Nanoscale Analysis of Surface Bending Strain in Film Substrates for Preventing Fracture in Flexible Electronic Devices

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With the rapid development of flexible electronics and soft robotics, there is an emerging topic of preventing fracture in materials and devices integrated on largely bending film substrates of >100 µm thickness. The high demand for strategically reducing strain in bending materials requires a facile method that enables one to accurately and precisely analyze the surface bending strain in a wide variety of materials. This study proposes the surface-labeled grating method that is the fundamental and efficient technique for measuring surface bending strains merely by labeling a thin, soft grating onto various film substrates composed of flexible polymeric and rigid inorganic materials. The surface strain with a single-nanoscale (<1.0 nm) can be quantified in real time with no need of material information such as Poisson’s ratio, Young’s modulus, and film thickness. The fracture limit of a hard coating overlying flexible substrates is successfully determined by the accurate and precise quantification of surface bending strains. Furthermore, a multilayer film substrate with surface bending strain reduced by 50% prevents fractures of hard coatings and organic thin film transistors (OTFTs) since the strains remain below the fracture limit under large bending.

Even by deformation at the nanometer scale, strain above the fracture limits inevitably damage any materials, which is the difficulty encountered in developing functional materials for soft robots, biomedical systems, and flexible electronic devices.[1–10] In flexible electronics, the surface strain of the bending film substrates exceeding the fracture limits of conductive and semiconductive materials causes the failure of the devices as shown in Figure 1a left.[9–13] This difficulty can be circumvented by exploiting an elementary mechanics that surface bending strain decreases linearly with a thickness of a substrate. For example, flexible substrates with a thickness of 10 µm experience peak surface strain of only 0.1% upon bending to the radius of curvature of 5 mm, and this strain remains well below the fracture limits of semiconductors (>1%), metals (1–2%), and hard coatings (1–3%); indeed, the use of a substrate within a range below tens of micrometers enables comparable growth, resulting in high-performance durable flexible devices for epidermal, implantable, and wearable applications (Figure 1b).[10–20] On the other hand, the development of foldable electronic devices that have thicknesses of hundreds of micrometers is an emerging challenge. This highlights the ever-growing importance of the substrates strategically designed to reduce surface strain without thinning (Figure 1a right and 1b). However, it is not yet possible to measure nanoscale surface bending strain in real time: none of the currently available advanced methods fulfill all of the necessary spatial-temporal resolution, accuracy, precision, and a wide range of measurable materials. Electrical strain sensors including strain gauges exemplify the most common strain analytical method.[21–23] Although they provide surface bending strains of materials targeted in real time, their...
low analytical resolutions are inadequate for the accurate and precise determination at the nanometer scale. Other methods that do not rely on electrical signals—such as of photoelasticity, Moiré patterns, and X-ray diffraction—overcome the above-mentioned drawback, but are still limited by a smaller variety of measurable materials and the lack of real-time analysis.[24–29] Herein, we present the surface-labeled grating method capable of real-time measuring the surface bending strain in various flexible film substrates, with high accuracy and precision in a single nanometer scale (<1.0 nm). We successfully determined a fracture limit of functional materials integrated on flexible film substrates via the quantitative analysis of their surface bending strain, merely by attaching a soft optical grating label on surface of target materials and measuring the diffraction angle of a probe beam. Furthermore, the surface bending strain was reduced by 50% through multi-layering of the film substrate, maintaining the original thickness; the surface bending strain remained well below the fracture limit. The use of the film substrate with reduced strain successfully suppressed the cracking of hard coatings and the breakdown of an organic transistor (Figure 1a right).

To measure the surface bending strain, a thin polydimethylsiloxane (PDMS) label with an optical grating (period \( \Lambda = 4 \mu m \)) was attached to the surface of a target film, as illustrated in Figure 1. a) Conceptual illustrations of flexible electronic devices. The common polymeric substrate damages the rigid and brittle electrical materials overlying it through its large surface bending strain that exceeds their fracture limits (left). The specialty substrate with a small surface bending strain that remains below their fracture limits prevents the breakdown of the electrical materials (right). b) Surface strain in a substrate bent with a certain radius of curvature as a function of substrate thickness. Horizontal axis shows the thickness of film substrates integrated into flexible electronic devices for epidermal, implantable, wearable, and next-generation foldable applications. Vertical axis is surface strain, and double arrows show fracture limits of materials such as glass, semiconductors, metals, and hard coatings.

