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Twisting and twisting fatigue of ITO/Ag/ITO multilayer films on PET substrates used in flexible electronic application

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Abstract

In recent times, there has been a large demand for flexible electronic devices, such as flexible solar cells, flexible circuits and flexible displays. However, the electrical failure of transparent conducting oxide layers in these products is one of the main reliability issues because these devices frequently work under mechanical and thermal stresses caused by various mechanical deformations. There is research focused on the electrical resistance changes under tensile and bending deformation. However, in addition to this tensile and bending deformation, twisting deformation is expected as another frequent deformation of flexible displays or other flexible electronics devices. Therefore, twisting tests and twisting fatigue experiments were conducted on multi-layered films of Ag-alloy based indium tin oxide (ITO) thin film deposited on polyethylene terephthalate (PET). In the twisting tests, crack development and electrical resistance were monitored *in-situ*. Cracks started at angle of $39^\circ \pm 2.4^\circ$ and propagated towards the direction of the sample length. In the twisting fatigue test two sets of experiments were performed; the first set of experiments were conducted to study the effect of twisting angle and temperature on ITO/Ag-alloy/ITO thin film-coated PET. The other set of experiments was conducted on specimens to study the effect of temperature in the absence of cyclic twisting deformation. Change in electrical resistance increased with twisting cycle number and with twisting angle. In addition, the highest change in electrical resistance was observed for samples subjected to cyclic fatigue at 100 °C , which is attributed to crack growth and oxidation of the Ag-alloy layer. The cracks were observed to initiate not only from coating defects but also from edge defects. Development of cracks is accelerated due to the combined effects of the external repeated stress with temperature. Therefore, it is suggested that controlling temperature when using ITO/Ag-alloy/ITO thin film under extreme mechanical stress is crucial for the electrical device performance.

1. Introduction

There is an increased interest in flexible optoelectronic devices because they offer the substantial advantages such as a large area, exciting new form factors, light weight and low cost. In order to realize the successful commercialization of such flexible devices, they must be able to withstand mechanical and thermo-mechanical loads during roll-to-roll processing and repetitive loading under different environmental conditions, as well as extreme handling both indoors and outdoors with a long-term operation period.

Indium tin oxide (ITO) grown on polyethylene terephthalate (PET) substrates has shown high conductivity and high transmittance in the visible region and so is widely used as the transparent anode layer in various optoelectronic devices including light-emitting diodes, solar cells and liquid-crystal displays [1,2]. However, the high cost of indium encourages the reduction of the quantities employed for film fabrication. It is difficult to reduce thickness under 200 nm in the case of a single ITO film owing to a decrease in electrical connectivity with thickness decrease. Therefore, a very thin metal film can be inserted between the ITO films to show higher conductivity than a single ITO layer of the same thickness [3]. Such a multilayer system has been shown effective to achieve conductive and transparent electrodes more adjusted to the required condition [4]. Usually, silver (Ag) film was used as the metal

layer because it has the lowest resistivity, approximately $2 \times 10^{-6} \Omega \cdot \text{cm}$ at 20 °C, in comparison with all other metals [5].

Owing to mechanical mismatches between the polymer substrate and the inorganic ceramic layer, which cause film cracking and delamination when they are under mechanical deformation during manufacturing and in service conduction [6], the mechanical response of different thin films has been extensively studied using mostly uniaxial tensile and buckling experiments. Cairns *et al.* investigated the electromechanical behaviour of ITO-coated PET by using a miniature tensile tester coupled with *in situ* optical microscopy. The onset of cracking was observed between 2.0 % and 2.5 % strain and this causes a sudden increase in the normalized electrical resistance. In addition, brittle ITO coatings deposited on polycarbonate substrates were tested under applied bending load by Bouten [7]. The electrical resistance was monitored *in situ*. He found that the ITO failed when exposed to strain of approximately 1.2 %.

