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Twisting fatigue in multilayer films of Ag-alloy with indium tin oxide on polyethylene terephthalate for flexible electronics devices

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Abstract

Twisting monotonic and fatigue experiments were conducted on multi-layered films of Ag-alloy based indium tin oxide (ITO) deposited on polyethylene terephthalate (PET). In the twisting tests, crack development and electrical resistance were monitored *in situ*. Cracks initiated at an angle of 39° ± 1.7° and propagated towards the direction of the sample length. Two sets of experiments were performed; the first set of experiments was conducted to study the effect of twisting angle and temperature on the film's electromechanical performance. The other set of experiments was conducted to study the effect of temperature in the absence of cyclic twisting deformation. The change in electrical resistance increased with number of twisting cycles and 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 mechanical stress is important for electrical device performance; temperatures in both fabrication and use should not exceed 50 °C.

Keywords: ITO/Ag-alloy/ITO, Polymer substrates, PET, twisting, Flexible electronic devices.

1. Introduction

There is an increased interest in flexible optoelectronic devices because they offer substantial advantages such as a large area, exciting new form factors, light weight and low cost [1]. 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 for 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, and usually fluctuating, cost of indium encourages the reduction of the quantities employed for film fabrication. It is challenging to reduce thickness under 150 nm in the case of a single ITO film owing to a decrease in electrical connectivity with thickness decrease [3,4]. Therefore, a very thin metal film can be inserted between the ITO films to induce higher conductivity than a single ITO layer of the same thickness [4]. Such a multilayer system has been shown to be effective in achieving electrically conductive and optically transparent electrodes by optimising the thickness of the ITO layer [5]. Usually, silver (Ag) film is used as the metal layer because it has the lowest resistivity of approximately 2×10^{-6} Ω. cm. in comparison with all other metals [6].

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 conditions [7], the mechanical response of different thin films has been extensively studied using mostly uniaxial tensile and buckling experiments. Cairns *et al*. [8] 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 [9]. The electrical resistance was monitored *in situ*. It was found that the ITO failed when exposed to strain of approximately 1.2 %.

As the number of applications for transparent conductive oxides on flexible plastics substrates increases, another deformation mode, which may be applied during fabrication or extreme handling, is twisting deformation. Lim [10] studied the electro-mechanical failure mechanisms of zinc tin oxide (ZTO) / Ag / zinc tin oxide (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 in the change of 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 [11] repeated dynamic loading forces for large number of cycles can cause structures to fail at stresses lower than those needed for failure under static load. Lechat *et al*. [12] showed that the cyclic loading stress was the cause for PET failure as it led to crack propagation at low stress.

Additionally, Gorkhali *et al*. [13] 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 while electrical 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 layer. After, 50,000 cycles catastrophic conductive failure occurred due to severe cracking. Also, Cho *et al*. [14] conducted cyclic loading experiments in the twisting mode. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) films printed on PET substrate were repeatedly twisted and untwisted using both sides of the sample at an angle of 30 °, and the change in electrical resistance was monitored *in situ*. It was observed that the change in electrical resistance is constant after 2,000 cycles indicating that such organic layers can provide high levels of twistability and flexibility. Hsu *et al*. [15], investigated the stability of an (20 nm) ITO film coated on PET substrate under tensile and compressive fatigue bending. They observed that both tensile and compressive stress can cause ITO failure and increase in electrical resistance and transparency. In addition, tensile stress was increased electrical resistance more easily compared with compressive stress. Moreover, the sheet resistance and optical transmittance were found to increase with increasing PET thickness regardless of whether the sample was under tensile or compressive stress.

In addition to external repeated mechanical stress, the thin film anode may also be subjected to high temperature such as 100 °C during the manufacturing process and perhaps up to 40 °C during the use of the devices. The temperature is likely to affect the mechanical, physical and electrical properties of the thin film layers over time, and to increase the oxidation of the metal film when used as intermediate layer between the transparent conductive oxide (TCO) layers. Because of the mismatches in the thermal expansion coefficients of substrate and thin film, both of them do not respond to temperature increases, in term of elongation, by the same percentage. The latter leads to thin film expansion or contraction resulting in cracking or/and delamination. Khalid *et al*.[16] studied the influence of temperature on the bending fatigue behaviour of copper thin film that deposited on a PET substrate by the sputtering technique. 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 conditions 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 a twisting and cyclic twisting apparatus developed in this project. The influence of factors including twisting angle and temperature and frequency on the fatigue behaviour of thin films deposited on flexible PET substrates are discussed. Further work on modelling the mechanical behaviour in order to provide a theoretical basis and lifetime predictions or estimates is in progress, in parallel with this study.

2. Experimental details

2.1. Samples

The ITO(~95nm)/Ag-alloy(~10 nm)/ITO(~95nm) sheets on PET (125µm) substrate with sheet resistance of 11Ω/sq were supplied by Dr G. Potoczny and 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 Bejitual *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 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 on a rigid frame. Metal grips were prepared and connected to the two goniometers to clamp the specimen. For *in situ* electrical resistance monitoring, a polymer plate was placed between each metal grip and each goniometer to provide a closed electrical circuit (see Fig.1). Then, two copper wires were attached to both grips and connected to a FLUKE 45 multimeter. A computer running National Instruments Lab View software was used to collect electrical resistance data. The twisting apparatus was placed underneath a confocal laser scanning microscope (CLSM) to monitor film crack initiation and propagation. The clamped sample was twisted in opposite directions by the grips at each end. 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 three-minute hold.

2.3. Twisting fatigue tests

Commercial rheometer machines equipped with a temperature-controlled oven are typically used to measure flow and deformation of materials under applied forces [17]. For this project a number of customisations were applied to allow investigation of the twisting fatigue behaviour of ITO/Ag-alloy/ITO coated PET. The sample was mounted by two jigs attached to the rheometer. The top jig is fixed to the stationary upper part of the rheometer while the other at the bottom, moves with a rotational driver, as shown in Fig. 2. During the experiment the lower jig oscillates about the vertical axis causing the specimen to twist in the clockwise or counter-clockwise direction. In a similar manner to the other twisting experiments, in order to close the electrical circuit and measure the electrical resistance change, the bottom jig is insulated from the base of the rheometer machine by using a polymer plate and plastic screws as shown in the inset of Fig. 2. As earlier, the electrical resistance is monitored by a multimeter and recorded by Lab View software. In order to keep the sample flat and stable, a small initial load was applied before starting the test. In addition, a calibration was performed to link the applied strain to the twisting angle. Both angle (17.5°, 22.5°, 27.5°) and temperature (RT, 50°C, 100°C) were selected as experimental parameters. The device's limiting twisting angle is 27.5° beyond which the sample does not twist. Also, the maximum temperature used was 100°C because this allowed measurements either side of the T_g of PET. Due to the device's limiting clamp dimensions, samples of the same dimension as those used in the twisting experiments were cut from a coated sheet (30 * 4 mm). The measured torques were ($3.7 * 10^{-3}$, $4.2 * 10^{-3}$, and $4.7 * 10^{-3}$ N. m) for the angles 17.5°, 22.5° and 27.5°, respectively. An air oven was used to heat the sample. 10 minutes were set aside before each material tested to reach the necessary temperatures. At any selected angle, such as at 17.5°, during one complete cycle the sample will twist in the following sequence 0° to; 17.5°, 0°, -17.5°, and then back to 0.

In order to assess whether occurring film damage was due to either cyclic twisting or temperature, a second set of experiments was performed. Without any mechanical loading applied, the samples were subjected to the same range of temperatures for 40 minutes (which is equal to the time required to perform 200 cycles at a frequency of 12 seconds/cycle). The electrical resistance was measured in situ. Scanning electron microscopy (SEM), X-ray diffractometry (XRD) and film transmittance tests were performed on tested and pristine films. SEM was also used to characterize film crack morphology after twisting and twisting fatigue experiments. Prior to SEM observations, the samples were sputtered with a 5 nm film gold layer to dissipate electron charges. The images were taken under an accelerating voltage of 15 kV and at a working distance of 10 mm.

3. Results and discussion

3.1. *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 measurement techniques are microscopy (CTA-M) and normalized electrical resistance (CTA-R) monitoring, both used to determine the critical twisting angle (CTA) for coating failure initiation. CTA-M is defined as the critical twisting angle at which the first cracks in the coating are observed, and CTA-R is defined as the critical twisting angle at which a 10% increment in electrical resistance occurs. The 10% increase was arbitrarily selected as the criterion for crack onset initiation [18].

CLSM micrographs of the cracks initiation and development on the ITO/Ag-alloy/ITO films at different angles are shown in Fig.3. Cracking is observed to appear at a CTA-M equal to 39° ± 1.7°. The imperfections or defects remaining after deposition in the layer coupled with edge defects resulting from specimen cutting are believed to be crack-initiation sites, Fig.3(a). It is suggested that this observation contributes to an increase in the energy released in the region [19]. The interface separation in the neighbourhood of an imperfection exhibits a larger energy release rate than that for a defect-free surface [19]. By increasing the applied twisting angle, the number of cracks initiated starts to increase and crack initiation continues along the whole sample length. However, it was found that the channel crack did not grow through the whole width of the film; they were arrested at a certain distance from the middle section of the sample width, as shown 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 propagating further as the applied twisting angle increases. This may be due to the substrate becoming plastic and not transferring the amount of stress required for crack propagation.

Fig. 5 shows the crack density and the change of electrical resistance of the conductive layer which is expressed as $\Delta R/R_o$, where $\Delta R = R - R_o$, (R_o is the electrical resistance value before applying stress and R is the value after applying a twisting stress). At the early stage of applying a twisting angle the normalized values of electrical resistance are negative. This could be due to the 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. This results are consistent with results reported by Potoczny [20] for ITO film on PET when subjected to compressive stress. This implies that during twisting tests sample was 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, (CTA-R) which promotes the first cracks in the conductive layer was observed to be 39.3° ± 3.5°. Above (CTA-R) the electrical resistance increased gradually due to the increased film crack formation [21], as the series of CLSM images show in Fig. 3. In addition, a finite electrical resistance was observed even at an applied twisting angle of 68°.

