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Direct measurement of intrinsic critical strain and internal strain in barrier films

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Resistance measurements during uniaxial tensile deformation of very thin (10 nm) conducting oxide films deposited on 150 nm SiN films on polyethylene naphthalate are discussed. It is first shown that certain characteristics of resistance versus strain curves are representative for the fracture behavior of the SiN film and not for that of the thin conducting oxide film. Subsequently, it is shown that the hysteresis in curves of resistance as a function of strain offers a way to directly measure the intrinsic critical strain of the SiN film without the need to determine internal strains from independent (curvature) measurements that rely on knowledge of moduli and geometry. The method should be applicable, in general, to measure intrinsic critical strain and residual strains of thin brittle films on polymers. Advantages and limitations of the method are discussed. © 2011 American Institute of Physics. [doi:10.1063/1.3624582]

I. INTRODUCTION

Flexible electronics offer commercial promise for two main reasons: they may enable new technologies and they may compete with already existing ones, capitalising on the possibilities offered by roll-to-roll processing. Although many possible applications exist (e.g., solar cells, lighting, and displays), the integrity of thin (often conductive) brittle films (for example, SiN or ITO) is crucial for the proper functioning of all of these devices. Such thin brittle layers may be electronically functional, e.g., as anode, or offer protection, for example, as environmental barrier layers. During fabrication and use, the devices are subjected to mechanical loads that depend on processing conditions, temperature, humidity, and intended use that vary with time. Whether a thin film remains intact or fractures depends in a complicated way on its cohesive properties, its thickness, the internal stress state, adhesion to the substrate, and its defect properties. A number of reviews exploring these issues have appeared in the past, e.g., Refs. 1–3. Moreover, the integrity depends on the interaction with the elastic^{4,5} and viscoelastic⁶ properties of the substrate and chemical interaction with the environment.⁷ For SiN derived from PECVD processes, such as discussed here, it is important to realize that film density, purity, internal stress, and elastic properties have all been shown to be correlated.⁸

Determination of the fracture properties of thin brittle films supported by polymers usually relies on optical microscopic or electrical methods or on a combination of those methods (e.g., Ref. 9). The optical method usually measures the density of cracks versus applied tensile strain. The electrical method (a.k.a. “electrofragmentation”^{10,11}) measures the resistivity or the normalized resistance versus tensile strain and is therefore limited to the presence of conductive

films. Tensile strain in the thin film may be applied either by uniaxial tension,⁹ 4-point bending,¹² 2-point bending,² or free bending.¹³ As a function of tensile strain, a succession of different fracture regimes characterizes the properties of the thin films: crack initiation and subcritical crack propagation, critical non-interacting cracks, critical interacting cracks, saturation, and finally transverse buckling. The results of the optical method have been used for sophisticated interpretation of these regimes in terms of the mechanical and statistical properties of the assemblies.¹⁴ The data from the electrical measurements have mainly been used to determine the critical strain ε_c .

A. Observed critical strain ε_c^{obs} versus intrinsic critical strain ε_c

The intrinsic critical strain ε_c can be defined by the Griffith criterion. This value also marks the transition from subcritical crack growth to critical crack growth. According to Griffith, the energy release rate G_c at ε_c is related to the surface energy 2γ of the crack surfaces:

$$G_c = 2\gamma. \quad (1)$$

The question is how ε_c can be derived from electrofragmentation experiments. The main part of Fig. 1 shows a typical $R(\varepsilon)/R_0$ curve. To assign a value to ε_c , a certain level $R(\varepsilon)/R_0 = x$ is usually chosen (where R_0 is the initial resistance) and related to a strain that we will call the observed critical strain ε_c^{obs} , in this case $\varepsilon_c^{obs,1,2}$.