As the number of applications for transparent conductive oxides on flexible plastic substrates increases, another deformation which may be applied during fabrication or extreme handling is twisting deformation. Lim [8] studied the electro-mechanical failure mechanisms of zinc tin oxide (ZTO)/Ag/ZTO coated PET using a lab-made twisting apparatus coupled with optical microscopy and electrical-resistance monitoring. The critical onset angle for cracking was determined to be 38°. They reported that the overlapped films after crack generation provided a conducting path and subsequent delay change of the electrical resistance.

Since flexible electronics need to remain functional after a load is repeatedly applied to the structure, repeated mechanical loading of ITO and ITO/Ag multi-layers under bending and twisting conditions is also vital. As reported in [9] repeated loading forces for large numbers of cycles can cause structures to fail at stresses lower than those needed for failure under static load. Lechat *et al.* [10] showed that the cyclic loading stress was the cause of PET failure as it led to crack propagation at low stress.

Additionally, Gorkhali *et al.* [11] reported results for the electro-mechanical properties of repeated loading of ITO-coated PET substrates using mandrel-bending over varying diameters ranging between 8 to 24 mm, and the resistance changes were continuously monitored. They observed that a rapid increase in electrical resistance was due to the dimensional change of the polymer substrate until an equilibrium size was attained, then a gradual increase in resistance was found due to cracking of the ITO. After 50,000 cycles catastrophic conductive failure occurred due to severe cracking. Also, Cho *et al.* [12] conducted cyclic loading experiments in the twisting mode. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) films printed on PET substrates were repeatedly twisted and untwisted from both sides of the sample at an angle of 30 °, the change in electrical resistance was monitored *in situ*. It was observed that the change in electrical resistance is constant after 2,000 cycles, this indicating that such structures can provide high levels of twistability and flexibility.

In addition to external repeated mechanical stress, the thin film anode may also be subject to high temperatures during the manufacturing process and during the use of the flexible electronic devices. The temperature is likely to change the mechanical, physical and electrical properties of the thin film over time for a wide range of materials and to increase the oxidation of the metal film when used as intermediate layer between TCO layer. Because of the mismatches in the thermal expansion coefficients of substrate and the thin film, both of them do not respond to temperature in term of elongation by the same percentage and the thin film is either stretched out or compressed and result cracking or/and delamination of the coating layer. Khalid *et al.* [13] studied the influence of temperature on the bending fatigue behaviour of copper thin film deposited on a PET substrate. They showed that high temperature caused a more rapid degradation of the conductive surface. Despite the importance of environmental issues combined with repeated mechanical stress for reliable long-term operation, to the best of

our knowledge no systematic investigation of the electro-mechanical behaviour of TCO film coated PET under the combination of twisting fatigue stress and harsh environmental condition has been published.

Therefore, the primary objective of this study is to focus on the flexing behaviour of ITO/Ag-alloy/ITO film coated PET by using twisting and cyclic twisting devices developed in this project. The influenced of factors including twisting angle and temperature and frequency on the fatigue behaviour of thin-film deposited on flexible PET substrates are discussed.

2. Experimental details

2.1. Samples

ITO/Ag-alloy/ITO sheets (200 nm thick) on polyethylene terephthalate PET (125 μm thick) substrate with sheet resistance of $11\Omega/\text{sq}$ were supplied by Dr G. Potoczny that deposited by a commercial roll-to-roll magnetron sputtering machine in CSEM (Brazil). Samples with dimension of (30 mm length, 18 mm gauge length and 4 mm gauge width) were cut from sheets using a Moore Hydraulic Press. The reliability is affected by the specimen size; a reduced volume of active brittle material leads to improved reliability due to the reduced number of intrinsic defects present in the film. As reported by Bejital et al. in reference [2], the crack onset strain of the smaller size specimens of ITO/PET was higher. This initial work used a standard specimen size for experimental convenience; a systematic study of specimen size effects would be useful further study.

