to form a protective coating of rGO over the entire area of the sample. Figure 2(a) reveals that the sample was still vulnerable to the tape test; upon removing the scotchtape, the bottom-half of the CuNW/rGO sample (inside the yellow box, where the tape was applied) had lost much of its nanowire network and, therefore, become non-conductive.

We imaged the bare CuNW sample as well as the CuNW/ZnO sample on a glass substrate using a SEM. Images were captured in both frontal view and edge view (at 5° grazing angle). These images are shown in Fig. 3. Figures 3(a) and 3(b) show, respectively, the frontal and edge views of a bare CuNW film deposited on a glass substrate. The CuNWs are seen to be elevated slightly above the flat surface of the substrate, which, in all likelihood, is the cause for their poor adhesion to the substrate. In contrast, in Figs. 3(c) and 3(d), CuNWs are seen to be covered and anchored to the substrate by the ZnO thin-film; the surface of the hybrid film also

appears to be smoother. Specifically, at the wire-wire junctions, the ZnO film appears to have flattened and smoothed the originally elevated surface of the CuNW network.

With the CuNW network buried under the ZnO thin film, our TCEs are mechanically stable and resistant to scotch-tape peel. However, both CuNW and ZnO are known to degrade over time in air, and more drastically, in hot and humid environments. In our previous work,¹⁷ we have demonstrated the effectiveness of using an rGO layer as passivation for improving the lifetime of CuNW TCEs in harsh environments. The carbon atoms in a 2-D graphene sheet are about 1.42 Å apart, while the oxygen and water molecules are about 3.5 Å and 2.7 Å in diameter, respectively. That, we believe, is the reason why a graphene coating layer prevents the penetration of water and oxygen molecules. We thus prepared and tested CuNW/ZnO/rGO samples together with unprotected CuNW/ZnO samples on both glass and flexible substrates in a controlled environment with 85% relative humidity at $85 \,^{\circ}$ C for four days. Figure 4(a) shows the optical transmittance spectra of CuNW, CuNW/ZnO, and CuNW/ ZnO/rGO samples deposited on glass substrates. Since we are using rGO platelets that have a lateral dimension of several micrometers, a stack of several rGO layers is needed to produce a rather complete coverage of the CuNW/ZnO thin film underneath. This explains the loss of optical transmittance (upon addition of the rGO layer) that is greater than the typical 2.3% for single layered graphene (see Figure 4(a)). The sheet resistance of the samples was monitored and recorded at 12 h intervals. Figure 4(b) shows the change of the sheet resistance during the four-day period of the study. It is seen that, while the sheet resistance of the unprotected CuNW/ZnO film deteriorates substantially over time, the protected CuNW/ZnO/rGO sample remains quite stable, with only a slight increase observed in its sheet resistance after four days of exposure to the harsh environment.

Figure 4(c) shows a frontal SEM image of a CuNW/ ZnO/rGO sample. While the embedded CuNWs are visible beneath the surface of the ZnO film, the rGO platelets are seen to blanket the entire surface of the hybrid CuNW/ZnO sample. In the top-left corner of the image, a few wrinkles are visible in the rGO layer. The rGO passivation prevents oxygen and moisture from attacking the nanowires through the pores (and occasional cracks) within the ZnO matrix, thereby improving the overall stability of the TCE in normal as well as harsh environments.



FIG. 4. (a) Transmittance spectra of CuNW, CuNW/ZnO, and CuNW/ZnO/rGO samples deposited on glass substrates. (b) Measured sheet resistance versus the number of days during which the samples were exposed to 85% relative humidity at 85 °C. The reduced graphene oxide (rGO) coating applied to the CuNW/ZnO film appears to prevent the penetration of moisture into the pores and cracks of the ZnO matrix, thereby prolonging the TCE's lifetime. (c) SEM image of a CuNW/ZnO/rGO sample showing embedded CuNWs beneath the surface, and wrinkles in the rGO layer in the upper left-hand corner of the imaged area.

Time [days]

IV. CONCLUSION

We synthesized high aspect-ratio CuNWs via a solution process and deposited them on glass and PEN substrates to fabricate high performance TCEs. Zinc oxide and reduced graphene oxide were deposited in sequence to strengthen the thin film electrode and to improve its stability. Our best Glass/CuNW/ZnO/rGO hybrid thin film has $R_s \sim 20 \Omega/sq$

Wavelength [nm]

and $T \sim 79\%$ at a wavelength of 550 nm. In addition, our hybrid TCE is resistant to scotch-tape peel and is stable when exposed to high humidity at elevated temperatures.

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The authors declare no competing financial interest.

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