A widely used analytic expression for the energy release rate of channeling cracks near bi-material interfaces has been given by Beuth.⁴ If the supported thin film is subjected to a uni-axial uniform tensile stress σ_c , it is found that

$$G_c = \frac{\pi h_f \sigma_c^2}{2 E_f} g(\alpha, \beta) = \frac{\pi}{2} h_f \varepsilon_c^2 \bar{E}_f g(\alpha, \beta), \quad (2)$$

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FIG. 1. Initial stages of cracking and the resulting $R(\varepsilon)/R_0$ for a conductive brittle film on a polymer substrate. Inset: cracks start growing from the sides inward, initiating on damage due to cutting. The cracks (more closely spaced in reality than in the drawing) restrict the current to an increasingly narrow path along the sample (gray area). The average width of this path determines the resistance. It is assumed that the crack pattern is more or less symmetric, which means that the effective length of the current path does not change until the crack arrays, starting from opposing sides, start to overlap. Main: roughly two regimes exist in $R(\varepsilon)/R_0$. These are separated by the observed critical strain, in this case, $\varepsilon_c^{obs,1.2}$. $R(\varepsilon)/R_0$ depends on w_0 and strain rate. Simulations show the effect of w_0 on $R(\varepsilon)/R_0$, using Eqs. (5), (6) and (7) for $2\Gamma = 2\text{J/m}^2$ and $nkT = 0.03\text{J/m}^2$ and a strain rate of 0.0003 s^{-1} . Left: effect of initial sample width. The arrow points from $w_0 = 0.001\text{m}$ to $w_0 = 0.01\text{m}$.

with h_f as the film thickness, $\bar{E}_f = E/(1 - \nu_f^2)$, and ν_f as the Poisson's ratio of the film. α and β are the Dundurs parameters characterizing the elastic misfit between coating and substrate defined as

$$\alpha = \frac{(\bar{E}_f - \bar{E}_s)}{\bar{E}_f + \bar{E}_s}, \quad (3)$$

$$\beta = \frac{1}{2} \frac{\mu_f(1 - 2\nu_s) - \mu_s(1 - 2\nu_f)}{\mu_f(1 - \nu_s) + \mu_s(1 - \nu_f)}, \quad (4)$$

with μ_f as the shear modulus of the thin film. In Eq. (2), G_c does not depend on the crack length $l(\varepsilon)$, which is only true if cracks are longer than a critical crack length l_c . For SiN on polymers, it has been found⁵ that, for cracks with a $l = 40h_f$, G still depends on the crack length. The function $g(\alpha, \beta)$ is a sensitive function of the substrate modulus in case it is much more compliant than the thin supported film.

The definition of ε_c^{obs} shown in Fig. 1 shows that the value depends on the geometry of the conducting path on the sample. The geometry of that path depends on the type of experiment. Methods that induce a homogeneous strain field (tensile loading, 4-point bending, free bending) are expected to lead to different crack patterns than methods that induce an inhomogeneous strain field (e.g., 2-point bending). For homogeneous loading, we assume that the crack pattern develops along the lines shown in the inset of Fig. 1: two sets of cracks initiate at damage along the edges of the sample and propagate inwards in a symmetric fashion.

As long as the two sets of cracks do not interpenetrate, it is possible to define an average crack length $l(\varepsilon)$. It can be shown (using, for example, finite element calculations) that current is effectively restricted to a path with width

$w(\varepsilon) = w_0 - 2l(\varepsilon)$ if the distance $d(\varepsilon)$ between the cracks is much smaller than their length $l(\varepsilon)$ (here, w_0 is the initial width of the conducting path on the sample). For the effective length $L(\varepsilon)$ of the conducting path, we can then simply take $L(\varepsilon) = L_0$, and it follows that

$$\frac{R(\varepsilon)}{R_0} \propto \frac{w_0}{w(\varepsilon)}. \quad (5)$$

It should be noted that $l(\varepsilon)$ at fixed $R(\varepsilon)/R_0$ depends on w_0 , so, strictly speaking, neither $l(\varepsilon_c^{obs})$ nor ε_c^{obs} can be a material parameter. Apart from this, there is a quantitative problem with the values of $R(\varepsilon)/R_0$ that are usually chosen (e.g., $R(\varepsilon)/R_0 = 1$,^{15,16} $R(\varepsilon)/R_0 = 1.1$,^{1,12} or $R(\varepsilon)/R_0 = 2$ ¹³). We note that $100 \times 160 = 16(\mu\text{m})$ is a conservative⁵ estimate of the critical crack length for edge cracks in our samples. In a typical experiment with w_0 on the order of 0.01 m , a value R/R_0 of $0.01/0.00999 = 1.001$ would indicate $l(\varepsilon) = l_c \approx 10$ microns. Noise interferes with such a precise determination in practice. Clearly, the crack lengths associated with R/R_0 of 1.1 or 2 are far longer, by a factor of 20 to 800.