Figure 1.

Figure 2a. A He–Ne laser beam (wavelength: 633 nm) was incident on a labeled film substrate placed on the laboratory-made optical setup (Figure 2b). The laser beam passing through the film diffracted depending on the grating period; thus, the increase in an applied strain (\( \Delta L/L \)) resulted in extensive bending of the film and simultaneously changed the distance between the diffracted beams (\( D \)) on the screen in Figure 2c and Movie S1 (Supporting Information). This change in the diffraction angle (\( \alpha \)) allowed the real-time quantitative determination of surface bending strain induced in the film, in the same manner as we previously reported.[30,31] However, the previous procedure required the
direct inscription of an optical grating on the surface of target materials using photochemical or lithographical technologies, thus limiting versatility of the method. To overcome this limitation, we employed a grating label that can be formed directly on various target films (Figure S1, Supporting Information). The label is very thin (≤1 µm) and soft (2 MPa modulus), as shown in Figures S2 and S3 (Supporting Information); hence, it never disturbs the bending of the films, enabling accurate measurement of the surface bending strain in various materials.

Figure 3a shows the surface bending strains in commercially available polyethylene naphthalate (PEN) films, as a common substrate used in flexible electronic devices. As the applied strain imposed on the PEN films with various thicknesses increased from 0% to 75%, the bending strains on the outer surfaces gradually increased from 0% to 0.7% (75 µm thickness), to 1.1% (100 µm thickness), and to 1.6% (125 µm thickness); conversely, the strains on the inner surfaces gradually decreased from 0% to −0.7%, −1.1%, and −1.6%, respectively. These results indicate that the outer and inner film surfaces are subjected to tension and compression as expected. The error bars showed only < ±0.05% strain, indicating that the surface-labeled grating method provides the precise surface bending strains. Remarkably, these strains are comparable to a nanoscale deformation. Figure 3c shows the relation between displacement (|ΔΛ|) and surface strain in the 75 µm thick PEN film. The displacement is on the nanometer scale (0.5–1.0 nm), even including error bars. Such quantification for surface bending strain in polymeric materials with a single nanoscale resolution has never been achieved through the other methods. Also note that the surface bending strain in the film remained unchanged even after the 100 000th bending (Figure 3d). Hence, the surface-labeled grating method is the powerful tool for achieving the accurate and precise measurement of the surface bending strain in the bending target flexible films with significantly high resolution and repeatability. The accuracy of this method will be elucidated later.

Compared to existing optical methods, the surface-labeled grating method is more versatile with respect to targeted materials because the label is merely attached to any surfaces as required; in the case of the others, targeted materials have to exhibit crystallinity or optical anisotropy, which significantly limits the types of measurable materials. To demonstrate this versatility, we measured the surface bending strains of

![Figure 3](image-url)
three representative samples: a cyclo-olefin polymer (COP) film exhibiting amorphousness and no optical anisotropy,[32] a polyimide (PI) film with colored appearance, and a glass plate as an amorphous inorganic material (Figure 3b). To prove the accuracy of this method, we used the modified Elastica theory which is an analytical model of curvature for a single-layer bent film that we recently reported.[33] As shown in Figure 3e, let s be the distance along the axis of the bent film from origin O; the expression for the angle between the line tangent to the bent film and the x-axis is θ (s). The angle θ (0) is also expressed by β, dividing the bending of a film into two groups: 0 ≤ β < π/2 (Figure 3e top) and β = π/2 (Figure 3e bottom). For an arbitrary β, the theoretical curvature (1/R; R denotes central radius of curvature) at each applied strain was obtained via the calculation of [dφ(s)/ds]−1/2 where φ(s) denotes arcsin[(θ/2)/sin(β/2)] from the experimental stress–strain curves (Figures S3 and S4, Supporting Information). These calculated results were consistent with the experimental curvatures (Figures S5 and S6, Supporting Information).