A potential reason for finite electrical resistance in ITO/Ag-alloy/ITO thin film, even at relatively high twisting angles, is that the channel cracks have not fully traversed across the sample width (see Fig. 4) so that the sample remains electrically conductive. Also, any overlapping film material at the crack (see Fig. 6(b)), contributes to the formation of conducting paths between the ITO fragmented films, which causes finite electrical resistance. This is consistent with a previous study conducted by Choa *et al*. [22] 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° ± 3.5° and it was in good agreement with CTA-M values determined by using CLSM images. Leterrier *et al*. [23] 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 $\Delta R/R_o$ *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. In the second region (see Fig. 5), the crack density reaches a saturation point at 60°, but the significant increase in normalized electrical resistance was observed above the crack saturation point. This is possible because at large angles the material no longer overlaps at the crack and the conductive path is no longer present. The stress produced on the ITO/Ag-alloy/ITO films after the saturation point leads previously formed cracks becoming deeper and wider and that can also be a reason for severe 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 [24].

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(a) shows that in some places the film was in complete separation due to the formation of wide cracks. 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. 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 a PET substrate equal to 38° [10].

The coating damage, under tensile strain, is caused by the creation of channel cracks, while under compression the film specimen may first delaminate from the polymer substrate and then buckle before the initiation of a crack [22]. This is in agreement with the surface morphology of twisted ITO/Ag-alloy/ITO multilayer samples observed in this work (see Fig. 6). The results of our work thus suggest that the twisting deformation induced tensile and compressive stress on the film simultaneously.

The thin film crack-initiation sites observed in this study are consistent with those previously reported by Sim *et al*. [25] for ITO thin films deposited on a plastic substrate. This is also consistent with a study of Bejitual *et al*. [2] who investigated the mechanical behaviour of patterned ITO coated PET substrates. They found that the cohesive crack originated from the edges of the pattern where the thin layer's surface is subjected to the tensile buckling mode. Consequently, edge etch control is important and may, in turn, enhance the reliability of the patterned thin film with increasing edge resolution. Furthermore, Lopez *et al*. [26] pointed out that the homogeneity of the edges has a significant effect on the initiation and propagation of cracks and bending reliability of flexible platinum lines patterned on polyimide.

3.2. 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.

3.2.1. Effect of twisting angle

The samples were tested at room temperature and a frequency of 12 second/cycle. Fig. 7 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 [27]. In 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 [27]. With further increment of the number of applied twisting cycles, a gradual increase of normalized electrical resistance is observed. This is likely to be due to progressive cracking and buckling [27], as shown in Fig. 8 (a),(b) and (c).

Fig. 9 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 27.5° shows the highest increase in normalised electrical resistance. Therefore, as the applied twisting angle increases, samples fail sooner. In addition, electrical resistance changed during loading and unloading as shown in the inset of Fig. 9. This change is believed to result from the wide opening and re-closing of microcracks in the film during twisting and untwisting of the sample [28]. Furthermore, resistance modulation repeated continuously during twisting cycles as shown in Fig. 9. The modulations in resistance of ITO/Ag-alloy/ITO multilayer film significantly depend on the twisting angle. The resistance modulation in the film with a higher twisting angle is higher than those of lower twisting angles. The resistance modulation phenomenon during bending test was reported by Park *et al.* [29] for Ga-doped ZnO (GZO/Ag/GZO) multilayer deposited on flexible substrate. They observed that modulation in resistance becomes stronger after subjecting samples to lower bending radius. In our study, 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. 10 (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 exhibit cracking.

However, a slight increase in electrical resistance with increasing number of cycles was noted. For example, we observe that at 200 cycles the change in electrical resistance is 9.3± 2.02 % for a 17.5° angle; and 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 [28]. Fig. 10 (c) is depicting the surface of the ITO/Ag-alloy/ITO samples after twisting cycles at 27.5°. It shows a few shallow and parallel to each cracks 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 film's electrical resistance (i.e. 28.6 ± 2.9 % after 200 cycles) compared to angles 17.5° and 22.5°, respectively.

3.2.2. 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 this work. In Fig.11, the normalised electrical resistance is plotted as a function of the number of twisting cycles at different temperatures and at constant twisting angle of 27.5° and constant frequency of 12 second/cycle, respectively. Regardless of temperature used, the electro-mechanical performance is consistent with that observed for fatigue twisting at different angles (see Fig 7.); after the first few cycles the normalized electrical resistance increased significantly until equilibrium is reached.

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 is noted. At 200 cycles, the change in electrical resistance for specimens tested at room temperature is found to be the lowest, whereas for specimens subjected to 50 °C resistance increases by about 78%, and for specimens subjected to 100 °C by 233%. Therefore, the combined action of externally applied torsional stress and temperature is considerable.

The significant difference in the normalized electrical resistance for the samples tested at 50 ° and 100 °C compared with those tested at RT could be due to the following reasons Firstly, the internal tensile stress has a direct effect on accelerating cracking of the thin film [30]. When the temperature increases to approximately 100 °C, the internal tensile stresses increases in the coating [31] due to the high thermal expansion coefficient of the substrate compared to the coating and also the mechanical mismatch increases between thin film and substrate resulting from the softening of the polymer substrate. Therefore, the thin film fractures easier, resulting in an increment in the electrical resistance. Secondly, once the crack has initiated under combined cycle stress and high temperature, it is easier for the oxygen in the air to penetrate into the Ag layer and react with it thus causing the Ag layer to partially oxidize. In general, oxidation occurs at a higher rate when the temperature is high [16]. Therefore, oxidation could be another factor, which might cause increments in the electrical resistance, in addition to the externally applied twisting stress.

The increase of crack density with temperature is shown by the confocal micrograph images Fig.12 (a), (b) and (c). It is found that crack density starts to increase as 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 ^{o}C are greater than that at room temperature, see Fig.11. In addition, ITO/Ag-alloy/ITO multilayer tested at higher temperature exhibits a larger 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, visible in the Fig. 13(b).

Similar electro-mechanical behaviour to that obtained in this work was reported for uniaxially strained ITO film coated PET substrates by Cairns *et al*. [27]. 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*. [16] 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. 14, the corner area at the end of the specimen exhibits the highest value of crack density, compared to the centre, because of the highest stress concentrated in that area. In the cases where cracks growth from one edge of sample to the other, the conductive path was reported to be severed; this means that the film lost its conductivities completely. This does demonstrate the property of an insulating material, which was not observed in our flexing test.

3.2.3. Film temperature response characterization

The samples were subjected to the same combinations of temperature (section 3.2.2) 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.15. shows no significant change in normalized electrical resistance over time for samples exposed to RT and 50 ^{o}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 stabilize after a certain period of time. This may result from microstructural rearrangements in the ITO [32] leading to shortening the distance between atoms and resulting in an increase of the electrical conductivity. To further understand the stability of the electrical resistance, SEM, XRD and optical transmittance tests were performed on the films exposed to different temperatures.

The lack of any cracks initiating in the surface of all samples in Fig. 16(b) and (c), confirms the electrical resistance stability. Fig.17 shows diffraction peaks of ITO/Ag-alloy/ITO for 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 for different temperatures.

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 [33]. It was also observed by Jin *et al.* [34] that the microstructure of an inserted Ag layer between ITO layer depend on its thickness. They reported that for a layer thickness greater than 10 nm no crystalline peaks were found in XRD, but for layers with thickness there was evidence of developing crystallinity. This suggests that the microstructure of the ITO and Ag film is not influenced by subjecting it to temperatures up to 100 °C. Fig.18 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.

4. 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 initiated at an angle equal to 39° ± 1.7° 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 from 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 for 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 to that at RT and 50 °C. It is believed that up to a temperature 100 °C the internal stresses are enhanced in the coating because of the thermal expansion coefficient mismatch between the polymer substrate and the 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 is associated with large electrical resistance modulation. Moreover, CLSM images suggest that no film cracking after exposure to (RT, 50°C and 100°C) in the absence of cyclic twisting. It is suggested that the combined action of an externally applied mechanical stress and temperature, both promoting cracking, should be taken into account when designing flexible optoelectronic structures for ensuring reliability.

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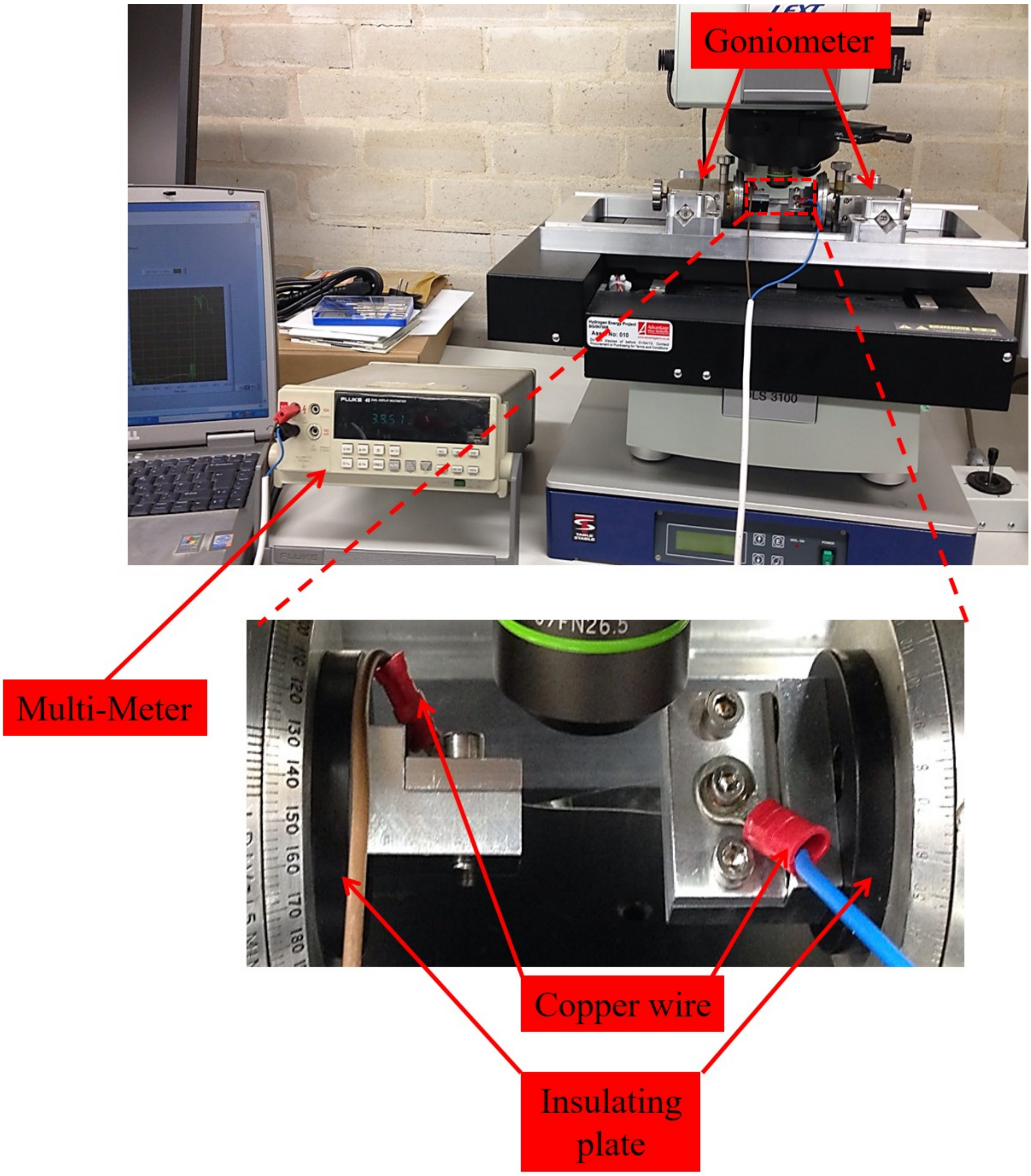

Fig. 1. Custom -built twisting loading apparatus.

