Buckle initiation and delamination of patterned ITO layers on a polymer substrate

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A R T I C L E   I N F O

Article history:
Received 17 March 2010
Accepted in revised form 9 November 2010
Available online 12 November 2010

Keywords:
Patterned ITO-structures
Buckling
Edge defects

A B S T R A C T

Buckle initiation and delamination of patterned ITO layers on a polymer substrate were studied. Various buckle modes have been observed depending on the type of etch defects and the crack patterns. The buckle density was found to be dependent on the number of etch defects, imperfections, applied uniaxial compressive strain and the loading time. Buckles originating from a specimen edge and from interior approaching the edge showed different type of behavior. Edge defects resulting from the specimen cutting were found to serve as a point of initiation of layer buckling. They also influence the propagating buckle from the interior of the specimen when it approaches the specimen edge. A propagating buckle front is arrested at an edge defect close to the specimen edge due to a reduction in the residual strains distribution in the vicinity of the edge defects.

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1. Introduction

Significant research efforts are being made to develop polymer-based layered structures for flexible devices, e.g., displays. Transparent conducting Indium Tin Oxide (ITO) materials are extensively used in display applications due to their excellent combination of mechanical, electrical and optical properties [1–6]. Moreover, ITO layers can be processed at low temperature compatible with the polymer substrates. Using ITO layers in displays requires not only a uniform layers, but also patterned ITO layers.

Buckle delamination is a common interfacial failure mode in layered structures that experience insufficient level of adhesion at the interface and/or high residual or external strains. The residual strains mainly arise from the difference in the thermal expansion coefficients of the layer and the substrate and the difference in the temperature during deposition and subsequent cooling to room temperature. In addition, the layered structures may also experience an external compressive strain during service. These residual and/or external strains may motivate defects or imperfections in the layer, the interface and/or the substrate to act as initiator for interfacial failure. The understanding of the mechanism leading to these types of failure in patterned ITO-structures is important in the production of reliable products.

Previous studies have studied some aspects of buckle initiation and propagation. Generally, layer buckling and delamination would be expected to occur when the energy release rate G equals to the interfacial toughness Γi for a certain defect size. Leterrier et al. [7–9] showed that layer cracking of thin ITO layers during tensile loading initiate at surface defects such as pinholes and imperfections in the layer and/or in the polymer substrate. For layered structures under compressive loading, the size of interfacial cracks needed to initiate layer buckling is typically Lc,≈20 hL [10], where hL is the layer thickness. Based on numerical solution of singular integral equations Yu et al. [11] studied the emergence of delamination from layer edges and the approach of delamination fronts towards layer edges. This paper intends to provide an improved understanding of buckle initiation and delamination from patterned ITO structures. However, due to the etching process, the presence of etch defects was found to have a significant effect on buckle initiation and propagation. In addition, the presence of edge defects due to cutting was also found to have a dominant effect on buckle initiation and propagation. Therefore, the emphasis of this paper will be on the effect of etch defects and edge defects on buckle initiation and propagation.

2. Experimental details

2.1. Materials

To study buckle initiation in a patterned structure, Indium Tin Oxide layers (ITO) were deposited on a polymer substrate (Arylite™) spin coated on both sides with a silica-acrylate hybrid coating, hereafter referred to as hard coat (HC). These layers improve the mechanical properties of the layered structure and act as a solvent barrier. A summary of the material’s elastic properties and thickness is given in Table 1.
Firstly, the silica-acrylate solution was applied on the Arylite and dried at 100 ± 2 °C. After that, the acrylate is cross-linked by UV at room temperature to result in the so-called HC layer. Secondly, A 250 nm and 350 nm ITO layers, which act as a transparent conducting oxide, were deposited on these substrates in a Leybold Z650 sputter system [12]. The target composition was 90 wt.% In_{2}O_{3} mixed with 10 wt.% Sn_{2}O_{3}. The deposition was started at room temperature and ended at approximately 100 °C, depending on layer thickness. The sputtering power was 600 W. The deposition rate was 20 nm/min, while the substrate carrier was rotated at 10 rpm. To etch the ITO layer, the ITO surface was covered with a layer of photo-resist (HPR504), as shown in Fig. 1. After the illumination through a mask the resist was developed and cured at 125 °C. The amorphous ITO layer normally was etched in 5% oxalic acid (C_{2}H_{2}O_{4}) at 45 °C, a typical etch rate being about 40 nm/min.