However, in the experiment, $R(\varepsilon)$ is measured and not $R(l)$, and the method is, in fact, valid if the crack speed below ε_c is effectively zero and at and above ε_c is extremely high. In that case, $l(\varepsilon) \sim w_0$ at ε_c . This means that the crack speed is also of importance for the interpretation of ε_c^{obs} . Relations between crack speed and driving force have been studied extensively in the past, e.g., in Refs. 7, 17–19. The prevailing view is of crack propagation as the thermally activated chemically and mechanically assisted formation of small protrusions along a crack front, in which case the propagation speed of the cracks is given by

$$v = v_0 e^{\frac{G}{nkT}}, \quad (6)$$

with

$$v_0 = f_0 a_0 e^{\frac{-G^{\text{trap}}}{nkT}} e^{\frac{-2\gamma - G^{\text{diss}}}{nkT}}. \quad (7)$$

Here, G^{trap} is an activation energy term and G^{diss} a dissipation energy term. Assuming a Maxwell-Boltzmann distribution of the active protrusions on the crack front, one finds for the frequency f_0 : $f_0 \sim kT/h = 6.25099 \times 10^{12}\text{ s}^{-1}$ for $T = 300\text{ K}$, and h is the Planck constant. a_0 is a characteristic distance associated with protrusions on the crack front. Assuming $a_0 \sim 2 \times 10^{-10}$, we find a value of the order of 1250 m/s for $f_0 a_0$. n is the bond density in the disordered material. For particularly disordered SiO₂, a value of about $8 \times 10^{18}\text{ m}^{-2}$ has been reported.⁷ Using that number, one finds $nkT = 0.03\text{J/m}^2$. The activation energy or trapping energy prefactor can be cast in the same form as that due to the effective surface energy and will likewise add to the critical strain. Including the trapping term in the surface energy term, one finds $2\Gamma = 2\gamma + G^{\text{diss}} + G^{\text{trap}}$. Assuming that the description is valid up to $G = 2\Gamma$, the limiting value of the crack speed is 1250 m/s , at which speed the crack would cross the sample in $1 \times 10^{-2} / 1 \times 10^3 \sim 1 \times 10^{-5}\text{ s}$. With the strain rate used in the experiment (usually $3 \times 10^{-4}\text{ 1/s}$), that

adds an uncertainty of the order of 10^{-9} in the strain, which is negligible. However, propagation of the crack in the sub-critical regime may lead to significant effects, as shown in Fig. 1.

The figure shows that, in general, $\epsilon_c^{obs} < \epsilon_c$. Temperature, strain rate, and sample width (shown in the figure) have an impact on ϵ_c^{obs} with higher strain rates and larger sample widths, leading to values closer to ϵ_c . This analysis shows that the interpretation of electrofragmentation experiments in the literature is often oversimplified.

B. Outline

Notwithstanding these problems, since electrofragmentation is comparatively simple compared to the optical method, it is of interest to extend the data analysis beyond the assessment of the critical strain. Examples can be found in Ref. 11, and this paper attempts to contribute toward that goal. Unlike most earlier papers in this work, we focus on cyclic measurements, consisting of at least a loading, unloading, and reloading step. It has been argued that the value of ϵ_c^{obs} may also differ from the intrinsic critical strain ϵ_c due to the presence of internal strains in the thin brittle film, due to, for example, growth processes, thermal, or hygroscopic effects.²⁰ We argue that the cyclic resistance measurements discussed here provide direct indications of the magnitude of the intrinsic critical strain ϵ_c and of the internal strain ϵ_{int} in the thin films. It is suggested that the method may be applicable to conductive and isolating thin brittle films on polymeric substrates. Furthermore, we combine electrical measurements and optical microscopy. This allows us to investigate the relation between the evolving crack pattern and the resistance in microscopic detail. In the set-up of the experiment and in the interpretation of the results, we will be using the simple hypothesis on initial stages of crack propagation in a conductive brittle film on a polymer substrate that is sketched in Fig. 1. The validity of this simple model will also be discussed in the paper, mainly based on the microscopic evidence.

