Robust Transparent Glass-fabric Reinforced Plastic (FRP) Films for Flexible Electronic Substrate Platform

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ABSTRACT

Optically transparent plastic films are developed by impregnating glass-fabric with refractive index matched siloxane hybrid resin (GFRHybrimer films). These films exhibit low thermal expansion coefficient (< 15 ppm/°C) and high modulus (> 10 GPa) with high thermal stability up to 350 °C, and are suitable for use in flexible substrate films. Furthermore, transparent conducting electrode (TCE) films are fabricated using metal (Ag or Cu) nanowire or nanotrough which are embedded into the surface of GFRHybrimer films (TCE-GFRHybrimer). The fabricated TCE films represent smooth surface roughness ($R_{rms} \sim 1$ nm), excellent opto-electrical performance (low sheet resistance with high transparency) and thermal/chemical robustness. To demonstrate suitability of the TCE films as a flexible substrate platform, flexible organic light emitting diode (OLED) and perovskite solar cells are fabricated on the TCE films.

Keywords: glass-fabric reinforced plastic (FRP), metal nanowire, metal nanotrough, crystalline ITO, perovskite solar cell

1 INTRODUCTION

A flexible substrate is one of the most important component for the implementation of flexible electronics. Recently, organic polymers such as PET and PEN are considered the most viable materials for flexible substrates due to their flexibility, transparency, lightweight and suitability for roll-to-roll process. However, most of these materials have insufficient properties such as low glass transition temperature ($T_g$) and high coefficient of thermal expansion (CTE). Optically transparent glass-fabric reinforced plastic (FRP) is considered a promising candidate for use as a flexible substrate. The transparent FRP is a fiber composite laminate that achieve improvement in terms of both the thermophysical property (low CTE and high modulus) and the optical property (high transparency).

We introduce a new class of transparent FRP (GFRHybrimer) film composed of a high refractive index sol-gel siloxane hybrid material matrix and E-glass fabric reinforcement. The GFRHybrimer film shows low CTE, high modulus and high thermal stability, so the film can be used as a high-performance flexible substrate. [1] In addition, various nanostructured transparent conducting electrode (TCE) materials such as metal nanowire (NW) and nanotrough are embedded into the surface of the GFRHybrimer film to confer conductivity to the film. The resulting TCE films (TCE-GFRHybrimer) exhibit high opto-electrical property, smooth surface and robust stability. To demonstrate potential suitability of the TCE-GFRHybrimer films as a flexible substrate platform, actual flexible optoelectronic devices are fabricated on the films.

2 EXPERIMENTAL

The TCE-GFRHybrimer film was fabricated via a vacuum-assisted bag molding process, a typical fabrication method for making fiber-reinforced sheet-molding composites (Figure 1(a)). Briefly, two sheets of E-glass fabric were placed on a glass plate and then impregnated with the matrix resin, which consisted of a UV-curable sol-gel hybrid (Figure 1(b)). On another glass plate, metal networks such as metal NW (Ag or Cu) and nanotrough are formed. Ag and CuNW were synthesized using polyol process and hydrothermal method, respectively. [2-4] The metal nanotrough network was fabricated by using electrospun polymer template and vacuum-deposited Au. [5] The impregnated sample was then covered with TCE-formed glass plate and was compressed in a vacuum-assisted bag molding process. Finally, the TCE-GFRHybrimer films were fabricated via the UV curing of the sample, followed by the separation of the two glass plates.

Figure 1. (a) Fabrication procedure for a TCE-GFRHybrimer film. (b) Molecular structure of sol-gel siloxane hybrid matrix.
3 RESULTS AND DISCUSSION

Figure 2 provides thermo-mechanical property of the TCE-GFRHybrimer film. Commercial polyimide films PI1, PI2, and CPI were used as references. Coefficient of thermal expansion (CTE) of the TCE-GFRHybrimer film was characterized using a thermomechanical analyzer (TMA), and the results are shown in Figure 2(a). The CTE of the TCE-GFRHybrimer film was calculated and was found to be 14 ppm/°C. It should be noted that the TCE-GFRHybrimer film showed CTE values comparable to those of commercial PIs and CPI, which was attributed to the use of E-glass fabric (5 ppm/°C). Moreover, from the TMA profiles, it can be seen that the TCE-GFRHybrimer film did not show any distinctive glass transition behavior, which would have been evidenced by the deflection at the glass transition temperature, as was seen in the case of CPI at around 270°C. The viscoelastic characteristic of the TCE-GFRHybrimer film was further investigated via dynamic mechanical analysis (DMA). As shown in Figure 2(b), over the entire temperature range, the TCE-GFRHybrimer film exhibited a level of storage modulus higher than those of the PIs and CPI. In addition, the TCE-GFRHybrimer film did not exhibit distinctive glass transition behavior. Thermal property of the TCE-GFRHybrimer film also analyzed using thermo-gravimetric analysis (TGA). The TCE-GFRHybrimer film shows no weight-loss during the analysis at 350°C after 60 min. This indicates that the TCE-GFRHybrimer film can be used as a robust flexible substrate for high temperature device fabrication process.