2.2. Twisting Test

Twisting tests were carried out using a twisting apparatus in order to investigate the twisting durability of the ITO/Ag-alloy/ITO coated polymer. The twisting apparatus as shown in Fig.1 was designed in this project and can be operated manually. Goniometers, originally used either to measure the angles between crystal faces in crystallography or to rotate the samples in X-ray diffraction, were selected as a method for rotating the ITO/Ag-alloy/ITO coated PET, enabling fine control of rotation angle to as low as 2° . The apparatus was attached in a rigid frame. Metal grips were prepared and connected to the two goniometers to clamp the specimen. For *in situ* electrical resistance monitoring, a plastic plate was placed between the metal grip and each goniometer (see Fig.1) to provide a closed electrical circuit, and then two copper wires were attached with both grips and connected to FLUKE 45 display multimeter. A computer running National Instruments Lab View software was used to collect electrical resistance data. The twisting apparatus were placed underneath a confocal laser scanning microscope (CLSM) to monitor crack initiation and propagation. The clamped sample was twisted in opposite directions. The twisting angle was increased stepwise to around 62° so that images and changes in electrical resistance could be recorded at each twisting step during a 2 minute hold.

Fig. 1. Custom -built twisting loading apparatus

2.3. Twisting fatigue tests

Commercial rheometer machines equipped with a temperature-controlled oven are usually used to measure flow and deformation of materials under applied forces [14]. However, for this project a number of customisations have been applied to allow investigation of the twisting fatigue behaviour of ITO/Ag-alloy/ITO coated PET take place. First of all, two jigs were prepared and attached to the rheometer machine to hold the sample. One jig which is on the top is fixed while the other one which is in the bottom is mobile with a rotational driver, as shown in Fig. 2. During the experiment the lower jig is rotated with the Z axis causing the specimen to twist in the clockwise and anti-clockwise direction. Similar to the twisting testing experiment, in order to close the electrical circuit and measure the electrical resistance change, the bottom jig was separate from the base of rheometer machine by using a plastic plate and also plastic screws was utilized as shown in the inset of Fig. 2. The electrical resistance is again monitored by a multimeter attached to the copper wire and recorded by the Lab View software. In order to keep the sample flat and stable, a small load was applied to it before the test was started. In addition, a calibration was performed to link the strain to the angle. Both angle (17.5° , 22.5° , 27.5°) and temperature (RT, 50°C , 100°C) were selected as the experiment parameters. The device limits twisting angle to 27.5° so the sample cannot twist with more than 27.5° angle. Also, a temperature above 100°C is not compatible with a flexible plastic substrate. Samples similar in dimension to those used in the twisting experiments were cut from the coated film and utilized. The measured torques were (37, 43 and 48 g.cm) for the angles 17.5° , 22.5° and 27.5° respectively. An air oven was

used to applied constant temperature to the sample. At any selected angle, such as at 17.5°, during one complete cycle the sample will twist in the following sequence: 0°, 17.5°, 0°, -17.5°, and 0°.

In order to assess whether the damage that occurred was due to the cyclic twisting or due to the temperature, a second set of experiments was performed. Without any mechanical loading applied, the samples were subjected to the same combination of temperature for 40 minutes, which is equal to the time required to perform 200 cycles at frequency of 12 seconds/cycle. The electrical resistance was measured *in situ*. SEM, XRD and film transmittance tests were conducted on the exposed and unexposed films.

Fig. 2. The twisting fatigue experiment set-up

2.4. Microscopy

Scanning electron microscopy (SEM) was performed to characterize the crack morphology of the ITO/Ag-alloy/ITO coated PET after twisting and twisting fatigue experiments. Prior to performing SEM observation, the samples were sputtered with a 5 nm film of gold to dissipate electron charges. The images were taken under an accelerating voltage of 15 kV and at a working distance of 10 mm.

2.5. Results and discussion

2.5.1. *In situ* twisting tests with confocal laser scanning microscopy

Twisting tests were carried out in order to investigate the critical twisting angle at which ITO/Ag-alloy/ITO film cracked and started to lose its electrical functionality. The two types of measurement techniques include microscopical (CTA-M) monitoring and normalized electrical resistance (CTA-R) were used to determine the critical twisting angle. CTA-M is defined as the angle at which the first cracks in the coating started to initiate and CTA-R is defined as the angle at which a 10% increment in electrical resistance occurred. This was arbitrarily selected as criteria for crack onset initiation [15].