The paper is organized as follows: in section III, we first discuss electrofragmentation experiments that establish that 10 nm indium-tin-oxide films are adequate probes for the fracture behavior of 150 nm silicon nitride films. We show that hysteresis occurs in $R(\epsilon)/R_0$ and use optical microscopy to interpret this effect in terms of the evolving cracks. Subsequently, we discuss the observed hysteresis in terms of the internal strain in the films. In section IV, we conclude that the hysteresis offers a way to directly measure the intrinsic critical strain ϵ_c and also the internal strain of such films without the need for supporting measurements of sample moduli and geometry.

II. EXPERIMENT

Conductive indium-tin-oxide (ITO) and non-stoichiometric SiN (also containing C and H) (SiN) were deposited by low temperature deposition techniques on sheets of polyethylene-naphthalate (PEN) approximately $15 \times 15 \text{ cm}^{-2}$. ITO-PEN and ITO-SiN-PEN samples were fabricated. The

ITO in all cases had a nominal thickness of 10 nm. For these films, a recipe for sputtering a 100 nm ITO film was used (as confirmed by profilometer measurements). With only 10% of the deposition time, a conductive layer with a sheet resistance of layer about $1000 \Omega/\text{square}$ is obtained, defined in the present paper as “10 nm ITO.”

The SiN films had a thickness of 150 nm and were made in two forms: one with a high compressive internal stress (ITO-SiN-PEN1) and one with a low internal compressive stress (ITO-SiN-PEN2). Curvature of the samples was determined for strips of about 8 cm length and 1 cm width of the PEN and of the high and low stress ITO-SiN-PEN material. Strips were clamped as cantilevers and imaged with a digital camera from the side. Points belonging to the cantilevers were isolated from the background using image processing techniques. The curvature was measured by performing a least squares fit of a circle through all the points. The curvature was measured from strips that were kept at constant humidity for a number of days until their curvature was observed to reach equilibrium. Two different values of relative humidity, 18% and 72%, were used. A value for the initial curvature of the base material was measured in the same way curvature was subtracted from these values. Samples of typical size $40 \times 9 \times 0.125 \text{ mm}$ were cut with a paper cutter. Table I shows the properties of the materials and stacks created.

Strain was measured optically from the distance between two lines drawn with a marker on the backside of the specimen. The tensile loading protocols were such that the films were loaded and unloaded cyclically to increasing loads. A typical sequence of loads is 50 N, 5 N, 75 N, 5 N, 100 N, and 0 N. The strain rate used was approximately $3 \times 10^{-4} \text{ s}^{-1}$. Viscoelastic relaxation effects were visible, but are neglected in the following. ITO-PEN and ITO-SiN-PEN samples were loaded in uniaxial tension, while the resistance was monitored real-time using a 4-point method. The tensile stage used was a Linkam TST 350-E with a 200 N load-cell. This stage allows temperature and humidity control, and it is suitable for use in an optical microscope. Transmission bright field microscopy ($25\times$) was used to image the crack pattern at various stages during the loading. In this mode, a slight defocus shows the cracks, due to phase contrast,²¹ caused by the slight differences in optical paths through a crack and close to a crack. Digital images were obtained with a Mikrotroon CMOS camera operating at 11 Hz. Rather elaborate image processing was needed to isolate the cracks from the background noise, due to dust and phase contrast inherent to the sample.

TABLE I. Properties of samples used in the paper.

Type	t_{PEN} (μm)	t_{SiN} (nm)	t_{ITO} (nm)	Curvature (m^{-1})	
				$RH = 18\%$	$RH = 72\%$
PEN	125	0	0	0.6 ± 0.1	0.6 ± 0.1
ITO-SiN-PEN1	125	150	10	4.4 ± 0.05	3.3 ± 0.05
ITO-SiN-PEN2	125	150	10	1.7 ± 0.05	0.8 ± 0.05

III. RESULTS AND DISCUSSION

A. Conductive 10 nm-ITO films as a fracture probe

First, we assess the suitability of the conductive 10 nm ITO films as a probe for the SiN fracture behavior. In the literature, this method is encountered in Refs. 10, 22, 23. The conductive layer should fulfill a number of requirements:¹⁰ 1: the cracks in the probe layer should be triggered by the non-conducting layer and not vice-versa; 2: the internal stress state of the non-conducting film should not be changed; and 3: the energy release rate of the stack (ITO + SiN) should not differ appreciably from that of the single SiN layer.

