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Enhancement of electrical properties of flexible ITO/PET by atmospheric pressure roll-to-roll plasma

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ABSTRACT

Flexible materials can significantly reduce the cost of the electronic devices because they can be manufactured by large-area roll-to-roll (R2R) processing. In this work, R2R atmospheric pressure plasma was used to modify flexible indium-tin-oxide films on polyethylene terephthalate foil (ITO/PET). Plasma treatment was performed in different feed gases consisting of various ratio between nitrogen and oxygen. A range of experimental techniques were used to study surface properties of ITO/PET, including X-ray and Ultraviolet photoelectron spectroscopies, four-point probe, Atomic force microscopy and UV–Vis measurement. We found that R2R plasma treatment decreased carbon contamination and increased the number of oxygen vacancies on the surface, whereas the ratio between indium and tin remained constant. UPS showed an increase in the work function from 3.9 eV for untreated sample to 5.1 eV for sample treated in plasma for very short time of 2 s. Four-point probe measurement demonstrated remarkable decrease in sheet resistance from 44.2 Ω/sq to 11.7 Ω/sq after plasma treatment for 2 s. The AFM and UV–Vis measurements revealed only slightly change on the surface morphology and transmittance of the ITO/PET. The plasma treated foils were stored under laboratory environment and inside of the glovebox to study the effect of the environmental conditions on the stability of the improved properties. The ITO surfaces stored in laboratory environment for 3 weeks preserved approx. 60% of the properties achieved by plasma treatment, e.g. work function of the samples was approx. 4.5 eV after 3 weeks (and 5 weeks) ageing time in the laboratory environment.

1. Introduction

Indium tin oxide (ITO) has gained significant interest because of its combination of several unique properties such as good electrical conductivity and high transparency, which designate it as an excellent material for transparent electrodes in flexible and printed electronics [1–5]. However, low work function of ITO [6] (3.8–4.6 eV), leads to various issues in design of the ITO-based electronic devices. The difference between work function of the ITO and host layer, e.g. organometal halide perovskite (~ 5.4 eV), is too large to provide efficient charge transport among the inter-layers [7–9]. Therefore, a number of additional inter-layers are often deposited to facilitate the charge mobility [10,11]. The additional inter-layer should possess work function higher than ITO and lower than the active layer to bridging the energy gap between them. For instance, several materials such as PEDOT: PSS and ZnO have been utilized as the inter-layers between the ITO and active layer [12,13]. However, fabricating each additional inter-layer increases manufacturing time and the cost of the final device [14,15]. Recently, surface modification of ITO without deposition of any additional layer have received great attention to optimizing ITO work function [16]. ITO surface was modified by wide range of procedures such as UV/ozone treatment [17], and electro-chemical methods [18]. Surface modification with electrical plasma is one of the most effective procedure used to improve ITO surface properties.

Work function of ITO was increased by low-pressure plasma treatment in hydrogen/oxygen [19], argon [20], and chlorine [21]. Although the achieved work function after plasma treatment was appropriate, the plasma generated at low pressure is not adequate for low-cost flexible electronics. Vacuum equipment increases the manufacturing time and makes the large-area roll-to-roll processing extremely challenging. Atmospheric pressure plasmas for ITO treatment have also been employed, for example Liao et al. [22] used atmospheric pressure plasma jet to treat ITO film on glass. Since the temperature of the plasma was high as 385 °C, the plasma treatment is not suitable when ITO is deposited on flexible polymeric substrate, which is thermally sensitive and cannot withstand temperatures higher than 150 °C. Increasing demand for flexible electronics requires to deposit semiconductors on plastics such as polyethylene terephthalate (PET) [23].

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Therefore, it is essential to perform plasma treatment of ITO/PET at low temperature and preferably at ambient conditions. For this reason, plasma jets that are operating in expensive noble gases are also inappropriate. Furthermore, plasma jets can provide only small treatment area of several mm^2, which is also not compatible with large-area requirements given of flexible electronics manufacturing. Sharma et al. [24], showed that plasma treated ITO is not stable because of the strong tendency of the surface to bond with carbon contamination from ambient atmosphere [25], this led to low quality of functional layers deposited on the ITO. Therefore, all fabrication steps, including surface modification and subsequent coating, should be accomplished continuously – by roll-to-roll fashion. Furthermore, since the glass transition temperature of PET is less than 100 °C, the deposition of ITO on PET should be done at low temperature, which makes the film low stable with elapsed time in preserve of its optoelectronic properties e.g. conductivity, work function, etc. [26].

Low-temperature plasma generated in dielectric barrier discharges (DBD) has shown as an effective procedure to surface processing without the need of vacuum equipment and can be utilized for treatment of thermosensitive materials [27,24,28]. Furthermore, DBD plasma in various feeding gas can generate different species and radicals [29]. In [30], effect of the argon/oxygen feeding gas on the DBD plasma treatment of the PET was studied and it was found that DBD with coplanar configuration of electrodes – a diffuse coplanar surface barrier discharge (DCSBD) can generate large-area plasma of high energy-density, whereas the temperature of the plasma is approx. 70 °C [31]. The DCSBD has been already used for treatment of various thermally sensitive materials, such as PET and PEN [32,33]. On the other hand, the roll-to-roll treatment of ITO has not been studied yet. In this work, we used novel plasma source with a curved DCSBD electrode to simulate roll-to-roll plasma treatment of ITO/PET. We studied the effects of the surface plasma generated in various working gases containing different N2/O2 ratio, with particular focus on 8:2 ratio, which is close to ambient air composition. A wide range of experimental techniques were employed to monitor electrical and optical changes induced by plasma treatment on ITO surface. The induced changes on the ITO surface were not stable in time and surface properties which developed after the plasma treatment had tendency to degrade. To investigate the stability of the plasma modified ITO/PET, the surface properties of the samples were measured with ageing time; form 3 days to 3 weeks after plasma treatment. The samples were stored under the two environments; in laboratory and inside of the glovebox. The surface parameters such as work function, sheet resistance, water contact angle and transmittance were measured.