CLSM micrographs of the crack initiation and development on the ITO/Ag-alloy/ITO films at different angles are shown in Fig. 3. Cracking first started to appear at a critical twisting angle (CTA-M) equal to $39^\circ \pm 2.4^\circ$. The imperfections or defects remaining after deposition in the layer coupled with edge defects resulting from specimen cutting were found to be crack-initiation sites, as can be seen in Fig. 3(a). It is believed that such observation

contributes to a highest energy presented at the region. Interface separation in the neighbourhood of an imperfection exhibits a larger energy release rate compared to that for a flat surface. By increasing the applied twisting angle, the initiated crack starts to increase and propagates along the whole sample length. It was found that the channel crack is not grown through the whole width of the film; it is arrested at a certain distance from middle section of the sample width, as could be observed in Fig. 4. This indicates that a maximum critical stress is produced over that specific region. It is clear to see that the cracks in the thin film are not developed further as applied twisting angle increases. In the other word, it is expected that the substrate becomes plastic and cannot transfer the stress required for further cracks.

Fig. 5 shows the crack density and the change of electrical resistance of the conductive layer [16] which is expressed as $\Delta R/R_0$, where $\Delta R = R - R_0$, (R_0 is the electrical resistance value before applying stress and R is the electrical resistance value after applying a twisting stress). As can be seen from the Fig. 5 at the early stage of applying a twisting angle the normalized increase of electrical resistance of ITO/Ag-alloy/ITO becomes negative. This could be due to shortening of the distance between adjacent atoms/grains present in the thin film, which can result in the decrease of physical barriers for moving electrons and improved mobility. These results are consistent with results reported by Potoczny [17] for ITO film on PET when subjected to compressive stress. This implies that during twisting tests the sample is applied to compressive stress. With further twisting, the normalised electrical resistance of the ITO/Ag-alloy/ITO started to increase. At 10% increase of normalized electrical resistance, the critical twisting angle (CTA-R) which promotes the first cracks in the ITO/Ag-alloy/ITO layer was observed to be $39.3^\circ \pm 3.5^\circ$. Above the critical twisting angle (CTA-R) the electrical resistance increased gradually due to the increased film crack formation [18], as the series of CLSM images show in Fig. 3. In addition, the finite electrical resistance was observed even at a high applied twisting angle of 68° .

A potential reason for finite electrical resistance in ITO/Ag-alloy/ITO thin film is that the channel cracks have not fully traversed across the sample width as confirmed by Fig. 4, so the sample is still conductive. Also, any overlapping film material at the crack after crack generation encouraged by Ag ductile layer (see Fig. 6(b)), contributes to the formation of conducting paths between the ITO films which causes finite electrical resistance. This is consistent with a previous study conducted by Choa *et al.* [19] who pointed out that the overlapping of the cracked IZO/Ag/IZO film, when it was twisted, provided a conductive pathway through the fragmented film and led to changes in the electrical resistance. The CTA-R value which was determined by using normalized electrical resistance was equal to $39.3^\circ \pm 3.5^\circ$ and it was in good correlation with CTA-M values determined by using the CLSM images. Leterrier *et al.* [16] also found good agreement between the initial crack growth in uniaxially-strained indium tin oxide (ITO) thin films measured from micrographs and the crack onset strain (COS) values which correspond to 10 % increase of normalized electrical resistance. Further understanding of the relationship between crack evolution density and variation in electrical resistance in the ITO/Ag-alloy/ITO film under twisting is explored in the following section.

Two distinct regions can be clearly observed in the crack density and $\Delta R/R_0$ vs angle. In the first region, as the applied twisting increases the crack density increases rapidly when channel cracks in ITO/Ag-alloy/ITO thin film start to advance through the sample length. As a result, the electrical resistance of the thin film increases in this region, which may suggest that the applied twisting angle is proportional to the number of cracks. However, above the crack saturation point, this is no longer applicable. As can be seen in the second region (see Fig. 5), the crack density reaches a saturation point at angle 60° , but the significant increase in normalized electrical resistance was observed above the crack saturation point. This is most likely to be due to the extension of the conductive path through the cracks where a large angle is applied. The stress produced on the ITO/Ag-alloy/ITO films after the saturation point leads to the previously formed cracks becoming deeper and wider, this can also be possibly the reason for serious conduction failure when the crack density is in a saturated state. This is in good agreement with previous observations of ITO deposited polymer substrates under bending stress [20].