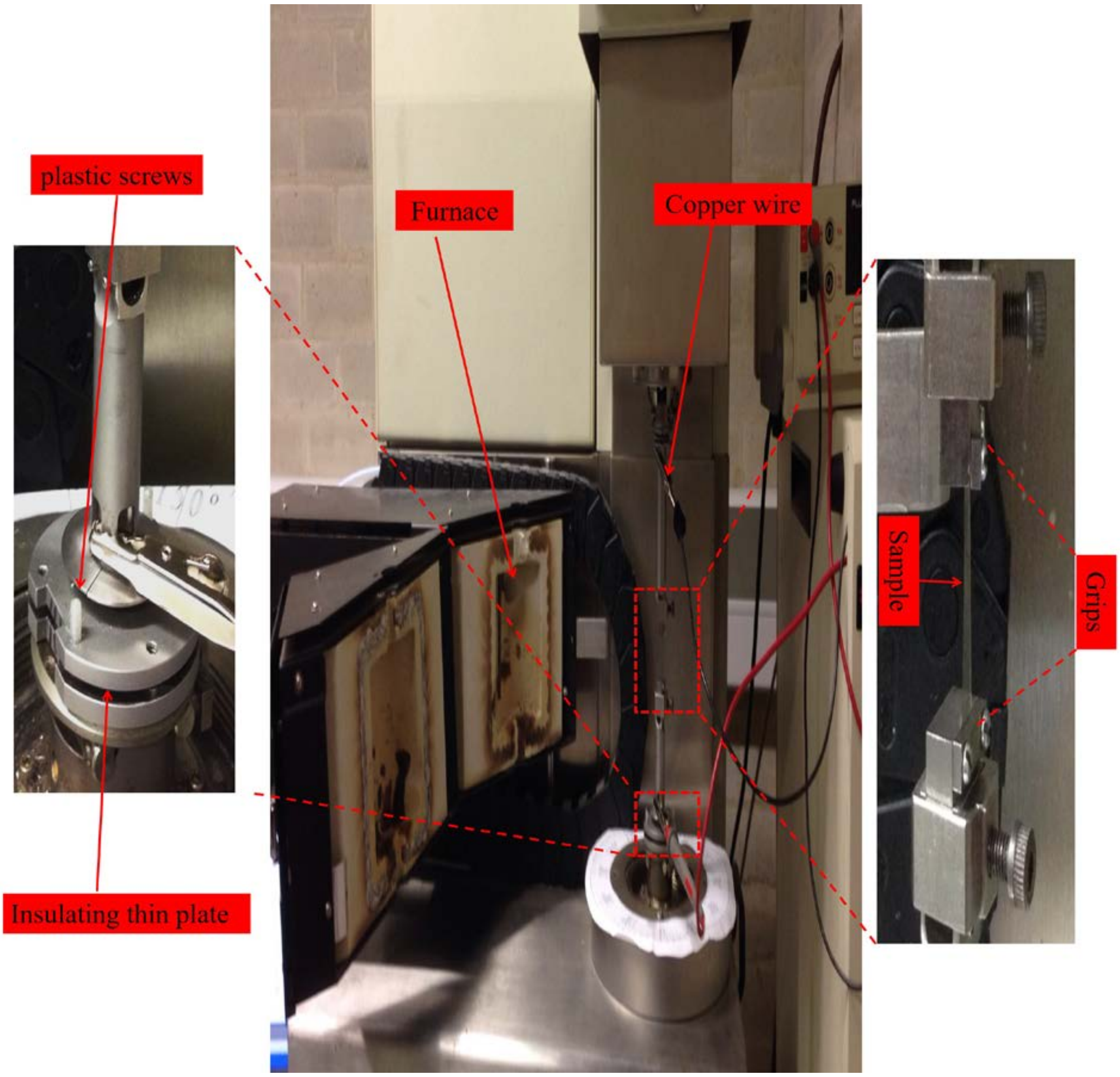

Fig. 2. The twisting fatigue experiment set-up used.

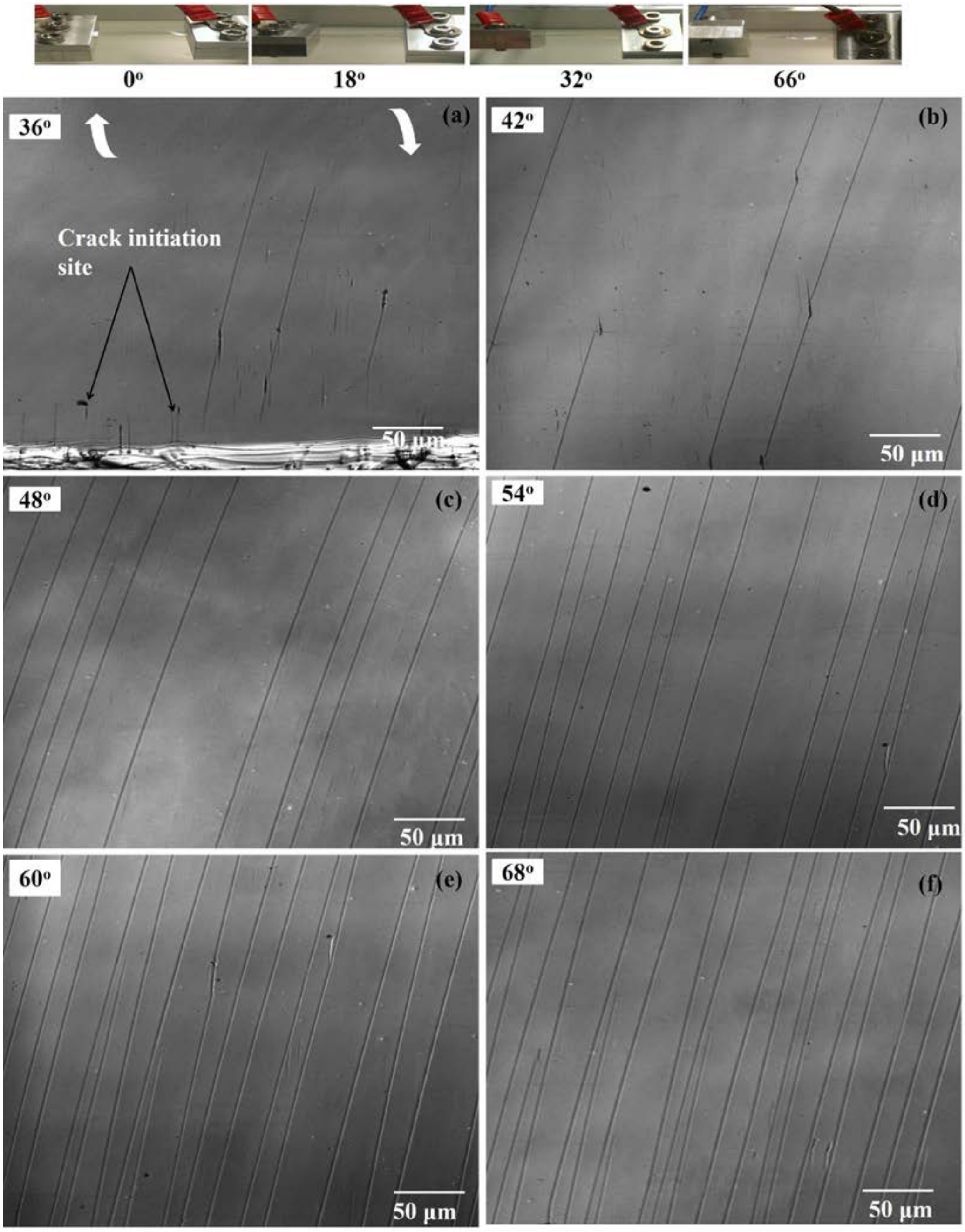

Fig. 3. *In situ* confocal laser microscope imaging of cracks development ITO/Ag/ITO of the multilayer thin film under twisting. The corresponding twisting angle values are indicated on the images. Twisted Arrows on image (a) indicated the twisting direction. The upper panel displays the steps of the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