On point 1, Fig. 2 shows a typical graph of $R(\epsilon)/R_0$ for ITO-PEN samples with 10-nm ITO films. We note that the maximum value of $R(\epsilon)/R_0$ reached during loading does not decrease during unloading. The observed critical strain for the 10 nm film is around 1.5%. Since the fracture strain of the 10 nm ITO film is much higher than that of the SiN films (also shown in the figure), it cannot be expected to trigger fracture in the SiN. On point 2, the 10-nm ITO film shown here was produced using exactly the same method as the ones eventually used as probes in the ITO-SiN-PEN samples. The highest temperature during production of these samples is reached during SiN deposition, and the thermal load during ITO deposition at room temperature is minimal (possibly 10 degrees C). The expectation is that the internal strain of the SiN is not significantly influenced by the ITO deposition. Using Hsueh's results²⁴ (see also section III C) it is possible to investigate whether the 10-nm ITO film on top of the SiN changes the value of ϵ_c by a significant amount. Even if it is assumed that the value of the critical strain for 10 nm ITO-PEN is completely due to internal strains, this would lead to only a 2% change in the internal strain of the SiN. Therefore, it can be safely assumed that this effect of the 10-nm ITO film is negligible. On point 3, assuming an equal Young's modulus for SiN and ITO and assuming that the ITO breaks at the same strain as the SiN, the ratio $G_{ITO-SiN}/G_{SiN}$ scales as $(t + t_{ITO})/t$. This means an increase in G of about 6.5% for the 10 (nm) film. Based on these three considerations it is

concluded that the 10 (nm) ITO films can be used as a probe for the fracture properties of the 150 (nm) SiN films.

B. Hysteresis

A typical $R(\epsilon)/R_0$ curve corresponding to measurements on a high stress ITO-SiN-PEN is shown in Fig. 2, together with a curve for the ITO-PEN. We note that the high stress ITO-SiN film fractures at much lower strain than the isolated 10-nm ITO layer. Also, after unloading ITO-SiN recovers its original conductivity (number 4 in the figure). On unloading, $R(\epsilon)/R_0$ initially remains constant at the highest value (number 2 in the figure) and then drops quickly to $R(\epsilon)/R_0 \sim 1$ (number 3). The first reloading curve (number 5) retraces the unloading curve until the strain becomes larger than during the first loading. At that moment, $R(\epsilon)/R_0$ starts increasing (number 7). So the material "remembers" the maximum resistance as well as the maximum strain that was reached earlier. It was found that repeating the same cycle leads to qualitatively similar behavior, but that the resistance after unloading (at point number 4) gradually increases after more cycles and that the drop (number 3), therefore, becomes less pronounced. Cycles to higher strains also show qualitatively similar behavior. For example, samples that were loaded to very high values of $R(\epsilon)/R_0$ 10 000 on unloading still return to $R(\epsilon)/R_0$ of the order of 1. Earlier^{3,13} hysteresis in $R(\epsilon)/R_0$ was observed, in which the initial resistance of the conducting film was almost entirely restored after unloading. A graph in Ref. 2 seems to show the same effect, although not as clear, since the strain was not completely relaxed. These observations were not explained.

Figure 3 shows $R(\epsilon)/R_0$ data for three cycles of increasing tensile strain for a high stress SiN film, during which *in situ* optical microscopy was performed. During this experiment, the loading cycle was stopped at maximum and minimum loads, mainly to adjust the focus of the microscope. The microscopic snapshots show the actual crack evolution in the 2nd and 3rd cycle that underlies the resistance data. Crack development during the first loading cycle did not occur in the limited field-of-view of the microscope at the center of the sample, so images from stages 1-6 are missing. During the second cycle, cracks became visible. During the 2nd unloading, the resistance initially stayed constant at a high level, which was reflected in the fact that the crack pattern remained unchanged. This geometry is shown in number 8. At minimum $R(\epsilon)/R_0$, (in this case, similar to the first maximum (number 6), where no cracks could be seen) the cracks are invisible; the cracks have closed. On reloading (numbers 11 and 12), the crack pattern that was present during the previous maximum is re-established until the strain reaches a new maximum value (number 13), after which existing cracks start growing and more cracks appear.