Ex situ scanning electron microscopy reveals additional fine details of the failure mechanisms of the ITO/Ag-alloy/ITO thin film. For example, Fig. 6 shows that in some places the ITO/Ag-alloy/ITO thin film was in complete separation due to the formation of cracks, as shown in Fig. 6(a) However, in the other places, overlapped film and buckling delamination of the multilayer stacking ITO/Ag-alloy/ITO thin film from the substrate are observed, as shown in Fig. 6(b). This is in agreement with the change in electrical resistance data observed after the crack saturation point. The critical twisting angle (CTA-R) of ITO/Ag-alloy/ITO thin film observed in this study is consistent with critical twisting angle of ZTO/Ag/ZTO multilayer deposited on to a PET substrate which was observed initiating cracks at a twisting angle of 38° [8].

The surface morphology of twisted ITO/Ag-alloy/ITO multilayer samples observed in this study (see Fig. 6) is consistent with the morphology of cracks and buckling delamination investigated in reference [19] for IZO/Ag/IZO multilayer thin films under both tension and compression buckling modes. This result indicates that the twisting deformation induced tensile and compressive stress on the film simultaneously.

The crack-initiation sites of ITO/Ag-alloy/ITO thin film observed in this study are consistent with those previously reported by Sim *et al.* [21] for ITO thin film deposited on a plastic substrate. This is also consistent with study of Bejital *et al.* [1] who observed the mechanical behaviour of patterned ITO-coated PET substrates. They found that the cohesive crack was revealed to originate from the edges of the pattern where the thin film is subjected to the tension buckling mode. Consequently, edge etch control is significantly important and may in turn enhance the reliability of the patterned thin film since the edge cracks would be diminished. Furthermore, Lopez *et al.* [22] pointed out that the homogeneity of the edges has significant influence on the initiation and propagation of cracks and consequent bending reliability of flexible platinum lines patterned on polyimide foil.

Fig. 3. *In situ* confocal laser microscope imaging of cracks development ITO/Ag/ITO of the multilayer thin film under twisting. The corresponding twisting angle values are indicated on the images. Twisted Arrows on image (a) indicated the twisting direction. The upper panel displays the steps of the twisting test as the increasing angles.

Fig. 4. Crack developments across the width of the sample under 68° twisting angle.

Fig. 5. Crack density and normalized electrical resistance versus twisting angle for ITO/Ag-alloy/ITO thin film coated PET substrate.

Fig. 6. SEM micrograph image with enlarged image showing (a) cracks on the surface (b) overlapping and buckling delamination of ITO/Ag alloy/ITO multilayer film at 68° applied angle under twisting tests. Black arrows indicate the cracks and twisted arrows on image indicated the twisting direction.

2.5.2. Twisting fatigue tests

Twisting fatigue experiments were performed to study the influence of both angle and temperature on electrical resistance behaviour of the ITO/Ag-alloy/ITO thin film under twisting fatigue.

2.5.2.1. Effect of twisting angle

The samples were tested at room temperature and a frequency of 12 second/cycle. Fig. 7 (a) shows how the resistance changes as a function of twisting cycles for ITO/Ag-alloy/ITO film. It is clear to see the sudden increase in electrical resistance after the first few cycles. This may be attributed to the dimensional change of the polymer substrate [23]. In the other words, the substrate does not appear to recover fully before the next cycle starts, but recovers over time. Therefore, after each loading cycle the gauge width of the substrate will reduce up to an equilibrium point attained between the applied load and the gauge width recovery [23]. With further increment of the number of applied twisting cycles, a gradual increase of normalised electrical resistance is observed. This is likely to be due to progressive cracking and buckling [23], as shown in Fig. 7 (b), (c) and (d).