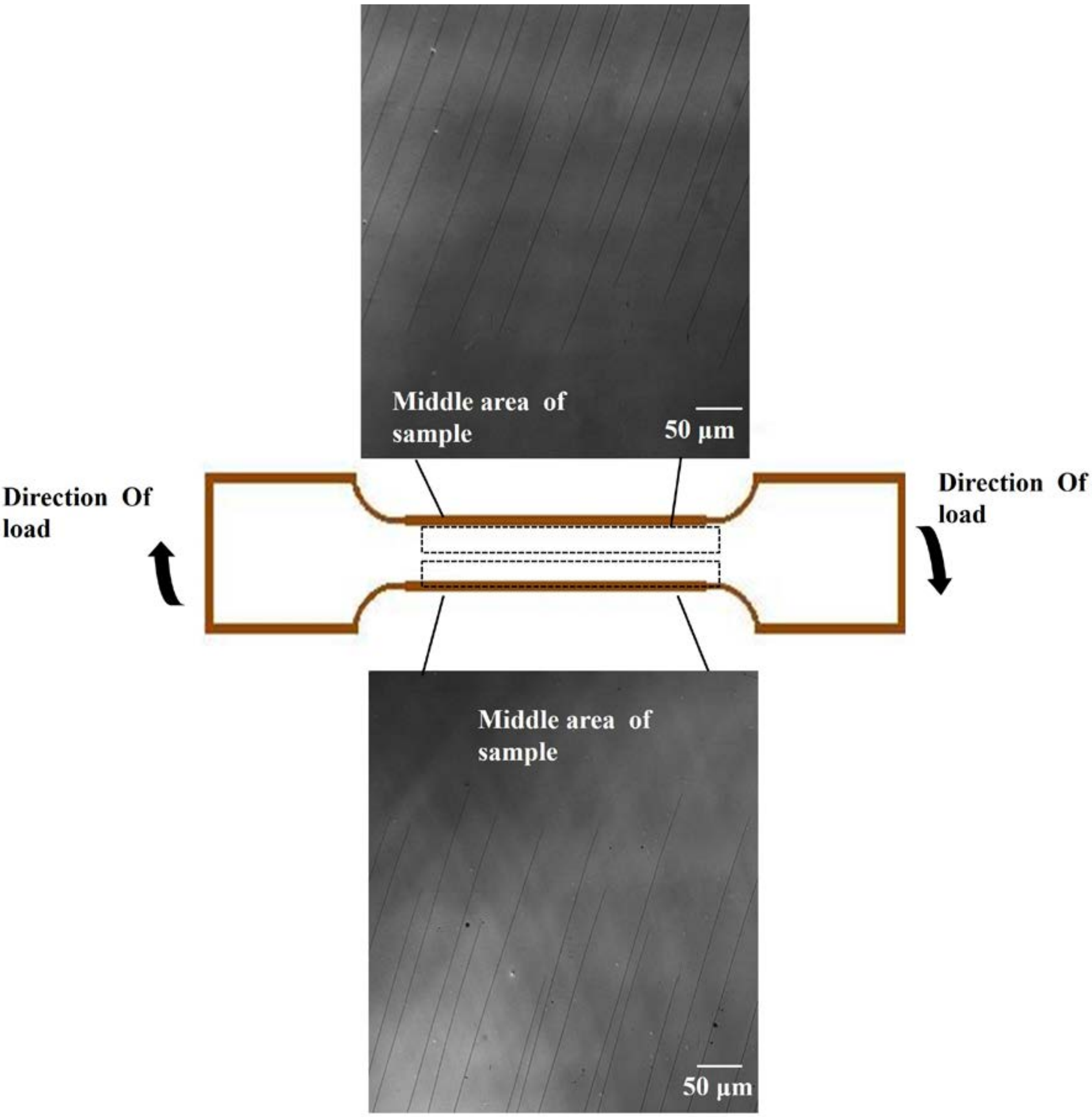

Fig. 4. Crack developments across the width of the sample under 68° twisting angle.

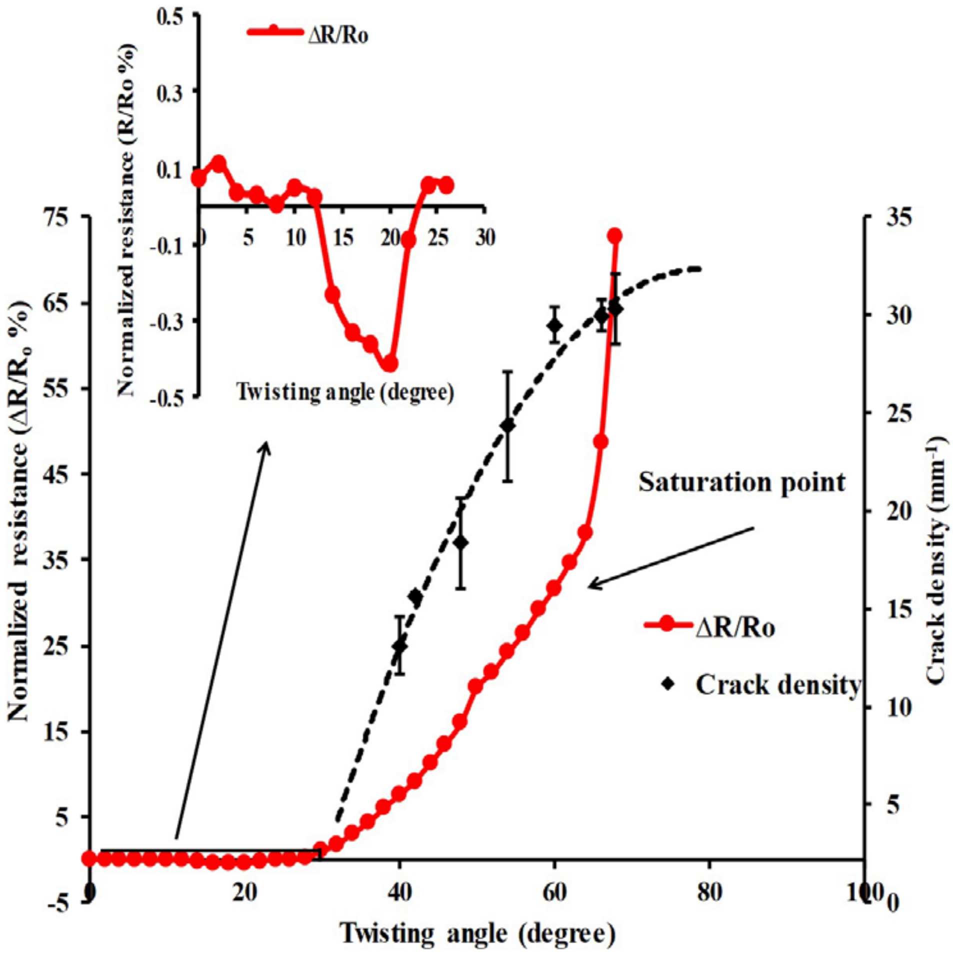

Fig. 5. Crack density and normalized electrical resistance versus twisting angle for ITO/Ag-alloy/ITO thin film coated PET substrate.

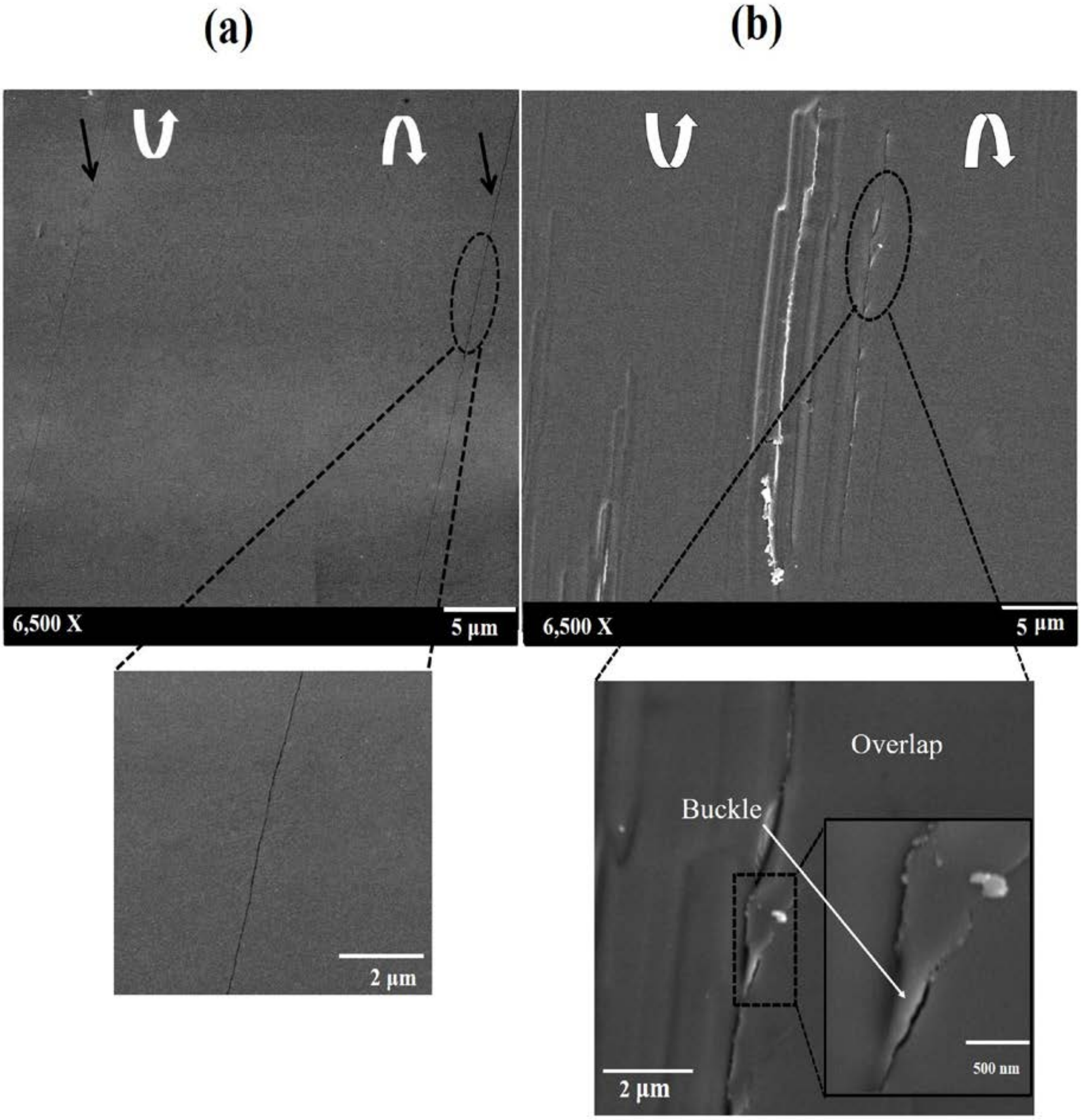

Fig.6. SEM micrograph with inset showing (a) cracks on the surface (b) overlapping and buckling delamination of ITO/Ag alloy/ITO multilayer film at 68^{o} applied angle under twisting tests. Black arrows indicate cracks and twisted arrows on image indicate twisting direction.