### 2.2. Experimental set-up

A mechanical bending device, shown in Fig. 2, was used to apply a deformation with constant curvature over a length of about 30 mm to the layered structures. As a result, the substrate is loaded in tension at the outer surface and in compression at the inner surface. Changing the distance between the bending plates will change the strain applied to the layered structure. Assuming that the neutral line is located at the mid-plane of the layered structure, the external applied strain $\varepsilon_{\text{app}}$ can be calculated from [13]:

$$
\varepsilon_{\text{app}} = \frac{(h_{s} + h_{f})}{2R}
$$

where $h_{f}$ is the thickness of the layer, the thickness of the substrate $h_{s} = h_{\text{Arylite}} + h_{\text{HC}}$ and $R$ is the bending radius. As Eq. (1) shows, a constant bending radius $R$ yields a constant strain along the sample length.

### Table 1
Material elastic properties and thickness.

<table>
<thead>
<tr>
<th>Material</th>
<th>Elastic modulus [GPa]</th>
<th>Poisson’s ratio [-]</th>
<th>Thermal expansion coefficient [ppm/K]</th>
<th>Thickness, μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arylite™</td>
<td>3.0</td>
<td>0.38$^*$</td>
<td>65</td>
<td>200</td>
</tr>
<tr>
<td>HC layer</td>
<td>6.5</td>
<td>0.3²</td>
<td>60²</td>
<td>3</td>
</tr>
<tr>
<td>ITO layer</td>
<td>120*</td>
<td>0.3²</td>
<td>10</td>
<td>0.25 and 0.35</td>
</tr>
</tbody>
</table>

* Estimated values [5].

**Fig. 1.** Schematic illustration of patterning the ITO structures. (a) The layered structure, (b) ITO surface covered with a photo resist, (c) After illumination through a mask, the photo resist is developed and cured at 125 °C, (d) After etching and (e) After resist removal.

**Fig. 2.** The mechanical bending device used to deform the layered structure, indicated by an arrow, which is mounted between two bending plates. The substrate is loaded in tension at the outer surface and in compression at the inner surface, i.e. the surface with the ITO layer.
2.3. Microscopy

The buckle morphology and profiles were observed by confocal optical microscope (μSurf™, equipped with a piezo-drive, NanoFocus, Oberhausen), and Environmental Scanning Electron Microscope (ESEM XL40 TMP, Tungsten electron source, FEI instruments, Eindhoven). For the ESEM examination a thin conductive gold layer was sputtered on top of the thin ITO layer in order to achieve optimal resolution by avoiding charging effects. Optical microscope (Polyvar™, Reicher-Jung, Austria) was also used to examine the crack pattern. Images of the initiation points were taken before and after applying a compressive strain on the specimen. In-situ observation of 12 × 30 mm² specimens compressed uniaxially was carried out using the mechanical bending device shown in Fig. 2 mounted under an optical microscope. The optical micrographs were used to analyze buckling failure of the thin layer.

2.4. Interfacial toughness

High residual strains in thin layers may result in buckling and delamination of these layers from the substrate. The value of the residual strain in the layers is required to estimate the interfacial toughness. A multilayer model was used to estimate the residual strain in a multilayer structure [14].

