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Mechanical properties of amorphous indium–gallium–zinc oxide thin films on compliant substrates for flexible optoelectronic devices
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Abstract
Amorphous indium–gallium–zinc-oxide (a-IGZO) thin films were deposited using RF magnetron sputtering on polyethylene naphthalate (PEN) and polyethylene terephthalate (PET) flexible substrates and their mechanical flexibility investigated using uniaxial tensile and buckling tests coupled with in situ optical microscopy. The uniaxial fragmentation test demonstrated that the crack onset strain of the IGZO/PEN was \( \sim 2.9\% \), which is slightly higher than that of IGZO/PET. Also, uniaxial tensile crack density analysis suggests that the saturated crack spacing of the film is strongly dependent on the mechanical properties of the underlying polymer substrate. Buckling test results suggest that the crack onset strain (equal to \( \sim 1.2\% \), of the IGZO/polymer samples flexed in compression to \( \sim 5.7 \) mm concave radius of curvature) is higher than that of the samples flexed with the film being in tension (convex bending) regardless whether the substrate is PEN or PET. The saturated crack density of a-IGZO film under the compression buckling mode is smaller than that of the film under the tensile buckling mode. This could be attributed to the fact that the tensile stress encouraged this crack formation originating from surface defects in the coating. It could also be due to the buckling delamination of the thin coating from the substrate at a lower strain than that at which a crack initiates during flexing in compression. These results provide useful information on the mechanical reliability of a-IGZO films for the development of flexible electronics.
Keywords: Polymer substrates, IGZO, PEN, PET, flexible optoelectronic devices, mechanical properties
1. Introduction

Electronic devices fabricated on flexible plastic substrates are expected to find a variety of new applications due to their attractive advantages, such as being mechanically robust, light weight and potentially having simple roll-to-roll-based fabrication and mass production [1,2]. Transparent oxide semiconductors, such as zinc oxide (ZnO), gallium-doped zinc oxide (GZO), indium tin oxide (ITO), zinc tin oxide (ZTO), and indium gallium zinc oxide (IGZO) have attracted many researchers with their large potential in flexible optoelectronic applications, such as transparent electrodes in solar cells,rollable displays, and channel layers in transparent thin film transistors (TFTs) [1,3], because of the capability of large-area, uniform deposition at low temperatures [4]. In particular, IGZO has drawn considerable attention as an extremely promising alternative to hydrogenated amorphous silicon (a-Si:H) for thin-film transistors (TFTs) due to its high electron mobility, processing compatibility with plastic substrates, good uniformity and high transparency in the visible wavelength region (400 - 700 nm) [4,5]. Polyethylene terephthalate (PET) and polyethylene naphthalate (PEN) have been widely used as the base substrates in the fabrication of flexible optoelectronic devices. This is due to their satisfactory optical transmittance, mechanical flexibility, light weight, transparency, low cost and ability to be manufactured through roll-to-roll processing. However, due to the low melting point of the polymers, transparent oxides must be fabricated on polymer substrates at a lower deposition temperature. The RF magnetron sputtering technique is one of the most commonly used methods to deposit a-IGZO thin films on flexible substrates at room temperature [6]. Many research groups have reported using radio frequency (r.f.) sputtering to fabricate a-IGZO layers for use in thin film transistors (TFTs) on flexible substrates [6]. However, transparent conducting oxide films are brittle by nature, and susceptible to cracking and/or buckling delamination under externally applied mechanical deformation, which significantly limits the flexibility of the devices [7]. Consequently, failure behaviour of the films under various loading modes such as stretching, bending, or twisting becomes a critical issue during both manufacturing processes and in service conditions [8]. Hence, this gives rise to the motivation for predicting the onset of failure such as critical strain and critical radius of curvature to provide this information to optoelectronic device designers.

Uniaxial tensile and buckling tests, coupled with in situ optical microscopy are commonly used to determine the failure strains of thin coatings adhering to a compliant substrate, where cracks first initiate, as well as any subsequent buckling and delamination that may occur [9]. For example, the mechanical behaviour of ZnO coated polymer substrates was investigated under compression tests by Sierros et al. and the critical onset strain for cracking was found to be approximately 2% [10]. Chen et al. [11] reported buckling experiments carried out on ITO, reporting that the crack onset strain (COS) of the film under tension at 1.1% was less than its value under compression. In addition, Ni et al. [12] investigated the fracture properties of AZO-coated on PET substrates under simple-support bending conditions. It was reported that 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. They explained that in tension, on the outer surface, the stored elastic energy went solely into crack formation; however in compression the elastic energy was distributed between crack formation and delamination, so the crack density is usually lower for bending testing on the compression side.