Fig. 8 shows a comparison for three different angles. It was found that the sample tested under an applied twisting angle equal to 17.5° shows an extremely slow increase in resistance followed by the sample tested under applied twisting angle equal to the 22.5° , while the sample tested under applied twisting angle equal to the 27.5° shows the highest increase in normalised electrical resistance. Therefore, as the applied twisting angle increases, samples fail sooner. In addition, the electrical resistances were varied during loading and unloading of sample as shown in the inset of Fig. 8. This variation is believed to result from the wide opening and re-closing of microcracks in the film during twisting and untwisting of the sample [24]. Furthermore, resistance modulation was repeated

continuously during twisting cycles as shown in Fig. 8. The modulations in resistance of ITO/Ag-alloy/ITO multilayer film significantly rely on the twisting angle. The resistance modulation in the ITO/Ag-alloy/ITO multilayer film with a higher twisting angle is higher than of those with lower twisting angles. The resistance modulations during bending test was reported by Park *et al.* [25] for Ga-doped ZnO (GZO/Ag/GZO) multilayer deposited on flexible substrate. They observed that modulation in resistance become stronger after subjecting samples to lower bending radius. The increasing number of microcracks and their growth in width and depth with increasing twisting angle, might be a primary cause of increased resistance modulation of the ITO/Ag-alloy/ITO multilayer with increasing twisting angle.

Fig. 9 (a) and (b) show SEM micrographs of the ITO/Ag-alloy/ITO samples after twisting cycles at 17.5° and 22.5° applied angles respectively. The thin film did not show any cracks. However, a slight increase in electrical resistance with increasing number of cycles was observed. For example we observe that at 200 cycles the change in ITO/Ag-alloy/ITO electrical resistance is 9.3 ± 2.02 % for 17.5° angle, 12.3 ± 0.88 % for 22.5°. This suggests that some microcracks might have been generated in the film, and then elastic recovery of the polymer substrate occurred, thus leading to the closure of the microcracks when the sample was unloaded [24]. Fig. 9 (c) is surface of the ITO/Ag-alloy/ITO samples after twisting cycles at 27.5° angle. It shows a few shallow and parallel cracks to each other with finite length. Closer observation of this image also reveals buckling formation besides the cracks. This is consistent with electrical resistance results, where the angle 27.5° shows higher change in ITO/Ag-alloy/ITO electrical resistance 28.6 ± 2.9 % after 200 cycle compared with angles 17.5° and 22.5°.

Fig. 7. (a) Normalized electrical resistance versus number of cycles for ITO/Ag-alloy/ITO multilayer coated PET substrate. (b), (c) and (d) CLSM images showing cracked ITO/Ag-alloy/ITO films after 100, 300, and 800 twisting cycles at 27.5°.

Fig. 8. Normalized electrical resistance as function of the number of fatigue cycles during cyclic twisting of ITO/Ag-alloy/ITO under different applied angle.

Fig. 9. SEM micrographs of ITO/Ag-alloy/ITO films after 200 cycles at maximum twisting angles of (a) 17.5 ° (b) 22.5 ° (c) 27.5°.

2.5.2.2. Effect of temperature

The influence of temperature on the electrical resistance of ITO/Ag-alloy/ITO multilayer film on PET substrates was also investigated. In Fig. 10(a), the normalised electrical resistance is plotted as a function of the number of twisting cycles at different temperatures, at a constant maximum twisting angle of 27.5° and constant frequency of 12 second/cycle. Regardless of temperature used, the electro-mechanical performance is consistent with that observed for fatigue twisting under different angle (see section **Error! Reference source not found.**); after the first few cycles the normalized electrical resistance increased significantly until an equilibrium take place.

Above the equilibrium point, which probably occurs between the applied stress and recovery of the dimensions of the compliant substrate, a gradual linear increase of the change in resistance with increasing number of cycle can be seen. After 200 cycles, the change in electrical resistance for specimens at room temperature is found to be the lowest, whereas for specimens subjected to 50 °C the resistance increases by 78%, and for specimens subjected to 100 °C by 233%. Therefore, the combined action of externally applied mechanical stress and temperature is considerable.