The elastic energy $G_o$ stored in a thin layer of thickness $h_t$ per unit width is defined by [15]:

$$G_o = \frac{1}{2} \frac{E_f}{1 - \nu_f^2} \varepsilon_f^2 h_t$$

(2)

where $E_f$ and $\nu_f$ are the elastic modulus and Poisson’s ratio of the layer, respectively. Upon layer buckling, the residual strain in the buckled layer drops to the critical buckle strain ($\varepsilon_c \approx \varepsilon_c$). Determination of the critical buckling strain $\varepsilon_c$ for a stiff layer on a compliant substrate is
given in Ref. [15]. Therefore, the elastic energy in the buckled region per unit width can be given by:

\[ G_c = \frac{1}{2} \frac{E_f}{(1-\nu_f)} \varepsilon_c^2 h_t \]  

(3)

Using the analysis in [16], buckling occurs when the energy release rate \( G \) equals the interfacial toughness \( \Gamma_i \):

\[ 2b\Gamma_i = 2bG = 2(b + l)(G_o - G_c) \]  

(4)

where \( b \) is the buckle half width, and \( l \) is a characteristic length defined as [17]:

\[ l = \frac{2h_t}{1-\alpha_D} \]  

(5)

which depends on the layer thickness \( h_t \) and the elastic mismatch as characterized by the Dundurs parameter [18] \( \alpha_D = (E_f - E_s)/(E_f + E_s) \). For a stiff layer on a compliant substrate, a certain width of the layer that still attached to the substrate along the delamination edge contributes to the buckling and delamination process. This width scales with the characteristic length \( l \) [17]. However, from Eq. (4) the energy release rate for buckling thus includes the net elastic strain energy, i.e., the difference in the elastic energy stored in the thin layer attached to the substrate \( G_o \) (unbuckled layer) and the elastic energy in the buckled portion of the layer \( G_c \). In this approximation the elastic energy released from the substrate is neglected.

3. Results and discussion

Before discussing the results for buckle initiation and delamination we deal with the residual strains induced in the layer during processing. The residual strains mainly arise from the difference in the thermal expansion coefficients of the layer and the substrate and the difference in the temperature during deposition and subsequent cooling to room temperature. Using the multilayer expression in [14] and the material properties shown in Table 1, the residual strain in the top 250 nm and 350 nm ITO layer was estimated to be \( \varepsilon_r = 0.41\% \) and 0.35\%, respectively. No layer buckling was observed due to this residual biaxial compressive strain.

3.1. The effect of etch defects on buckle initiation and propagation

In this section, buckle initiation and delamination in patterned ITO lines lying perpendicular to the compression axis and ITO lines lying parallel to the compression axis are investigated. These ITO lines have different width, length and spacing between the lines. No layer buckling was observed when a uniaxial compressive strain was applied on the patterned ITO lines lying perpendicular to the compression axis; the layer remained attached completely to the substrate. Buckling was observed when a uniaxial compressive strain was applied on the patterned ITO lines lying parallel to the compression axis. In addition, V-shape and U-shape initiation points with different size were designed deliberately in order to study buckle initiation from these points (the images of these designed initiation points are not shown in this paper). However, etch defects resulted from the processing of the patterned structure and edge defects

![Fig. 5](image-url) Buckle initiation and propagation from etch defects after applying a compressive strain for 10 min along the x-direction: (a) \( \varepsilon_{app} = 0.95\% \) and (b) \( \varepsilon_{app} = 1.25\% \), buckle initiate from the crack pattern at the etch defect and then develop along the crack pattern. The etch defects have directional angle \( \perp 80^\circ \). (c) \( \varepsilon_{app} = 1.0\% \) and (d) \( \varepsilon_{app} = 1.25\% \), buckle initiate from the crack pattern at the etch defect and then develop perpendicular to the compassion axis away from the crack pattern. The etch defects have directional angle \( \perp 60^\circ \).
resulted from poor cutting edge of the specimen were found to influence buckle initiation dramatically. Since buckles were found to initiate from the designed initiation points with etched defects rather than those without etch defects. Therefore, our focus in this paper will be mainly on the effect of etch and edge defects on buckle delamination of the thin layers from the polymer substrate.