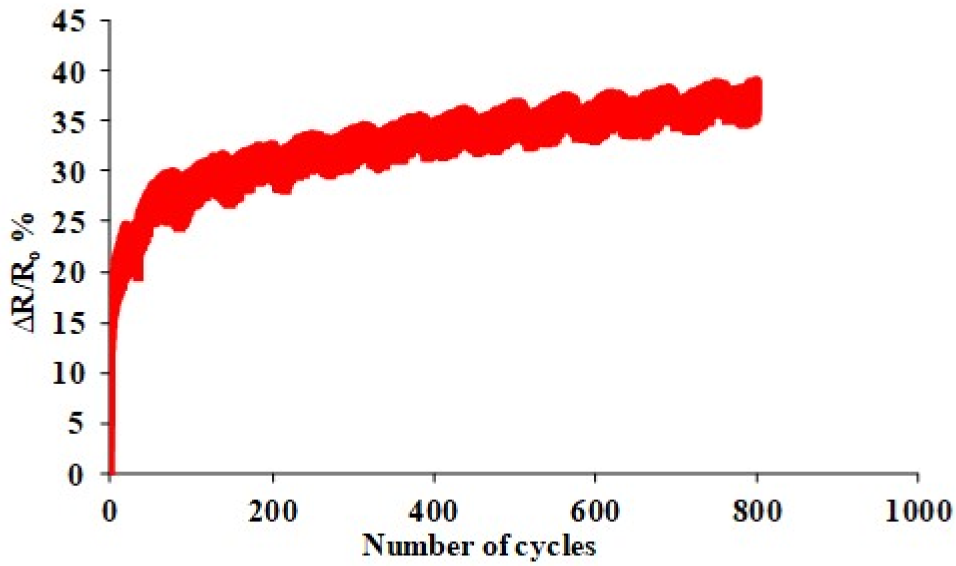

Fig. 7 Normalized electrical resistance versus number of cycles for ITO/Ag-alloy/ITO multilayer coated PET substrate.

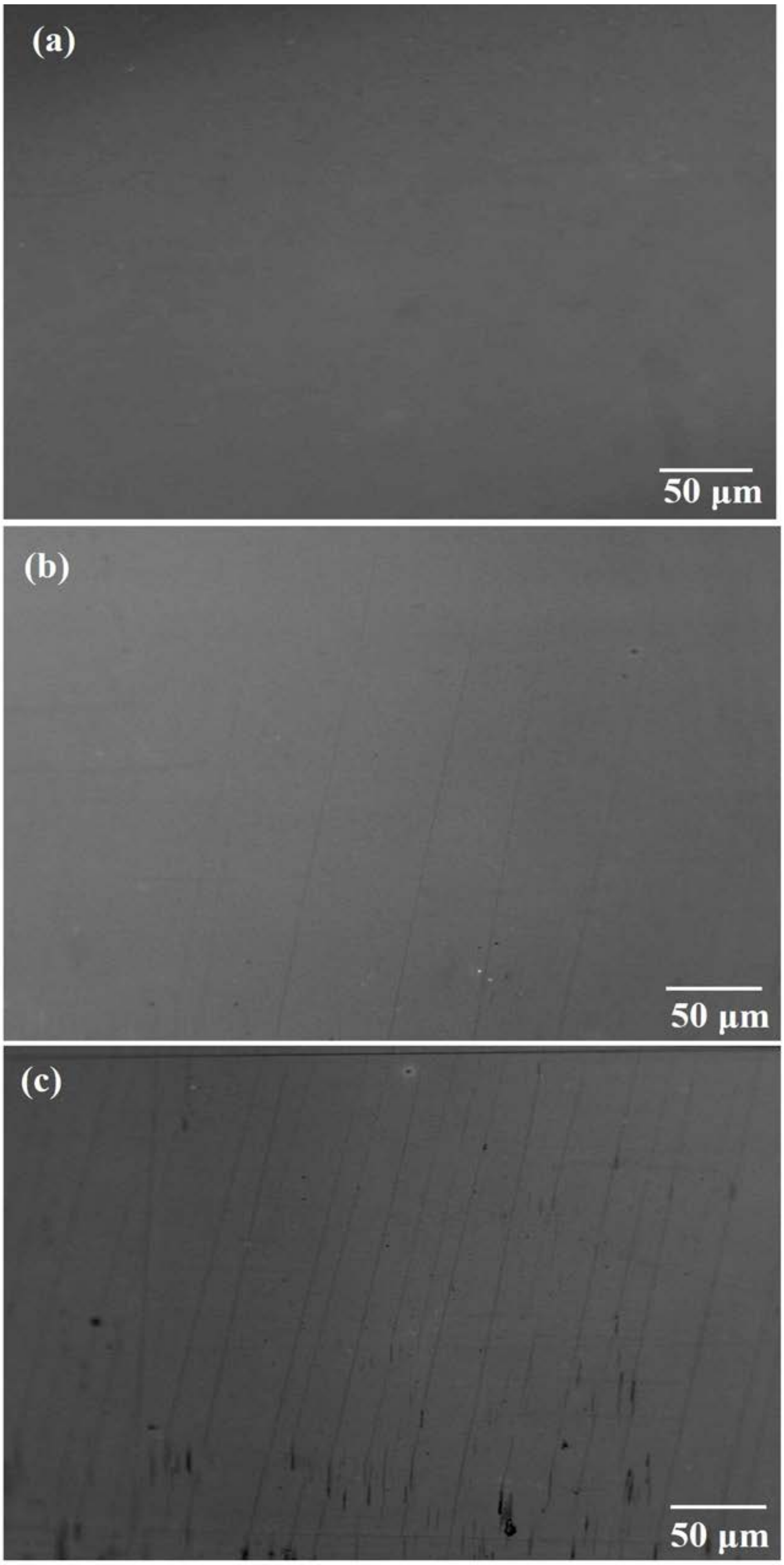

Fig. 8 CLSM images showing cracked ITO/Ag-alloy/ITO films after 100 ,300 and 800 twisting cycles at 27.5 °.

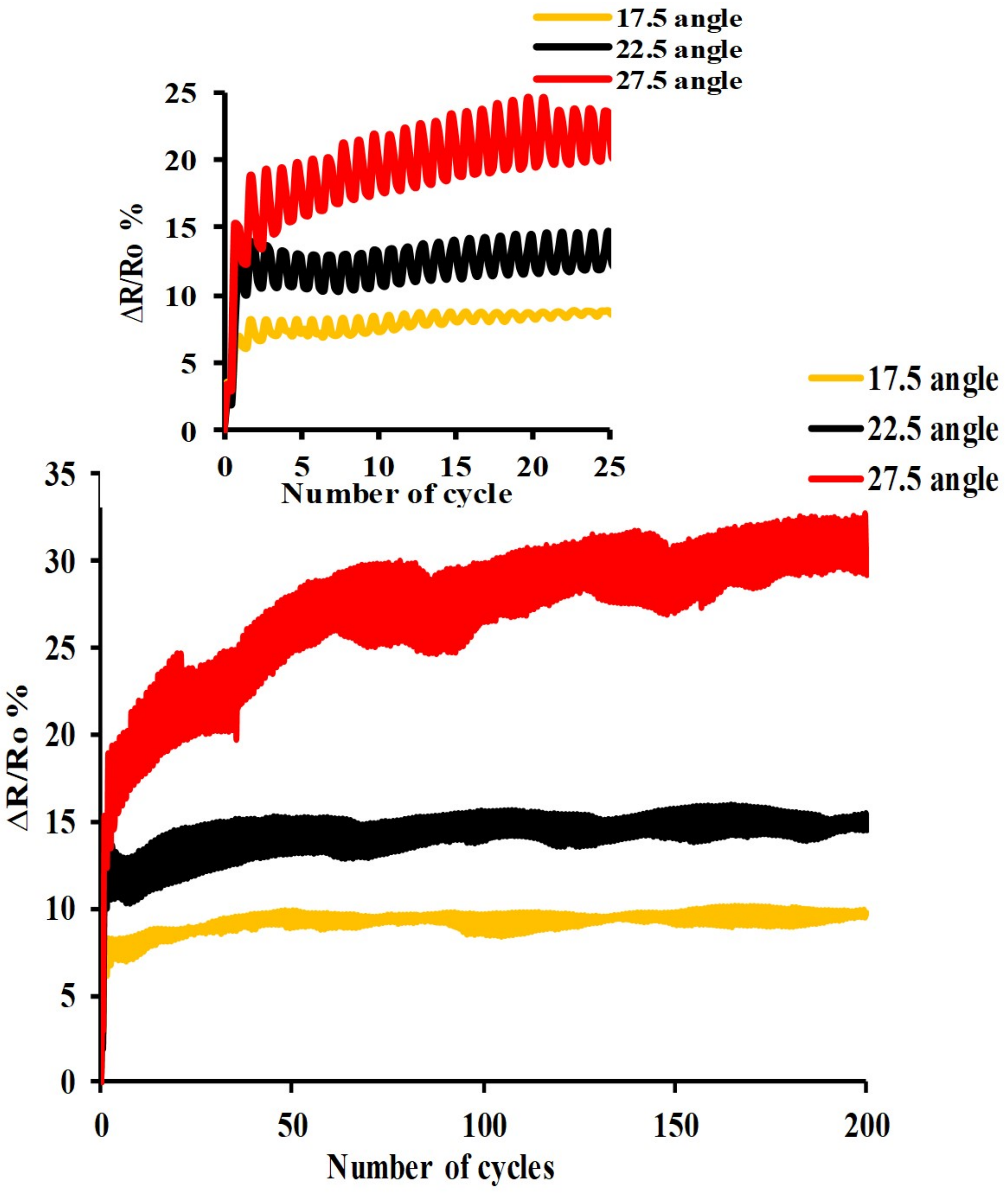

Fig.9 Normalized electrical resistance as function of the number of fatigue cycles during cyclic twisting of ITO/Ag-alloy/ITO under different applied angle.