The question that remains now is why these cracks close before the applied strain is zero. On unloading, the crack opening is expected to decrease smoothly until it reaches zero, when the strain in the film $\epsilon_f = 0$ is zero, at which point $R(\epsilon)/R_0$ should drop. In fact, this is not observed in Figs. 2 and 3. Rather, $R(\epsilon)/R_0$ begins to drop at an appreciable value of strain. On reloading, $R(\epsilon)/R_0$ increases at exactly that

FIG. 2. (Color online) $R(\epsilon)/R_0$ hysteresis curves for ITO-PEN (right) and for high stress ITO-SiN-PEN (left). Stages 0-1: loading; 2-3: unloading; 4-7: reloading.

FIG. 3. Crack initiation, growth, and closure in a high stress ITO-SiN-PEN sample during loading and unloading cycles. Top: resistance measurements. Numbers 1-7 correspond to those in Fig. 2. Numbers 8-13 represent analogous stages in the 2nd unloading and reloading. Numbers with “a” indicate static parts. The upper curve qualitatively shows the applied strain; the lower curve shows $R(t)/R_0$. Bottom: processed micrographs. Numbers correspond to resistance measurements shown above and in Fig. 2. Note that stage 8 (maximum resistance after 2nd loading) and 12 (resistance plateau during 2nd reloading) that have similar resistance show similar crack patterns. Stage 10, that shows the same resistance as stage 6, shows only noise in accordance with the fact that, during stage 6, no cracks were visible. Stage 13 and 13a, that show increasing resistance, show growth of cracks as well as appearance of new cracks.

strain. And since the crack already exists, this can be imagined as the opening of a crack with interface energy $\gamma = 0$. The conclusion must be that zero film strain $\varepsilon_f = 0$ and zero applied strain $\varepsilon_{appl} = 0$ do not coincide.

C. Effect of internal strain on determination of ε_c

Importantly, during the experiment, the strain in the film ε_f consists of two parts: the internal strain ε_{int} and the applied strain ε_{app} . The internal strain ε_{int} may be due to growth stresses and thermal and hygroscopic mismatches. Its presence is betrayed by a curvature κ of the sample. In our case, the sample consists of three layers: the PEN substrate, the SiN film of interest, and the very thin ITO film. The strains in the assembly can be analyzed following Hsueh.²⁴ Consider all films to have an unconstrained growth strain in a stress free condition. Subsequently apply a stress to each film to achieve a homogeneous strain c , at which all the layers are in registry for a zero net force on the assembly. Subsequently clamp the layers together and let the assembly relax according to the stress imbalance that now exists. A bending strain $(z - t_b)/r$ will develop. Here, t_b is the neutral line of strain and r is the radius of curvature of the assembly. For the strain ε of the assembly, it follows that

$$\varepsilon = c + (z - t_b)/r. \quad (8)$$

For the relation between the internal stress in a layer, for example, the internal stress $\sigma_{int, SiN}$ in the SiN layer and the strain ε , it is found that

$$\sigma_{int, SiN}/E_{SiN} = \varepsilon - \varepsilon_{g, SiN} = \varepsilon_{int, SiN}, \quad (9)$$

with $\varepsilon_{int, SiN}$ as the internal strain. $\varepsilon_{g, SiN}$ replaces the thermal strains in Hsueh's formulation and encompasses all strains that develop during or after fabrication. It is clear that the value of $\varepsilon_{g, SiN}$ depends on the geometry and moduli of the stack. For a very thick and stiff substrate, $\varepsilon_{int, SiN} = -\varepsilon_{g, SiN}$.

During the experiments described here, we increase the applied strain, thereby adding to the initial, internal strain $\varepsilon_{int, SiN}$ until fracture occurs at ε_c^{obs} , so

$$\varepsilon_{int, SiN} + \varepsilon_c = \varepsilon_c, \quad (10)$$

with ε_c as the total strain in the film at breaking. Interpreting the measurement data of ε_c^{obs} , we can, of course, use

$$\varepsilon_c^{obs} = \varepsilon_c - \varepsilon_{int, SiN}. \quad (11)$$

A tensile internal strain ($\varepsilon_{int, SiN} > 0$) leads to $\varepsilon_c^{obs} < \varepsilon_c$ and a compressive growth strain to $\varepsilon_c^{obs} > \varepsilon_c$. In a partially cracked film, such as shown in Figs. 1 and 2, the internal strain (compressive in this case) is pushing the crack faces into contact during unloading. But, clearly, G_c for the cracked portion of the film has dropped to approximately 0. So the reloading curve should only show the effect of the internal strain, and the difference in strain between the loading and reloading curves is therefore the true or intrinsic fracture strain ε_c of the thin film. The position of the reloading curve itself should reflect the internal stress state and may be measured in the same way (and with the same caveats) as the critical strain as $\varepsilon_{int}^{obs, 1,2}$. Figure 4 shows measurements on the low stress and high stress ITO-SiN-PEN samples. The relative positions of the reloading curves (at lower strain for the low stress film) is consistent with this interpretation.