Fig. 3 shows optical micrographs of patterned ITO lines. Both the 250 nm and 350 nm ITO layers showed crack patterns before etching. After etching these cracks showed significant etching defects. After lacquer removal, the samples are not seriously cleaned to avoid further crack propagation. The images of the etched ITO lines in Fig. 3 show clearly residual ITO material in the etched region and characteristic etch defects features at the crack end due to etching of the crack faces below the mask. Initiation and propagation of layer buckling were found to depend heavily on these crack pattern and the etch defects. Therefore, etching has an important effect on buckle initiation and propagation. In this section the effect of the etch defects and their crack patterns on buckle initiation and delamination are discussed.

A constant etching rate resulted in etching defects having approximately the same shape: width $W \approx 10 \mu m$, length $L \approx 15 \mu m$ and top angle $T \approx 30°–35°$. However, the directional angle of the etch defects ($D \approx 90°$) varies from $60°$ to $80°$ and can be used to characterize buckle initiation and delamination, as shown in Fig. 3(c).

Applying a uniaxial compressive strain $\varepsilon_{app} = 1.25\%$ on the patterned ITO lines lying parallel to the compression axis for 30 min resulted in buckling and delamination of the ITO layers from the substrate, as shown in Fig. 4. The width of the ITO line shown in Fig. 4 is 100 $\mu m$ and the spacing between lines is 25 $\mu m$, 50 $\mu m$ and 100 $\mu m$, respectively. Layer buckling was found to initiate from etch defects and then to develop perpendicular to the compression axis towards the other end of the etched edge of the ITO lines. Moreover, the orientation of the buckles is related to preferential etching along the layer. The total number of initiated buckles was found to depend also on the total number of the etch defects and their orientation normal to the compression axis, the width of the ITO lines and the spacing between lines. However, only the effect of the etch defects will be discussed in details in this stage.

Figs. 5 and 6 illustrate the process of buckle initiation from etch defects having a different directional angle. The average width of the initiated buckle is 9 to 13 $\mu m$, while the average buckle height is ranging from 0.1 to 0.3 $\mu m$. In general, buckling starts from the sharp point of the etch defect where the stress concentration is high. By increasing the applied compressive strain the initiated buckle starts to propagate perpendicular to the compression axis until it spanned the whole width of the ITO lines or until it is arrested at an imperfection or at another etch defect. After initiation, mainly two types of buckle trajectories can be distinguished. First, a buckle that follows the path of the crack pattern (Fig. 5(a)–(b)). In this case the etch defect directional angle is approximately 80°. Second, the buckle may run perpendicular to the compression axis as shown in Fig. 5(c)–(d) and the directional angle of the etch defect in this case is 60°. The buckling of the first type is affected by the crack pattern (buckle with layer cracking) and of the second type the buckle delamination tends to propagate perpendicular to the compression axis (buckling without layer cracking). For the two types of buckling, increasing the uniaxial applied compressive strain resulted in an increase in the buckle size, as shown in Fig. 5.

**Fig. 6.** Buckle initiation and propagation from etch defects after applying a compressive strain for 10 min along the x-direction: (a) $\varepsilon_{app} = 0.87\%$ and (b) $\varepsilon_{app} = 1.0\%$, buckle initiate from the etch defect having directional angle $\approx 90°$ and then followed the crack pattern, (c) $\varepsilon_{app} = 1.0\%$ and (d) $\varepsilon_{app} = 1.25\%$. Buckle initiate from the etch defect having directional angle $\approx 90°$ and develop perpendicular to the compression axis.
For an etch defect with directional angle of 90°, buckling with layer cracking on top was observed to initiate from the crack pattern at $\varepsilon_{\text{app}} = 0.87\%$ (Fig. 6(a)), while buckling without layer cracking was observed to initiate from the etch defect at $\varepsilon_{\text{app}} = 1.0\%$ (Fig. 6(c)). For the latter, increasing the applied compressive strain from $\varepsilon_{\text{app}} = 1.0\%$ up to $\varepsilon_{\text{app}} = 1.25\%$, resulted in cracking of the already existing buckle, as shown in Fig. 6(d). Whether the initiated buckle follows the crack pattern or develops perpendicular to the compression axis depends on the crack pattern and the orientation of the etch defects with respect to the compression axis.