However, relatively little research to date has been reported about the mechanical behaviour of a-IGZO coated on polymers. Cherenack et al. [2] investigated the performance of amorphous thin film transistors (a-IGZO) under mechanical bending. It was pointed out that the films can be flexed down to 10 mm radius of bending curvature and, still, can remain functional. Also Munzenrieder [13] investigated the behaviour of a-IGZO TFTs on flexible substrates under tensile and compressive stress conditions. It was found that the mechanical stress has considerable impact on the TFT mobility and threshold voltage. Gleskova et al. [14], demonstrated that the amorphous silicon TFTs fabricated on polyimide foil can be strained more in compression than in tension. No mechanical failure was noted in compression for strains smaller than 2%, while in tension, mechanical failure was found at a strain of 0.5%. They also pointed out that the failure mode was the formation of periodic cracks
perpendicular to the straining direction. Such cracks interrupt the current path if the source-drain current path and the strain direction are parallel.

In this work, we report on the mechanical flexibility of a-IGZO thin film grown on PET and PEN substrates via RF magnetron sputtering at room temperature for use in flexible optoelectronics. We utilize two different polyesters in an effort to elucidate the effect(s) of the underlying substrate on the resulting mechanical performance of the sputtered films since the applied stresses are transferred from the substrate to the coating through the interface. We examined the mechanical integrity of a-IGZO by using uniaxial tensile fragmentation and buckling tests coupled with in situ optical microscopy to further understand the failure mechanism under different mechanical deformation modes. Although the performance of the coated substrates will be modified once they are in a complete device, with potentially several other layers above or below, an understanding of the mechanical properties of the IGZO/polymer layers remains of fundamental importance.
2. Experimental Procedure

The polymer substrates used were two semi-crystalline polyesters, 0.125 mm thick polyethylene terephthalate (PET Melinex ST 504) and 0.125 mm thick polyethylene naphthalate (PEN Teonex Q65FA). Samples of both were supplied in the form of A4 sheet (DuPont Teijin Films, UK). Thermal and mechanical properties of both substrates were measured by using differential scanning calorimetry and uniaxial tension (Instron 4410) respectively. a-IGZO film of thickness ~50nm was deposited on to polymer substrates using RF magnetron sputtering from a In$_2$O$_3$:Ga$_2$O$_3$:ZnO (1:1:1) target (99.99% purity), the samples having a dog-bone shape (50 mm length , with 18 mm gauge length and 4 mm gauge width). The substrates were cut from sheets using a Moore Hydraulic Press. Prior to introduction inside the sputtering chamber, the polymer substrates were ultrasonically cleaned in acetone, ethanol, and then in deionized water for 5 min each. Deposition was performed (without heating the substrate) in an argon atmosphere and without an oxygen feed. A 4-inch diameter ceramic target, 20 cm from the substrate, was used under a base pressure of $5.1 \times 10^{-6}$ Pa; constant RF power of 55 W; deposition pressure of 0.5 Pa; power density of 0.7 W/cm$^2$; Ar flow rate of 50 sccm (sccm denotes standard cubic centimeter per minute at STP conditions) and deposition rate of ~3.3 nm/min. In order to remove contaminant on the surface of the target, the a-IGZO target was pre-sputtered for 5 min before the deposition of the film. The optical transmittance of the films was measured in the visible range from 400 to 800 nm using a Jenway 6310 spectrophotometer. Moreover, X-ray diffraction was used to examine the structural properties of the a-IGZO films. The IGZO deposition conditions were previously optimised to produce thin film transistors with a high mobility, low threshold voltage and large switching ratio. Examples of TFT characteristics have been reported previously in [15].