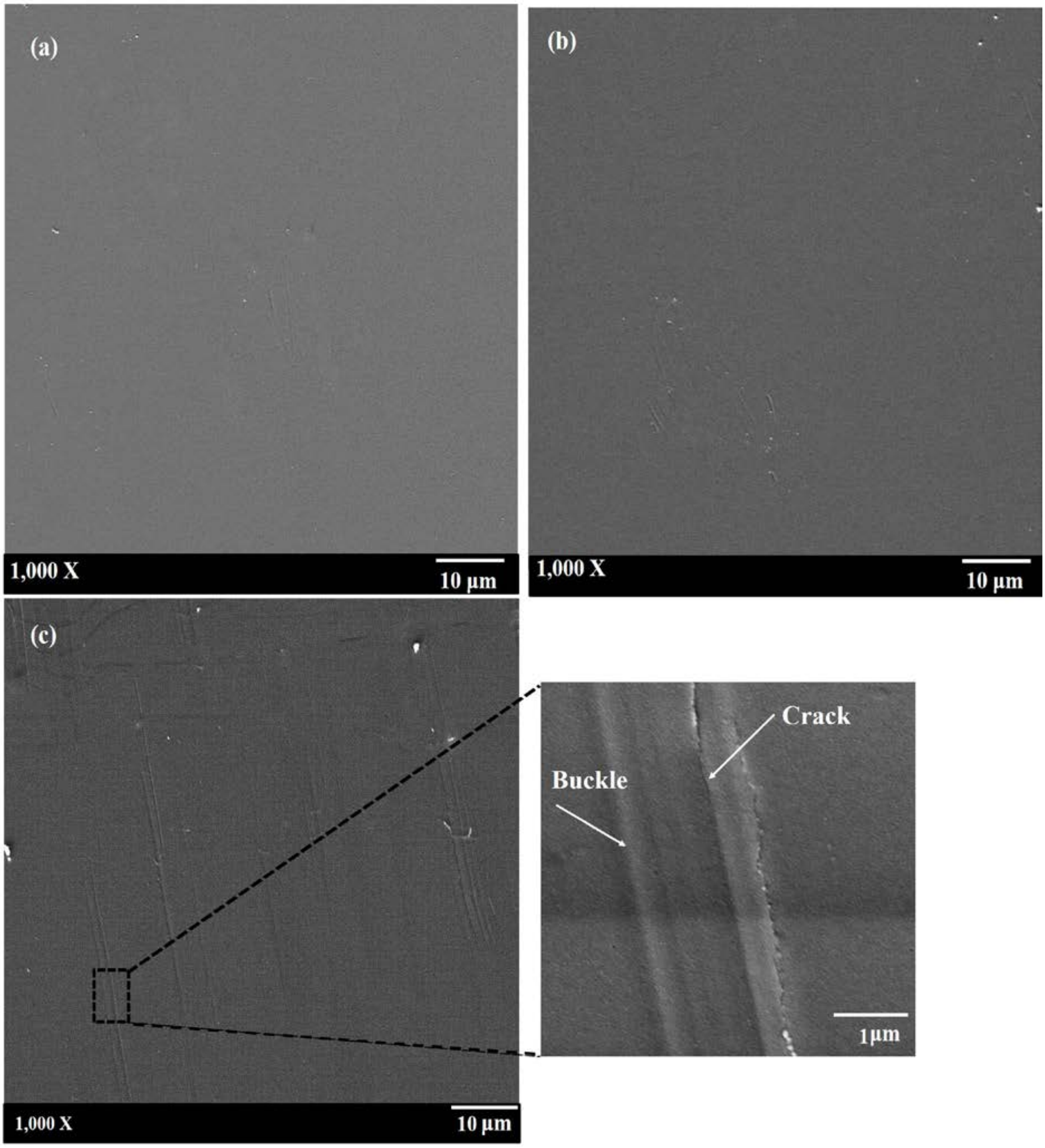

Fig. 10 SEM micrographs of ITO/Ag-alloy/ITO films after 200 twisting cycles at (a) 17.5 ° (b) 22. 5 ° (c) 27.5° applied angle.

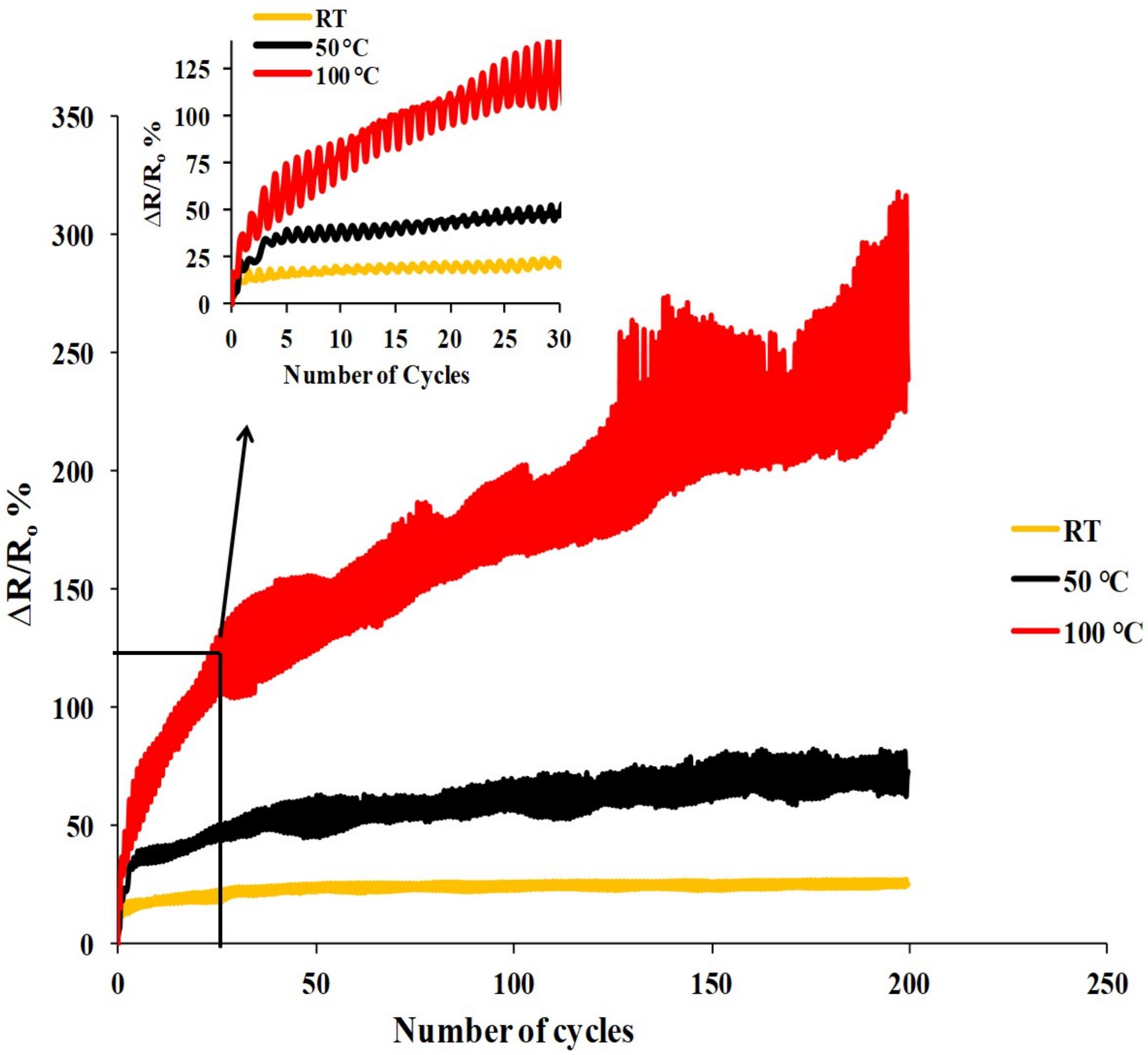

Fig. 11 Normalized electrical resistance as function of applied number of cycles during cyclic twisting test of ITO/Ag-alloy/ITO under different applied temperature.

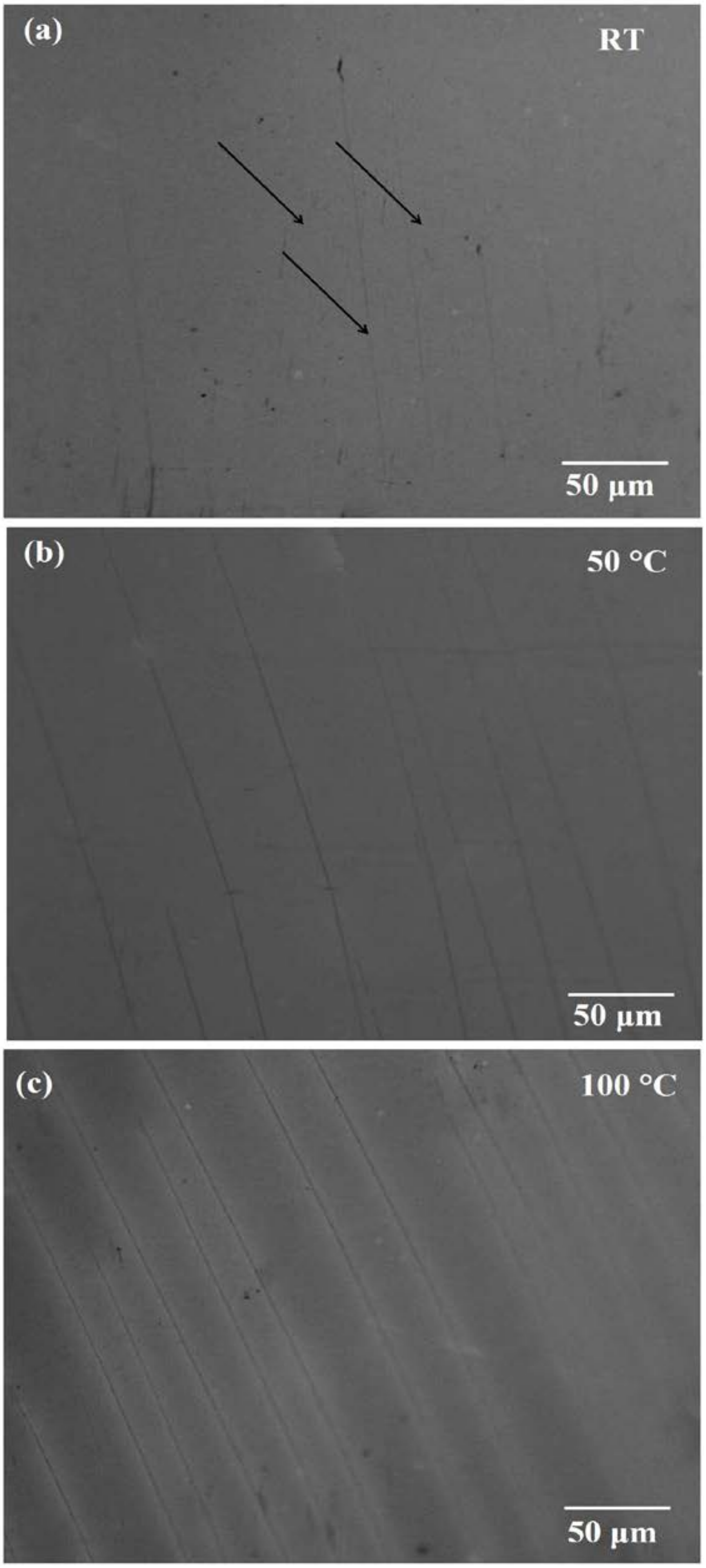

Fig. 12 CLSM images showing surface of ITO/Ag-alloy/ITO films after 200 twisting cycles at RT, 50 °C and 100 °C temperature respictively. The black arrows show cracks on the coating.