2. Experimental part

2.1. Plasma treatment

Indium tin oxide (ITO) film coated on the polyethylene terephthalate (PET) (Sigma Aldrich, product No. 639303) was used as a substrate. The surface of the ITO/PET was protected by plastic foil removed before exposure to the plasma. R2R plasma treatment of ITO/PET was carried out by using DCSBD with curved electrode design, manufactured by Roplass, Czech Rep. The surface plasma with area of $20 \times 8\ cm^2$ was generated at atmospheric pressure and the power density was kept at $2.5\ W/cm^2$. The DCSBD is discussed in more detail in [34]. The curved DCSBD design is depicted in Fig. 1. The curvature and circumference of the curved DCSBD roller was $6.7\ m^{-1}$ and 92.9 cm respectively. The inlets of the DCSBD chamber with different flow rate ranging from 2 to 8 L/min provided various N_2/O_2 compositions of the feeding gas. ITO/PET flexible sheets with thickness of 120 μm were fixed on the guiding roll and the distance between the guiding roll and the curved ceramic surface was approx. 0.3 mm. The speed of the roller was adjusted according to treatment time, which varied from 18.6 to 4.1 cm/s corresponding to 0.25–2 s treatment time.

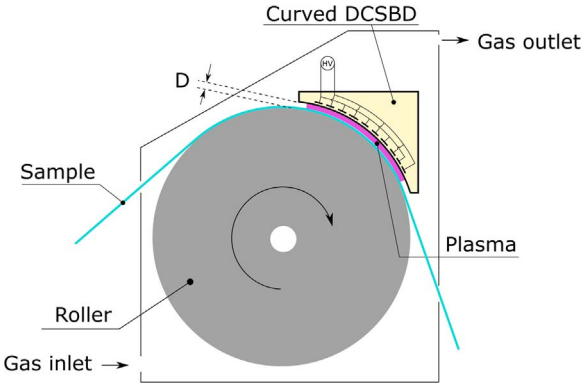

Fig. 1. Schematic of the roll-to-roll DCSBD source with curved electrode.

For longer plasma treatment times (> 2 s), samples were treated in multiple and continuous shorter periods, e.g. 8 s treatment time was achieved by four continuous periods with 2 s treatment time.

2.2. Materials characterization

Chemical composition of the samples was determined immediately after plasma treatment by X-ray photoelectron spectroscopy (XPS) Al Kα ESCALAB 250Xi (ThermoFisher Scientific). The XPS spectra were acquired from two spots (650 μm) with a takeoff angle of 90° in 10^{-8} mbar vacuum at 20 °C. Ultraviolet photoelectron spectroscopy (UPS) was performed by Kratos Supra under normal emission using He I (21.22 eV). The spectra were calibrated at the Fermi edge, which is the energy of fastest emitted electron. Work function was calculated by subtraction of biding energy at the secondary electron cut off (energy of the slowest emitted electron) from the energy of the incident light. To separate the secondary electron cut-off of the samples from that of the detector, negative bias was applied to the samples. Each measurement was performed on the two spots of the sample. Surface morphology of the samples was evaluated by using atomic force microscopy (AFM), Ntegra Prima (NT-MDT) from two different 2×2 μm scans taken in semi-contact mode. The root mean square (RMS) was calculated from two spots of each sample. UV–Vis spectrometer, Cary 5000i, was employed to measure optical properties of the ITO/PET at the wavelengths between 380 to 700 nm. Electrical properties of the samples were measured by four-point probe method. The probe spacing was 1.06 mm and the applied voltage and current were 1.05 mV and 1 mA. The sheet resistance was calculated from $R_S = 1.5 \times 10^{-2}$ V/I. The measurement was performed on 10 points for each sample and mean sheet resistance as the average of the measured values. The surface wettability of plasma treated ITO/PET surface was studied by sessile droplet (2 μL) contact angle measurements of demineralized water using See System (Advex Instrument, Czech Rep). In total, eight measurements per sample and four different samples were used to calculate water contact angle of the ITO/PET.

To investigate the behavior of the plasma treated ITO/PET as a function of storage time and environmental conditions, the samples were stored under two different environments: i) the samples were kept in a laboratory under open air with relative humidity between 30–40% and temperature 25 °C, ii) the samples were stored under dry nitrogen atmosphere (purity 4.8) inside of a glove box Jacomex GP Campus. The moisture and O_2 content values were < 10 ppm at temperature 25 °C.

3. Results and discussion

Fig. 2 shows the carbon concentration on the ITO surface after plasma treatment as a function of the various ratio between N_2 and O_2. A gradual decrease of the carbon concentration with the plasma treatment time indicates that plasma treatment led to cleaning of ITO