The mechanical flexibility of the a-IGZO films deposited on the polymer substrate was evaluated by uniaxial tensile and buckling tests. The uniaxial fragmentation test was performed using a Miniature Materials testing machine. The test was coupled with in situ optical microscopy; images were taken every 3 seconds during the test in order to monitor the critical onset strain and development of the cracking of thin film as the applied tensile strain increases. Equipment originally designed to determine the critical failure strain of optical fibres was slightly modified to test the a-IGZO/polymer samples.
shows the experimental set-up used in this case. The sample is clamped between the two parallel plates, where one plate is movable, while the other plate is fixed. The distance between the two parallel plates was measured using a side-view digital imaging system and image analysis software (Image J). Crack initiation and propagation were carefully monitored by using confocal microscopy. In situ optical observation was used as a simple and effective way to determine the crack-initiation strain of thin film, particularly as the film is non-electrically conductive [16]. The values of the resulting strain from buckling were calculated using the following equation [17].

\[ e = \frac{h_s}{R} \]

where \( R \) is the radius of curvature and \( h_s \) is substrate thickness.

Scanning electron microscopy (SEM) was performed to investigate the microstructure of the IGZO coatings and to characterize the cracking morphology of the a-IGZO films after testing. (The specimens were coated with a 5 nm thick Au layer before SEM investigation in order to increase their conductivity).

Atomic Force Microscopy (AFM) was employed in order to examine the coating fragmentation as a result of uniaxial straining. The atomic force microscope (JPK Instruments, UK) was operated in contact-mode conditions. Si cantilevers with a spring constant of 0.3 N/m were used with an operating frequency of 330 Hz.
3. Results and discussion

3.1 Characterisation of polymer substrate and IGZO thin film

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Table 1 shows that the glass transition temperature and Young's modulus of PEN are slightly higher than those of PET due to the substitution of the phenyl ring of PET by the naphthalene double ring of PEN [18]. This indicates that the first Dundur's parameter $\alpha$ for PEN (~0.96) will be slightly lower than that of PET (~0.97) as determined according to Eq (2), indicating also a lower mismatch in mechanical properties of the oxide coating on a PEN substrate compared with a PET substrate.

$$\alpha = \frac{E_s}{E_f} + \frac{E_f}{E_s} - 1$$

where $E$ is the Young's modulus, the subscripts f and s stand for the film and the substrate, respectively. $E_f$ is taken as 200 GPa using the rule of mixtures [19] based on separate measurements of the substrate and composite film modulus.

It is observed that both films exhibit high transparency equal to ~82% in the visible region.
illustrates the XRD patterns for IGZO/PEN and PEN substrate. Strong diffraction peaks in the range of 24 to 29 degrees were observed for both IGZO/PEN and PEN substrates and corresponds to the semi-crystalline polymer substrate. The lack of any other peaks confirms the amorphous nature of the IGZO.

Inset Error! Reference source not found. shows AFM pictures of IGZO thin films deposited on polymer substrate. The root mean square (RMS) roughness of the films was approximately 1.12 nm, the surface appearing smooth and featureless, which contributes to the high electrical performance of the proposed device [20], since surface defects are primary candidates for inducing cracks in the film under application of external stresses [21].

### 3.2 Uniaxial fragmentation test

Uniaxial fragmentation tests were performed in order to investigate the critical onset strain (COS) at which the IGZO-coated PET and PEN started to crack. Fig. 3 (a) and (b) show a series of representative optical microscopy images of crack progression for the IGZO coating on PEN and PET substrates, respectively. These were optically monitored in situ during the tensile tests. The cracks can channel across the film and may arrest at the film-substrate interface. The channel crack initiation and evolution processes in the IGZO/PEN films are quite similar to those in the IGZO/PET samples. Upon loading, the initial channel cracks begin to initiate from microscopic defects such as pinholes in the coating and surface defects on the underlying polymer substrates. The cracks then grow to span the whole sample width direction, and are propagating perpendicular to the loading direction. However, the IGZO/PEN sample exhibits a higher crack onset strain (COS) of ~ 2.9% than that IGZO/PET at ~ 2.4%. Such a slight difference in critical strain for the IGZO layer deposited on the two types of substrates may be due to the lower mechanical mismatch between the (IGZO) coating and the PEN. Cracks grew into the thickness of the film, as can be seen in the cross-sectional view of a channel crack in (b).