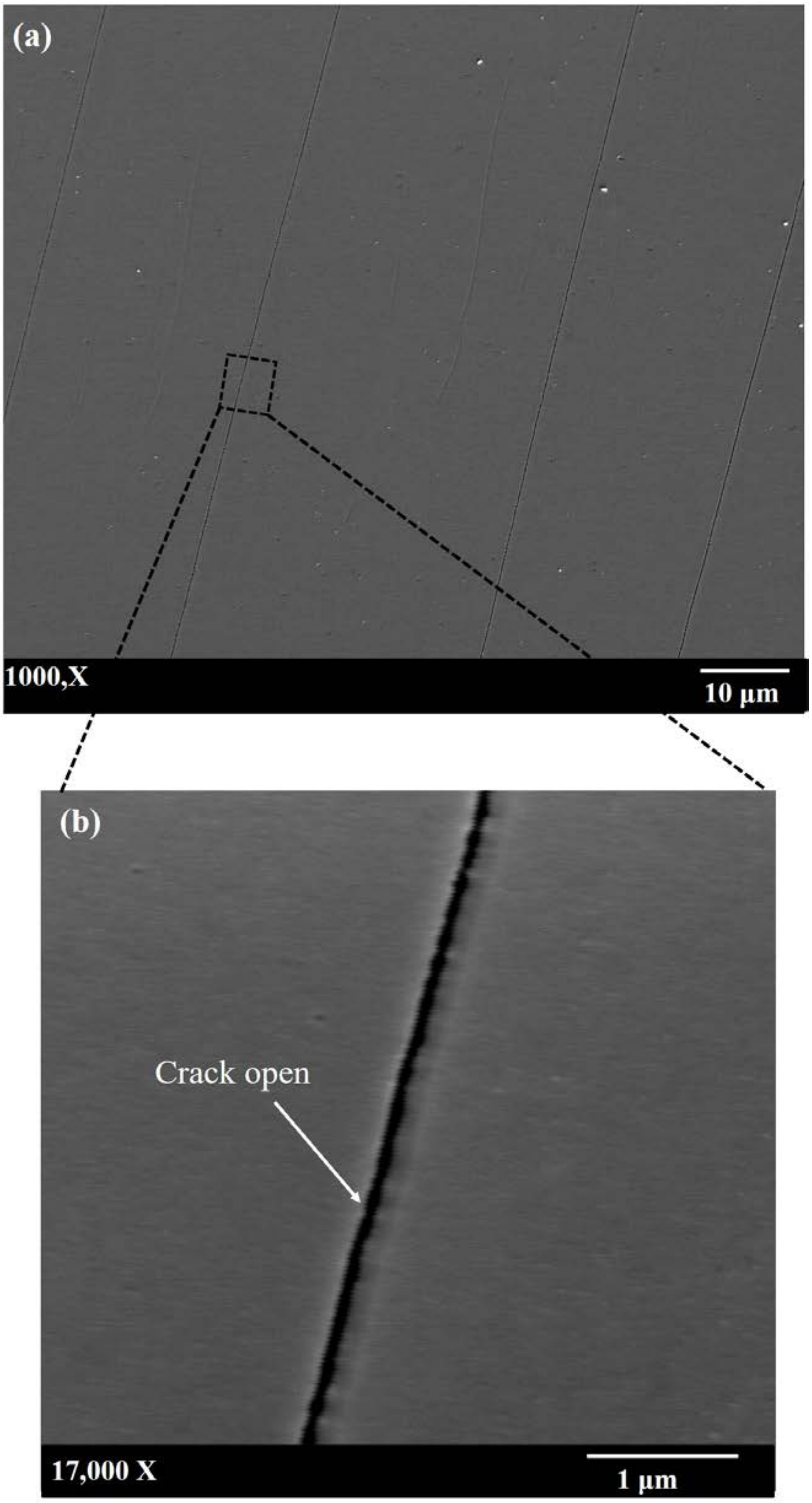

Fig. 13 SEM images of surface of ITO/Ag-alloy/ITO films after 200 twisting cycles under 100 °C temperature.

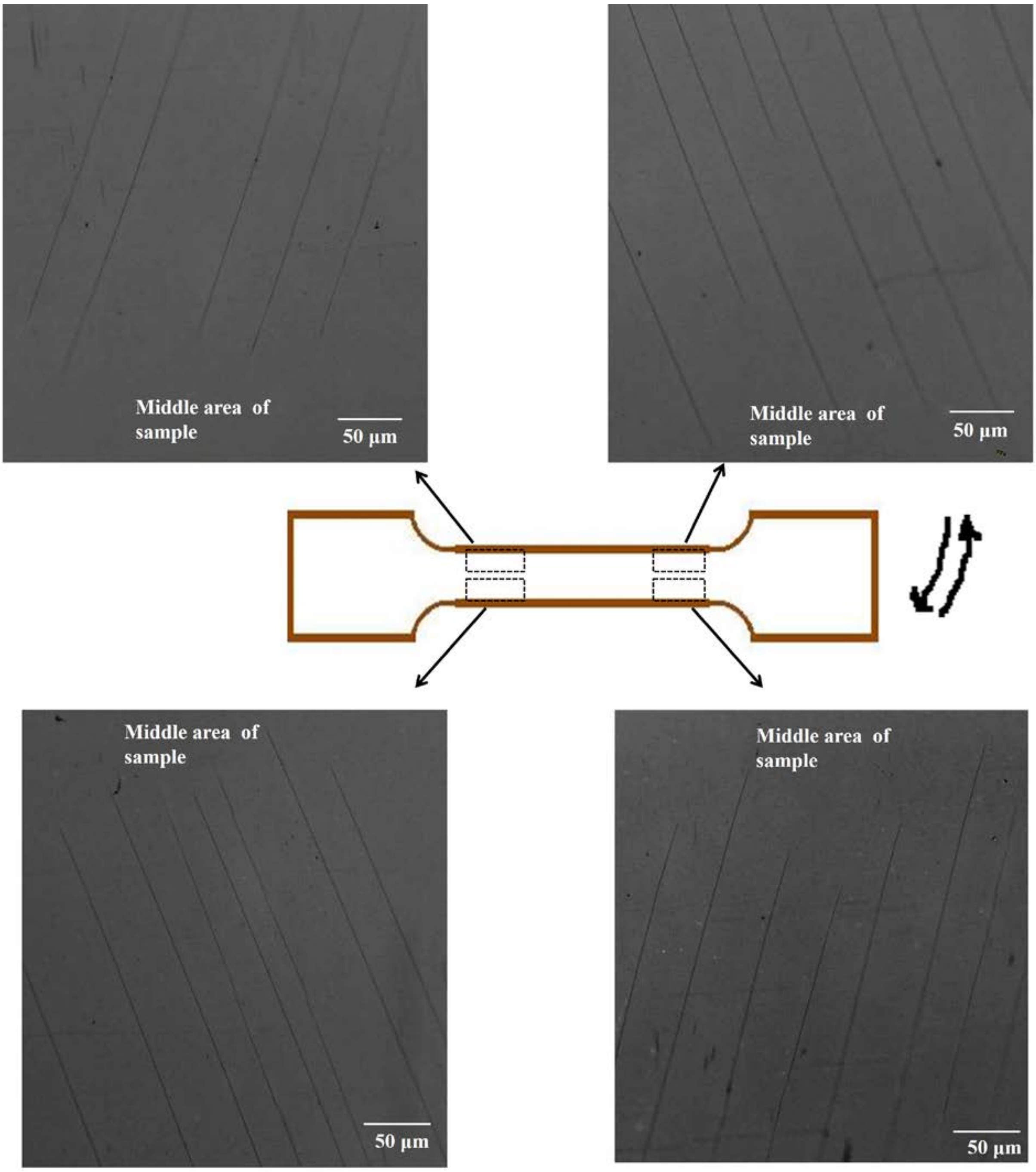

Fig. 14 Confocal laser microscopy images showing crack distribution in surface of ITO/Ag-alloy/ITO films after 200 twisting cycles at 100 °C.

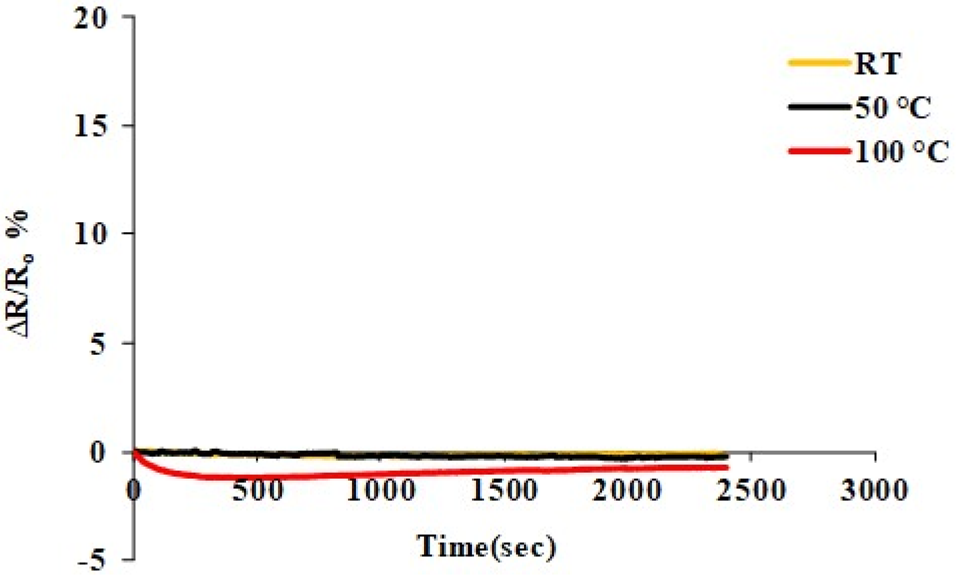

Fig.15 Normalized electrical resistance of ITO/Ag-alloy/ITO as function of time at different applied temperature.