Apart from buckle initiation from etch defects, buckles were also observed to initiate from imperfections or defects in the layer, as shown in Fig. 7. Buckle initiation from imperfections is believed to be due to an increase in the energy available at the imperfection. The energy release rate $G$ for interface separation in the neighborhood of an imperfection is high relative to that for a flat surface. Moreover, the imperfection was also observed to affect the propagating buckle (Fig. 7(c)–(d)).

3.2. The effect of edge defects on buckle initiation and propagation

The ESEM image in Fig. 8 shows the edge quality of the specimen. Many defects were observed at the specimen edge due to cutting. These edge defects serve as points of initiation for layer buckling and delamination and straight buckles were observed to initiate from these edge defects.

From Fig. 9, random layer buckling was observed to initiate from the edge defects and then to propagate perpendicular to the compression axis. The total number of buckles increases by increasing the compressive strain from 0.87% up to 1.25%, and as a consequence, the spacing between buckles becomes smaller. The buckle density will depend on the interfacial toughness and the density of edge defects.

In addition, edge defects were also found to affect buckles that initiated from the interior of the specimen propagating towards the specimen edge, perpendicular to the compression axis. Buckles were observed to arrest within a certain distance from the specimen edge due to the presence of the edge defects. In-situ observations of individual buckles at a constant applied uniaxial-compressive strain $\varepsilon_{\text{app}} = 1.0\%$, were performed under the optical microscope in order to study the effect of edge defect on buckle delamination. An example of

![Fig. 7. Buckle initiation and propagation from layer imperfections, indicated by arrow, after applying a compressive strain for 10 min along the x-direction: (a) $\varepsilon_{\text{app}} = 0.87\%$ and (b) $\varepsilon_{\text{app}} = 1.0\%$, (c) the propagating buckle is affected by the imperfection indicated by arrow, $\varepsilon_{\text{app}} = 1.0\%$ and (d) $\varepsilon_{\text{app}} = 1.25\%$.](image)

![Fig. 8. ESEM image show edge defects initiated upon cutting the specimen.](image)
the various steps of buckle initiation from the interior of the layer and propagation towards the specimen edge is presented in Fig. 10. The buckle was observed to arrest at the edge defects for a certain time, as indicated by a plateau in Fig. 10(c), and then start to propagate again until it arrested completely at a certain distance from the specimen edge. The edge defects divide the buckle into several segments, depending on the distance between the edge defects that originate from the specimen edge. From the analysis of the optical micrographs taken with intervals of 10 s the buckle delamination rate for each segment was determined from data of the buckle delamination length versus time (Fig. 10(c)). The buckle delamination rate for segments 1, 2, 3, 4 and 5 was 0.34, 0.27, 0.18, 0.10 and 0.08 μm/s, respectively.

It thus appears that layer defects and buckling are coupled. Buckles initiate and then stop at the defects and after certain incubation time the buckle starts again to propagate to the next defect. Layer cracking consumes energy available around the crack and as a result the propagating buckle will arrest when the energy available is less than the interfacial toughness. This was observed when the buckle front approaches the specimen edge where the number of defects increases. By subcritical growth the buckle the buckle jumps across the layer cracking and propagates further until it approaches the next defect and the same scenario is repeated again.
From the confocal microscope image shown in Fig. 11, the buckle width for the segment 1, 2, 3, 4 and 5 are 9.69, 9.37, 8.75, 9.71 and 7.51 μm, respectively, while the corresponding buckle heights are 0.206, 0.218, 0.139, 0.140 and 0.115 μm, respectively. From Fig. 11(a), an increase in the buckle height in the vicinity of the crack path was observed. Therefore, poor cutting affects not only buckle initiation but also buckle propagation rate and morphology.