A more common way to determine the value of ε_{int} is by curvature methods. Using a formula proposed by Timoshenko,²⁵ it is possible to determine the residual strain in the thin oxide film supported by a polymer, provided that the Young's moduli and Poisson's ratios of substrate and thin film are known. Measuring the curvature $\kappa(\varepsilon_{int})$, the strain ε_{int} can be found using

$$\kappa(\varepsilon_{int}) = \frac{6\varepsilon_{int} \left(\frac{h_f}{h_s} + 1 \right)^2}{(h_c + h_s) \left(3 \left(\frac{h_f}{h_s} + 1 \right)^2 + \left(\frac{E_f h_f}{E_s h_s} + 1 \right) \left(\frac{h_f^2}{h_s^2} + \frac{E_s h_s}{E_f h_f} \right) \right)}. \quad (12)$$

FIG. 4. (Color online) $R(\epsilon)/R_0$ hysteresis curves for ITO-SiN-PEN samples with high stress and low stress SiN. Drawn lines with double headed arrows indicate the intrinsic critical strain, dashed lines with single arrows the internal strain for $R(\epsilon)/R_0 = 1.2$.

Hsueh²⁴ derives similar but more general expressions that are valid for any number of layers.

There are a number of issues with the determination of ϵ_{int} in this way. Firstly, in practice, measurement of the elastic properties of thin films supported by polymers is difficult and not often performed. Usually, one of the few available literature values for the moduli is used. For ITO, values of 88.4 ± 11.3 GPa (Brillouin light scattering),²⁶ 92 GPa (Vickers indentation),²⁶ 99.8 ± 13.6 ,²⁷ 112 GPa (nanoindentation on ITO coatings deposited on glass substrates),²⁸ 116 GPa,²⁹ and 118 GPa³⁰ have been given in the literature. For SiN derived from PECVD processes, it is important to realize that film density, hydrogen content, internal stress, and elastic properties have all been shown to be correlated.⁸ Secondly, for the systems discussed here, with a low substrate modulus, the displacements that occur can be rather large, even though the strains remain small. This means that the assumptions of linear elasticity underlying Hsueh's approach are, in general, not valid. In this case, solutions based on non-linear elasticity are appropriate, as was shown in Ref. 31. Solutions for rectangular strips were shown to be in accordance with the experiment in, e.g., Ref. 32. We will use

FIG. 5. (Color online) Measured curvature (at RH = 18% and RH = 72%) for high-stress ITO-SiN-PEN1 and low-stress ITO-SiN-PEN2. Derived stresses are according to non-linear analysis [Ref. 31]. Linear relation between curvature and stress is according to Ref. 25, shown for comparison.

TABLE II. Properties of the materials used in the paper.

	PEN	ITO	SiN
Young's modulus E	5 GPa	100 GPa	100 GPa
Poisson's ratio ν	0.3	0.3	0.3

the expressions given in these papers to relate measured curvature (See Table I and Fig. 5) to stresses in the SiN, assuming that the ITO has the same modulus as the SiN, (see Table II for the material parameters used) so that the system effectively consists of 2 layers.

We can now compare the two sets of measurements for the internal strain and the intrinsic critical strain. Table III show values determined for $\epsilon_c^{\text{obs}, 1,2}$, for the intrinsic critical strain derived directly from the hysteresis curves, ϵ_c^{hys} , and indirectly from curvature measurements, ϵ_c^{curv} , and for the internal strain determined directly from the hysteresis curves, $\epsilon_{\text{int}}^{\text{obs}, 1,2}$, and indirectly from curvature measurements, $\epsilon_{\text{int}}^{\text{curv}}$.