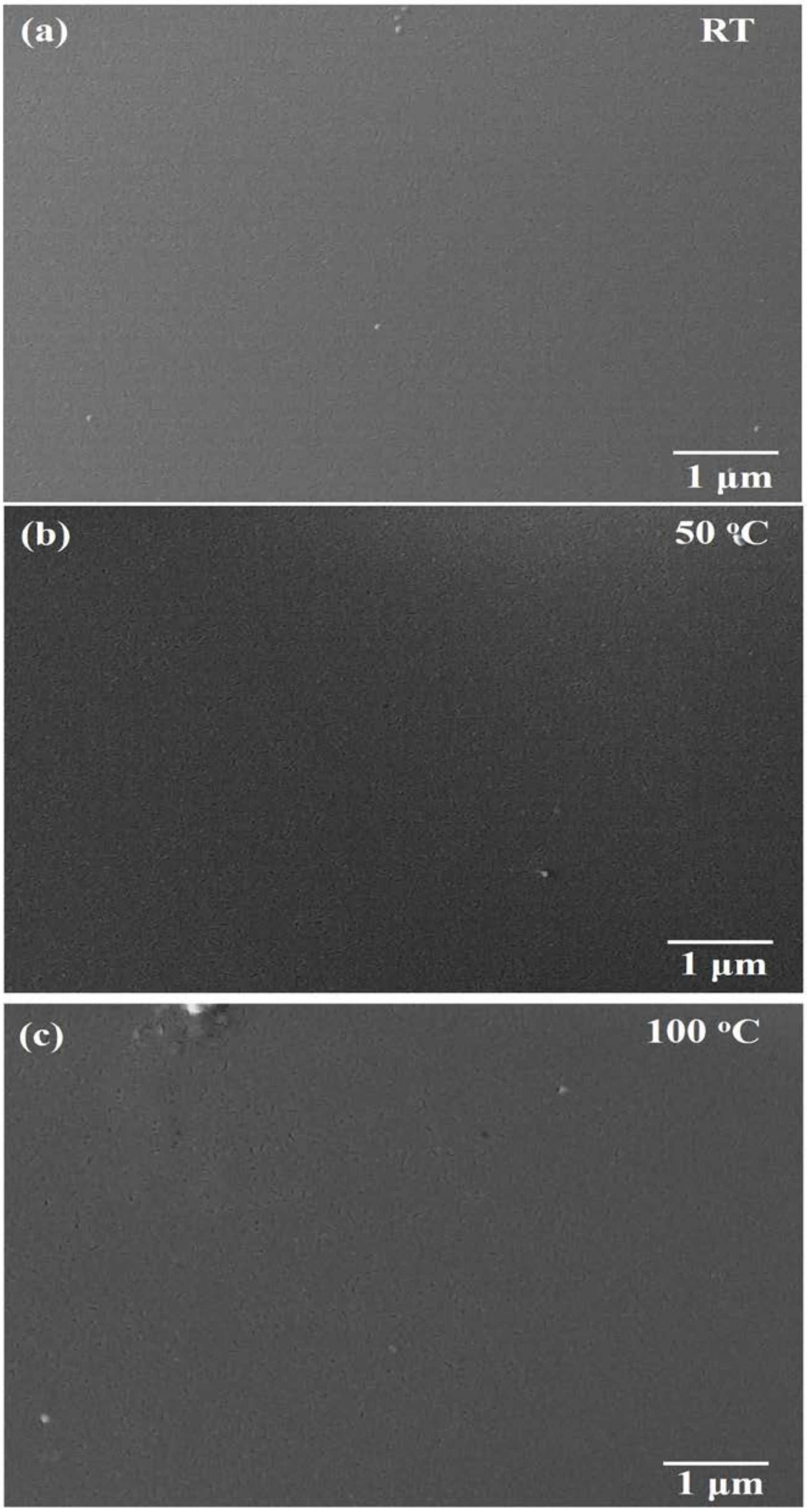

Fig. 16 SEM images of surface of ITO/Ag-alloy/ITO after exposure to different temperatures for 40 minutes.

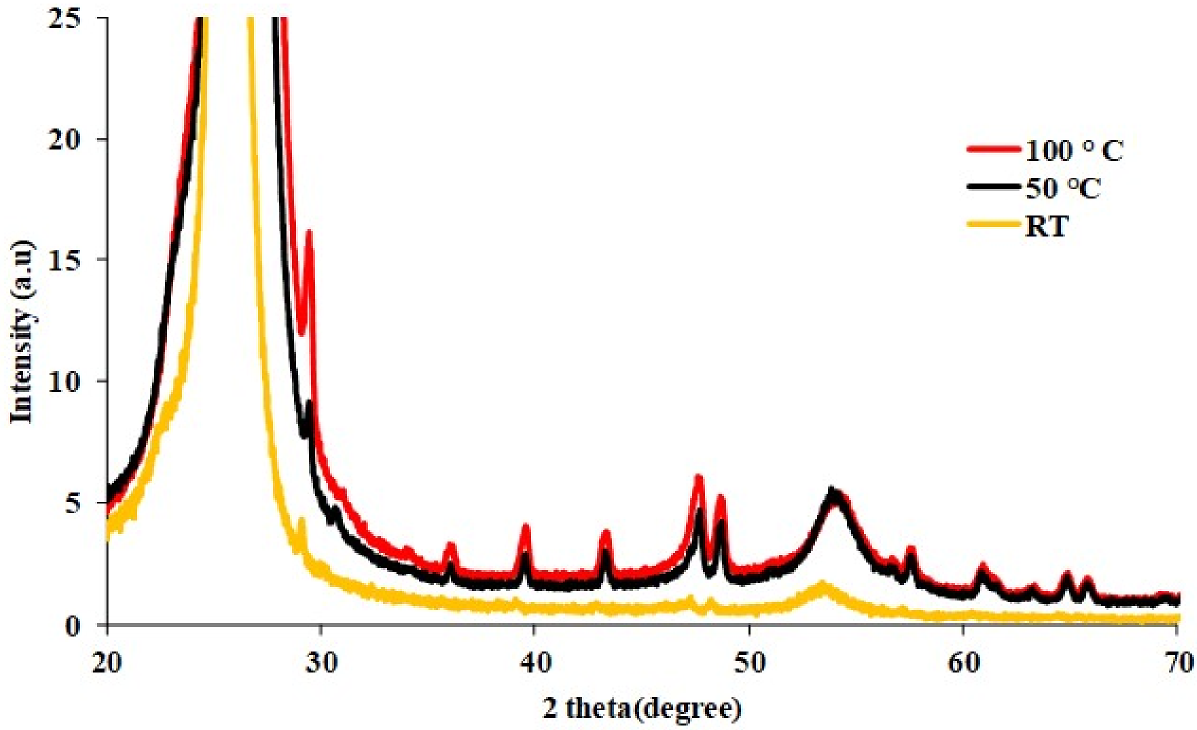

Fig.17 XRD diffraction patterns of the ITO/Ag-alloy/ITO film exposed to different temperatures (RT, 50 °C and 100 °C).

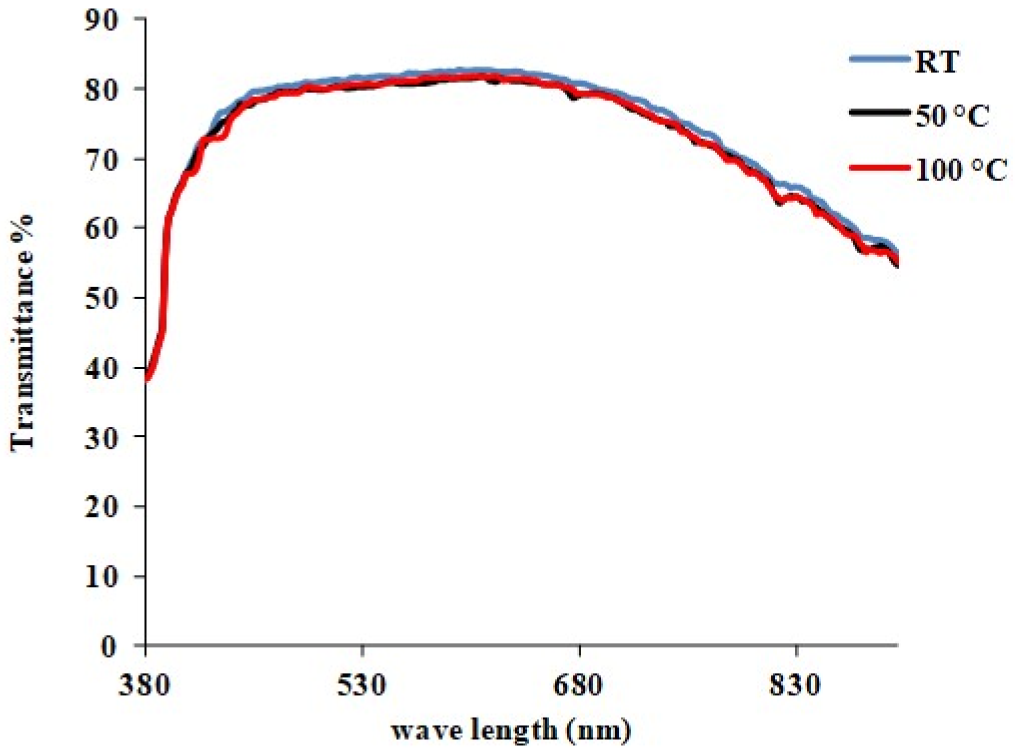

Fig. 18 Optical transmittance spectra of ITO/Ag/ITO thin film with different temperature exposures.