As the strain level increases, at almost ~6.8% and ~5.4% strain of IGZO coated PEN and PET respectively, an adhesion-related failure appears in the form of buckling of the IGZO film. Cracks on the buckle top were not visible during in situ optical microscopy observations indicating closed buckle delamination. However, SEM analysis confirm that there are cracks present on the top of the buckle, parallel to the applied tensile strain, and these secondary crack indicating open buckling zones, as Fig. 5(a) and (b) show. The secondary cracks and buckling of the film appear to be due to the lateral contraction mismatch between the substrate and thin film [22,23]. It is important to note that the IGZO/PEN samples have fractured at the edges of the debonded zone while for the IGZO/PET delamination is continuous except for the cracks on the buckle-top, as double sided arrows indicate in Fig. 5 (a) and (b). Also, a slightly higher adhesion level in IGZO/PEN systems is expected compared with IGZO/ PET due to the large buckling width of IGZO/PET sample, as shown in Fig. 5(b).

The cracks and buckling morphology of IGZO observed in this work are consistent with a study conducted by Frank et al. [24] who pointed out that the load introduced into a thin tantalum coating on a polyimide substrate during uniaxial tensile strain causes the formation of parallel cracks and at later stages lead to film buckling. The IGZO cracking was quantitatively characterized under tensile strain, in terms of crack density, defined as the number of channel cracks per unit length in the straining direction.
Fig. 66 shows the evolution of the coating crack density as a function of the applied strain for both IGZO/PEN and IGZO /PET samples. It is observed that there is a significant increase in crack density as the applied strain increases. However, with further increases in strain, the crack density gradually saturates at certain value, above which no new cracks can form. Furthermore, it was found that the IGZO/PEN samples exhibit a higher value of saturated crack density compared with the IGZO/PET specimens. The quantitative measurements of the progression of crack density at saturation state indicate that the IGZO on a highly stiff polymer substrate develops more cracks to relax the applied tensile stress. On the other hand, if a less stiff polymer substrate is used the stress concentration can influence the debonding formation between the polymer substrate and IGZO, hence the stress is absorbed by the polymer substrate in the debonded zone. Similar observations have been demonstrated previously by Tsubone [25] for diamond-like carbon films coated on polymer substrates. The above results suggest that the crack initiation and the density of channel cracks are highly related to the Young’s modulus of the polymer substrates. In general, the high mechanical reliability of a-IGZO film coated on polymer substrate is attributed to the following possible reason. There are many grains with preferred orientation in the thin film when it exhibits a polycrystalline structure, therefore is very prone to cracking due to intergranular defects in the grains under an external force [26]. However, an amorphous IGZO film delays crack initiation due to the absence of grain boundaries.

3.3 Buckling test analysis
The buckling test was used to evaluate the mechanical failure behaviour of a-IGZO films on PET substrates under both compression and tension buckling conditions.

Fig. 7 and Error! Reference source not found. illustrate the development of IGZO film cracking under tension and compression buckling modes respectively. Channel cracks in IGZO/PET are observed when samples are flexed in tension down to 6.4 mm and flexed in compression down to 5.7 mm radius of curvature, which correspond to strains of ~0.9 and 1.1%, respectively. Regardless of the type of deformation mode, it is noted that the number of cracks increased dramatically with an increase in applied strain. The cracks were initiated from surface defects for specimens under tension mode and then develop perpendicular to the direction of bending, which are comparable with the results obtained from uniaxial tensile experiments.

Based on the optical images, a comparison of crack density of IGZO/PET under tension and compression modes is determined and presented in Error! Reference source not found. It is observed that the saturated crack density of the film in the tension buckling mode was significantly higher than that of the film in the compression buckling mode and the discrepancy is observed to be around 58 mm⁻¹. The first reason for this might be because of surface defects such as pinholes and imperfections in the film and/or in the substrate [27]. These are also
detectable in optical images of crack development of IGZO/PET sample as shown in Fig. 7(a). It illustrates crack initiation from pre-existing defects in the IGZO film under tension, which contributes to the formation of cracks in IGZO film earlier as compared with that under compression mode. Thus, it is believed that applying stresses to a specimen under compression buckling leads to closed rather than open microcracks, as also suggested by Potoczny [28]. The second reason for the discrepancy in the saturated crack density between the film under tensile and compression buckling mode is attributed to the various failure
Fig. 7 and Error! Reference source not found.. In particular, the cracks in IGZO film under tensile bending mode are straighter and parallel to each other while zigzag shaped cracks are observed for the IGZO film under the compression-bending mode. This is also confirmed by SEM images of cracking morphologies of IGZO film shown in Fig. 10. Fig. 10 (a) shows the IGZO/PET film after the specimen is bent in tensile bending mode to a radius of 2.7 mm, which is equivalent to a strain of 2.3%. It is observed that the IGZO film is fractured completely due to formation of channel cracks. However, coating delamination and channel cracking are observed when the specimen is bent in the compression buckling mode with the same radius of 2.7 mm, as shown in Fig. 10(b). This can be due to the contraction of the polymer substrate induced by applying stress in the compressive mode. The present findings are consistent with those found by Lu et al. [29] who found ITO film failures are caused by channel cracks when the sample is under tensile strain bending conditions while under compressive strain conditions the film experiences buckling delamination and cracking. The results from these experiments indicate that the film subject to tension buckling mode is more apt to fail than the film under compression buckling mode (see Section 1 and [13].)