Figure 3 shows the structural analyses of the metal NW-embedded TCE-GFRHybrimer (metal NW-GFRHybrimer) film. Large area (10 x 10 cm²) metal NW-GFRHybrimer films were fabricated. Metal NW and nanotrough TCEs are embedded into the surface of the GFRHybrimer films, resulting extremely smooth surface topography (Rrms < 1 nm, peak-to-peak value < 6 nm). In addition, strong adhesion of the TCEs are achieved because most part of the metal NW is held by hybrimer matrix. Surface and tilted SEM images reveal microstructure of the metal NW-GFRHybrimer films. Glass-fabric reinforcements are located in the middle of the film and covered by hybrimer matrix. The thickness of the metal NW-GFRHybrimer films 60 μm.

The TCE-GFRHybrimer films exhibit excellent opto-electrical performances compared with commercial indium tin oxide (ITO) TCEs. AgNW- and CuNW-GFRHybrimer films show sheet resistance (Rsh) of 22 Ω/sq at transmittance (T) of 94 % and Rsh of 25 Ω/sq at T of 91 %, respectively. Metal nanotrough-GFRHybrimer also shows good opto-electrical performance, Rsh of 2 Ω/sq at T of 90 %.
Thermal stability of the metal NW-GFRHybrimer films is evaluated by annealing the films on a hot-plate (ramp rate = 5 °C/min). Rsh of the films were traced every minutes during annealing. Figure 4(a) and 4(b) represent plots of Rsh vs. temperature for AgNW- and CuNW-GFRHybrimer films, respectively. Both films show improved thermal stability compared to bare metal NWs on glass substrates. These results are attributed to the metal NW TCEs are protected by the thermally-insulating sol-gel siloxane hybrid matrix.

Mechanical bending durability of the TCE-GFRHybrimer film was tested using lab-made bending test tool. The bending radius was 1 mm, and inner/outer bending of the TCE-GFRHybrimer film was conducted. Figure 5 shows sheet resistance change of the TCE-GFRhybrimer film and a reference ITO/PET sample. The TCE-GFRHybrimer film endured 10^4 bending cycles resulting in no change of sheet resistance values. This can be attributed to the excellent bendability of the GFRHybrimer film and tight anchoring of the TCE in the film.

To evaluate potential suitability of the TCE-GFRHybrimer films as a robust flexible TCE/substrate platform, flexible OLED and perovskite solar cell devices were fabricated on the TCE-GFRHybrimer films. The flexible OLED device is fabricated on the CuNW-GFRHybrimer film. The device structure is CuNW-GFRHybrimer / PEDOT:PSS / Super Yellow / ZnO / Al as shown is Figure 6(a). A windmill-shaped electrode pattern is produced on the CuNW-GFRHybrimer film by directly transferring a CuNW network identically predefined on a donor glass using a maskassisted spray-deposition of CuNW solution. The fabricated OLED device exhibits a stable operation even in a flexed state. The characteristic current density-voltage (J-V) and luminance-voltage (L-V) curves of the OLED device and of a reference device fabricated on ITO/glass (sputtered ITO on glass substrate) are shown in Figure 6(b-c). Although the OLED fabricated on the CuNW-GFRHybrimer film shows a small leakage current below 5 V in the J-V plot, both devices exhibit comparable performances. This current leakage might possibly be due to interfacial defects at the CuNW/PEDOT:PSS interface which may have been created during the spin-coating of the hygroscopic PEDOT:PSS solution.

The flexible perovskite solar cell devices were fabricated on the metal NW-GFRHybrimer films. Thin crystalline ITO top layer was adopted for further protection of the bottom metal NW networks. It is challenging to fabricate the perovskite solar cells directly on metal NW TCEs due to the high reactivity of the metal NWs toward halides. The device structure is c-ITO/metal NW-GFRHybrimer / PEDOT:PSS / perovskite / PCBM / BCP / Ag. Figure 7 shows the representative current density-voltage (J-V) characteristics of the perovskite solar cell devices on c-ITO/AgNW-GFRHybrimer, c-ITO/CuNW-GFRHybrimer, ITO/glass, and ITO/PET under 100 TechConnect Briefs 2016, TechConnect.org, ISBN 978-0-9975-1173-4
mW/cm² AM 1.5 G illumination. The reference devices on the ITO/glass and ITO/PET show PCE values of 15.38 % and 12.08%, respectively. The devices on the c-ITO/AgNW- and c-ITO/CuNW-GFRHybrimer films exhibit PCE values of 14.15% and 12.95%, respectively. It should be noted that the performance of the devices on the c-ITO/metal NW-GFRHybrimer films are comparable to or even superior to those of the reference devices. It is worth noting that the excellent chemical stability of the c-ITO/metal NW-GFRHybrimer films against perovskite precursor solution enables stable integration of the perovskite layer. Furthermore, bending durability of the solar cell devices were evaluated with bending radius of 2.5 mm. The devices endured 500 cycles of bending test without performance degradation. However, reference device on ITO/PET sample showed immediate degradation of its performance after few cycles of bending.

Figure 6. Flexible OLED devices on the TCE-GFRHybrimer film. (a) Device structure. (b) A photograph of the device. (c) J-V and (d) L-V characteristics of the device.

Figure 7. Flexible perovskite solar cell devices on the TCE-GFRHybrimer films. (a) The device structure. (b) Photovoltaic performance.

REFERENCES