A significant discrepancy in the normalized electrical resistance for samples tested at 50 ° and 100 °C compared with samples tested at RT could be due to the following reasons. Firstly, the internal tensile stress has a direct effect on accelerating the cracking of the thin film [26]. When the temperature increases up to approximately 100 °C, internal tensile stresses increase in the coating [27] due to the high thermal expansion coefficient of the substrate compared to the coating and also the mechanical mismatch between the thin film and substrate resulting from softening of the polymer substrate. Therefore, the thin film fractures more easily, resulting in an increment in the electrical resistance. Secondly, once the crack has started under combined cycle stress and high temperature, this makes it easier for the oxygen in the air to penetrate into the Ag layer and react with it thus causing the Ag layer to be partly oxidized. In general, oxidation occurs at a higher rate when the temperature is higher [13]. Therefore, oxidation could be another factor which might cause increments in the electrical resistance, in addition to the externally applied twisting stress.

This is confirmed by the confocal micrograph images shown in Fig. 10(b), (c) and (d). It is found that crack density starts to increase as the temperature increases. With further increasing temperature, the growth of cracks in the conductive layer is more pronounced and they become wider. Thus, the increment of electrical resistance for the sample at 50°C and 100 °C are greater than that at room temperature, see Fig. 10(a). In addition, ITO/Ag-alloy/ITO multilayers tested at higher temperature exhibits a higher resistance modulation when it is twisted and comes back to its initial position. This may be attributed to the existence of cracks opening with width of ~ 90 nm which are clearly visible in the inset of Fig. 11.

Similar electro-mechanical behaviour to that obtained in this work was reported for uniaxially-strained ITO film-coated PET substrates by Cairns *et al.* [23]. They suggested that the increase of resistance with temperature is dependent on the thermal properties of the substrate.

This result is also consistent with work conducted previously by Khalid *et al.* [13] who studied the influence of temperature on the bending fatigue behaviour of copper thin film deposited on a PET substrate. They observed that the electrical resistance change of the samples tested at higher temperatures (100°C) is greater than that tested at both 0°C and 50°C temperature. It was believed that the failure of the Cu functional layer is oxidation dominated.

It is worth noting that the electrical resistance of the material was still finite even after being subjected to temperature of up to 100 °C. This indicates that the cracks form locally and have not propagated through the whole length and width of the sample from one edge to the other. As shown in the confocal microscope image in Fig. 12, the corner area of the end of the specimen has the highest value of crack density other than in the centre because of the highest stress concentrated in that area. In the cases that cracks grown from one edge of the sample to the other, the conductive path is completely severed; the film loses its conductivity completely and demonstrates the electrical properties of an insulating material, which is not observed in our flexing tests.

Fig. 10. (a) Normalized electrical resistance as function of applied number of cycles during cyclic twisting test of ITO/Ag-alloy/ITO under different applied temperature. (b), (c) and (d) CLSM images showing surface of ITO/Ag-alloy/ITO films after 200 twisting cycles at RT, 50 °C and 100 °C temperature respectively. The black arrows show cracks on the coating.

Fig. 11. SEM images of surface of ITO/Ag-alloy/ITO films after 200 twisting cycles at 100 °C

Fig. 12. Confocal laser microscopy images showing crack distribution in surface of ITO/Ag-alloy/ITO films after 200 twisting cycles at 100 °C.

2.5.2.3. Film temperature response characterization

The samples were subjected to the same combinations of temperature (section 2.5.2.2) for 40 minutes without involving cyclic twisting, in order to determine whether the damage to thin film occurs as a result of cyclic twisting or temperature. The electrical resistance was monitored *in situ*. Fig. 13(a) shows no significant change in normalized electrical resistance over time for samples exposed to RT and 50 °C. However, in the early stages of subjecting samples to high temperatures (above the glass transition temperature of PET) a slight decrease in electrical resistance is observed and then it tends to be more stable after a certain period of time. This may result from rearrangements of the atoms in the ITO [28] which leads to shortening distance between atoms and resulting increase in the electrical conductivity. To further understand the stability of the electrical resistance, SEM, XRD and film transmittance tests were employed on the films exposed to different temperatures.