4. Conclusions
In summary, the mechanical durability of RF–magnetron sputtered a-IGZO thin films on PEN and PET substrates was studied by using uniaxial tensile and bending tests coupled with in situ optical microscopy. During uniaxial tensile tests, it was found that the crack initiation strain is mostly dependent on the mechanical mismatch between the coating and substrate. High COS was observed for IGZO deposited on PEN. In addition, a relatively high value of saturation crack density was observed for IGZO film coated on PEN substrates. Furthermore, bending test results show that thin films subject to the compression buckling mode exhibit better bending durability than the films subjected to tensile buckling mode. Surface defects on thin films under the tensile mode can cause the a-IGZO film cracking to occur at strains less than those of the film under the compression buckling mode. Also, delamination of the thin film under compression from the polymer substrate can reduce the rate of crack growth. The results of this study may provide a better understanding of the failure processes of IGZO thin films on polyesters under different deformation stress modes. This in turn is expected to aid device designers to develop the next generation of flexible optoelectronic applications.
Acknowledgments
The authors would like to thank DuPont-Teijin for donating polymer samples. We would also like to thank Mr Frank Biddlestone for his technical support and Mr Warren Hay for his help in the workshop. Financial support from the Kurdistan Regional Government HCDP program is gratefully acknowledged. The atomic force microscope used in this research was obtained, through Birmingham Science City: Innovative Uses for Advanced Materials in the Modern World (West Midlands Centre for Advanced Materials Project 2), with support from Advantage West Midlands (AWM) and partly funded by the European Regional Development Fund (ERDF). R.W. gratefully acknowledges funding from the EPSRC Centre for Doctoral Training in Photonic Systems Development.
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Table 1 Thermal and mechanical properties of PET and PEN
Fig. 1 The bending test set-up used in this study.
Fig. 2. XRD patterns of the bare PEN substrate and IGZO films deposited on PEN at room temperature. Inset shows AFM images of IGZO on PEN substrate.
Fig. 3 Progressive cracking in the IGZO (50 nm) coating on PEN Substrate (a) and on PET substrate (b) at different applied tensile strains. The arrows show failure initiation on the coating.
Fig. 4 (a) 3D - AFM image of channel crack path of (50 nm) IGZO/PEN sample, white arrows show straining direction; (b) Cross section view of the channelling crack of (50nm) IGZO/PEN.
Fig. 5  FIB-SEM image of buckling delamination of IGZO (50 nm) film deposited on PEN substrate (a) and on PET substrate (b). Note that black arrows indicate loading direction for 13% applied strain in both cases.
Fig. 6 Density vs applied strain for IGZO (50 nm) coating on PET and PEN substrates.
Fig. 7 Sequence of optical micrograph images of cracks morphology in a-IGZO films coated PET under (a-d) tensile buckling mode at different strain bending curvature. The white arrow at 0.9 % strain indicates a crack initiation.
Fig. 8 Sequence of optical micrograph images of cracks morphology in a-IGZO films coated PET under (a-d) compressive buckling mode at different strain bending curvature.
Fig. 9  Plot of crack density of a-IGZO thin film coated PET as a function of applied tensile and compression buckling strain.
Fig. 10 SEM micrograph showing crack morphology of a-IGZO after flexed down to 2.7 mm radius of curvature in (a) tensile (b) compression buckling condition
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