From the table, it can be seen that there is quite a good agreement between the two methods. We think this shows that the hysteresis curves offer a more direct way of measuring the ϵ_c and ϵ_{int} . Considering the problems associated with the determination of the internal strain using curvature, that seems very attractive.

There are a number of limitations to this direct method of determining the intrinsic critical strain and the internal strain. The first is that the strains have to remain small. Clearly, plastic deformation may prevent the cracks from closing at unloading. This is the reason that the measurements shown here are restricted to very low values of $R(\epsilon)/R_0$. In practice, a particularly strong layer may only break in the plastic region of the substrate. However, for typical barrier layer-polymer substrates combinations, the critical strain is between 0.5% and 1% and the method is expected to work.

Also, in the case of tensile internal stresses, a tensile experiment, such as described here, will not work, since it is not possible to load the film in compression. A bending experiment would be needed, in which the curvature of the sample can change from positive to negative. This is certainly interesting to investigate.

Finally, one might expect the roughness of the crack faces to be of importance. Apparently, in this case, the cracks can close almost perfectly; whether that is true for all materials and thicknesses remains to be seen.

TABLE III. Directly and indirectly measured fracture properties of high stress and low stress SiN films on PEN. Observed critical strain $\epsilon_c^{\text{obs}, 1,2}$; ϵ_c^{hys} : intrinsic critical strain from hysteresis; $\epsilon_{\text{int}}^{\text{curv}}$: internal strain derived from curvature; $\epsilon_{\text{int}}^{\text{obs}, 1,2}$: internal strain derived from reloading curve; ϵ_c^{curv} : intrinsic critical strain using curvature measurements $\epsilon_c^{\text{obs}, 1,2} - \epsilon_{\text{int}}^{\text{curv}}$. A comparison with Fig. 1 shows that, for these SiN films, $2\Gamma \sim 2J/m^2$.

Type	$\epsilon_c^{\text{obs}, 1,2}$ (%)	ϵ_c^{hys} (%)	$\epsilon_{\text{int}}^{\text{curv}}$ (%)	$\epsilon_{\text{int}}^{\text{obs}, 1,2}$ (%)	ϵ_c^{curv} (%)
ITO-SiN-PEN1	0.55 ± 0.05	0.4 ± 0.05	0.1 ± 0.05	0.1 ± 0.05	0.45 ± 0.05
ITO-SiN-PEN2	0.80 ± 0.05	0.35 ± 0.05	0.5 ± 0.05	0.45 ± 0.05	0.3 ± 0.05

IV. CONCLUSIONS

The conductivity of 10 (nm) films of ITO deposited on top of 150 (nm) SiN films is an effective probe of the fracture properties of the SiN films. It was found that the ITO layer could not be expected to influence the internal strain in the SiN, that it was not expected to induce fracture in SiN, and that it added only a small amount to the energy release rate. Based on these observations, it was concluded that a 10 (nm) ITO film constitutes a good probe for the fracture behavior of SiN.

Using this as a basis, we studied $R(\varepsilon)/R_0$ during loading, unloading, and reloading to low strains. The rise in $R(\varepsilon)/R_0$ during loading is associated with initiation and propagation of cracks in the SiN.

The operational definition of the ε_c^{obs} was shown to be invalid in principle. However, it is correct in practice if the difference in propagation speed between subcritical and critical cracks is large enough. A simulation indicated that ε_c^{obs} usually underestimates ε_c by an amount depending on, among other factors, strain rate and sample geometry.

On unloading and reloading the ITO-SiN-PEN, $R(\varepsilon)/R_0$ shows a steep drop that is associated with crack closure, as observed from microscopy. The location of the drop corresponds to a zero strain level in the thin film, and therefore, the difference in between the rising and dropping parts of $R(\varepsilon)/R_0$ corresponds to the intrinsic critical strain ε_c . ε_c can therefore be measured directly from the hysteresis curves without the need to perform independent measurements of curvature substrate, film thickness, and film moduli.

This also means that the internal strain ε_{int} can be measured directly from the $R(\varepsilon)/R_0$ curves. However, in this case, it is necessary to choose a level, as was the case for the critical strain earlier.

In conclusion, the observed hysteresis loops in the $R(\varepsilon)/R_0$ during loading and unloading of thin brittle conductive films offers a way to directly measure the intrinsic critical strain and internal strain of such films without the need for supporting measurements of sample moduli and geometry.

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