The buckle characteristic length \( l \) represents the width of the layer still attached to the substrate along the edge of the delamination that contributes to the buckle delamination process. For the 250 nm ITO/HC/Arylite layered structure the elastic mismatch between the ITO layer and the HC layer is \( \alpha_D = 0.897 \), resulting in \( l = 4.8 \) μm. For the interior of the specimen the interfacial toughness was calculated from Eq. (4) in combination with \( \varepsilon_f = 0.41\% \) and \( 2b = 9.69 \) μm results in \( \Gamma_i = 6.5 \) J/m\(^2\). An estimation of the residual strain at each segment can be made assuming the interfacial toughness is constant throughout the specimen, \( \Gamma_i = 6.5 \) J/m\(^2\). From measured buckle width and height with the confocal microscopy, the residual strains were calculated at point 1, 2, 3, 4 and 5 as 0.40%, 0.39%, 0.36%, 0.40% and 0.31%, respectively. The presence of edge defects thus causes a small variation in the residual strain in the vicinity of the specimen edge, but not significant decrease. Only for segment 5 the residual strain is somewhat lower.

Since the confocal microscopy has a limited resolution, AFM is tried. Fig. 12 shows AFM image and profile of buckle measured at the edge defect (\( 2b = 6.2 \) μm and \( w = 0.18 \) μm). Again, assuming the

![Confocal microscope image](image)

**Fig. 11.** (a) Confocal microscope image showing the effect of edge defects at the specimen edge on buckle delamination. Edge defects divided the buckle delamination length into five segments. (b) to (f) Buckle profile of segment 1, 2, 3, 4 and 5, respectively. The buckle width and height are \( 2b \) and \( w \), respectively. The shape of the buckle profile indicates the occurrence of layer cracking on the buckled layer.
interfacial toughness is constant throughout the specimen, $\Gamma_i = 6.5 \text{ J/m}^2$, and from the buckle width at line-5, the residual strain was calculated $\varepsilon_o = 0.24\%$ consistent with the result from the confocal microscope measurements. The presence of edge defects causes thus a small reduction in the residual strains in the vicinity of the specimen edge. This reduction in the residual strain at line-5 resulted in a decrease in the energy available for the delaminated buckle front to propagate further and therefore the buckle arrest.

In the case of buckle propagating from the interior of the specimen, interface defects are believed to be responsible for buckle initiation, while for buckle propagation from the edge of the specimen, an edge crack is responsible for the initiation. Hutchinson et al. [10] reported that the buckling condition can be expressed in terms of the width or height of delaminated buckle front to propagate further and therefore the buckle arrest. A reduction in the delamination rate was also observed when the buckle delamination front approaches the specimen edge. The size of initial defect needed to initiate layer buckling from the interior of the specimen is in the order of $15h_i$, where $h_i$ is the layer thickness.

Acknowledgements

This work is part of the research programme of the ‘Stichting voor Fundamenteel Onderzoek der Materie (FOM)’, which is financially supported by the ‘Nederlandse Organisatie voor Wetenschappelijk Onderzoek’ (NWO). Kees Mutsaers is acknowledged for providing samples.

References


Fig. 12. (a) AFM image showing buckle arrest due to the presence of edge defect at the specimen edge. (b) Buckle profile at line-5. The buckle width and height are $2b$ and $w$, respectively. The shape of the buckle profile indicates the occurrence of layer cracking on the buckled layer.