The lack of any cracks initiating in the surface of all of the samples in Fig. 13(c) and (d), confirms the electrical resistance stability. Fig. 14 shows diffraction peaks of ITO/Ag-alloy/ITO at different temperature. All diffraction peaks were attributed to the semi-crystalline polymer substrates. The film did not show any additional diffraction peaks, indicating the amorphous nature of the top and bottom ITO layers and Ag layer. In addition, there was no appreciable change between XRD spectra of different temperature except there was a slight increase of peak intensities for semi-crystalline PET due to a slight increase in crystallinity of PET.

As previously reported ITO films up to 100–200 nm thick are amorphous and processing temperature above 100 °C or increasing film thickness can provide crystalline growth [29]. It was also observed by Jin *et al.* [30] that the microstructure of an inserted Ag layer between ITO layer depend on its thickness. They reported that for a layer thickness of 10 nm no crystalline peaks were found in XRD, but for layers with thickness greater than 10 nm there was evidence of developing crystallinity. This suggests that the microstructure of the film is not influenced by subjecting it to temperatures up to 100 °C. Fig. 15 shows the transmittance spectra of the ITO/Ag/ITO thin film with various temperature exposures as a function of wavelength. The transmittance of all of the films was approximately 75% in the visible light region. This shows that temperature does not necessarily affect the optical properties.

Fig. 13. (a) Normalized electrical resistance of ITO/Ag-alloy/ITO as function of time at different applied temperature. (b), (c) and (d) SEM images of surface of ITO/Ag-alloy/ITO after exposure to different temperatures for 40 minutes.

Fig. 14. XRD diffraction patterns of the ITO/Ag-alloy/ITO film exposed to different temperatures (RT, 50 °C and 100 °C)

Fig. 15. Optical transmittance spectra of ITO/Ag/ITO thin film with different temperature exposures.

3. Conclusions

In this research twisting tests and twisting fatigue experiments were conducted on ITO/Ag-alloy/ITO coated PET. In twisting tests, it was found that cracks started at angle of $39^\circ \pm 2.4^\circ$ and propagated towards the sample length. The crack intensity increased with increasing applied angle, resulting in electrical resistance increases. The cracks were observed to initiate not only from coating defects but also from edge defects. These findings suggest that improving coating quality and sample edges can lead to preservation of the integrity of the thin film. In addition, good correlation between the CTA-R value which was obtained by using normalized electrical resistance and CTA-M values obtained by using the CLSM images was observed. SEM results reveal cracking and buckling delamination failure which indicates that both tensile and compressive stresses have been induced in the films by the twisting motion. In twisting fatigue experiments, the analysis of resistance has revealed that as the number of cycles increases the normalized resistance increases due to crack initiation and propagation. In addition, normalized resistance change of the samples was higher at higher applied angles. This was caused by higher applied stresses which led to more thin film cracking resulting in greater changes in electrical resistance. Furthermore, the percent change in electrical resistance for samples during cyclic fatigue at 100°C temperature was higher compared with that at room temperature and 50 °C. It is believed that up to a temperature of 100 °C the internal stresses are enhanced in the coating because of thermal expansion coefficient mismatch between the polymer substrate and the thin film. Therefore, a combination of the applied external stress with internal stresses accelerating crack initiation and propagation and then leads to an increment in electrical resistance. Open cracking observed during twisting fatigue at 100 °C promotes oxidation of the Ag layer and associated with high electrical resistance modulation. Moreover, CLSM images showed that no crack appeared in ITO/Ag-alloy/ITO film after exposure to (RT, 50°C and 100°C) in the absence of cyclic twisting. This suggests that the combined action of an externally applied mechanical stress and temperature which both promote cracking should be taken into account for ensuring reliability.

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