Surface bending strain in the underlying film substrate of practical devices is an important controlling factor that causes the fracture of the overlying functional materials, e.g., hard-coatings and electrodes. On substrates whose surfaces exhibited different bending strains, such as single-layer polyethylene terephthalate (PET) films with different thicknesses of 125, 188, and 250 µm (Figure 4a and Figure S8, Supporting Information), we formed 7 µm thick hard coatings with a pencil hardness of 6H on them (HCPET125, HCPET188, and HCPET250) as shown in Figure S9 (Supporting Information). Following the bending of hard-coated PET films (Figure 4a), we plotted the surface bending strain (%), curvature (1/R), strain (∆L/L), and crack density as a function of curvature (1/R) and strain (∆L/L) for PET films with thicknesses of 125, 188, 250 µm, and a triple-layer film with a thickness of 200 µm. Plots and lines correspond to the values obtained using the surface-labeled grating method and the geometric relation: εs = h/2R, where εs, h, and R represent surface strain at the center of a bent film, film thickness, and radius of curvature at the center of a bent film. Inset shows schematic of the triple-layer film. Optical micrographs of the hard coating formed on the 250 µm thick PET film, Corresponding curvatures (1/R) and applied strains (∆L/L) are shown in images. Crack density is a function of surface bending strain in substrates. Images of bent films whose curvatures (1/R) are approximately 0.20 mm−1. The normalized mobility of OTFTs during bending was measured.
PET films, cracking was eventually observed at their center (Figure 4b); the curvatures at which their first cracks appeared were 0.23 mm\(^{-1}\) in HC\(_{\text{PET250}}\), 0.15 mm\(^{-1}\) in HC\(_{\text{PET188}}\), and 0.11 mm\(^{-1}\) in HC\(_{\text{PET125}}\). With the increase in curvature, the crack density\(^{[15-38]}\) which was defined as the number of cracks formed on the hard coating layer per unit length, increased in the hard coatings, as shown in Figure 4c and Figure S10 (Supporting Information). Interestingly, the hard coatings began to fracture at the same surface strain of 1.45% regardless of the thickness and curvature of the PET substrates (Figure 4d). This result clearly shows that the surface strain in the bending substrates determines the fracture limit of the hard coatings.

Cracking of the hard coatings is prevented by using a substrate that exhibits the surface bending strain below the fracture limit. This motivated us to reduce surface bending strain in a substrate used. Here, we employed the multilayering strategy because no material information is required for quantification of surface strain in the multi-layers by our method; on the other hand, material properties of Poisson's ratio and Young's modulus are inevitable for simulations and theoretical calculations of the multi-layers. For single-layer PET films, their surface bending strains were in accordance with the geometric relation (\(\varepsilon_s = h/2R\)) and proportional to the film thickness and curvature (Figure 4a). However, this geometric relation was not applied to a film with a sandwich-like structure composed of two 50 \(\mu\)m thick PET layers with a 100 \(\mu\)m thick PDMS layer between them (inset of Figure 4a). This film was 200 \(\mu\)m thick, yet exhibited a surprisingly small surface bending strain: the strain on the triple-layer film surface decreased by approximately 50% compared with the geometric relation (yellow line in Figure 4a). This decrease is due to multiple neutral mechanical planes, where bending strain becomes zero, generated by the shear deformation of the PDMS layer, as reported on several theoretical studies.\(^{[19,40]}\) Note that the surface bending strain of the triple-layer film was even smaller than that of the single-layer 125 \(\mu\)m thick PET film despite the same curvature as the single-layer PET films (Figure 4e), and its maximum value was only 1.0%. Since the triple-layer film exhibited smaller surface bending strain than the fracture limit of a hard coating (1.45%), bending-induced cracking in the hard coating was successfully suppressed (HC\(_{\text{Tri200}}\)) (Figure 4d,e).

This triple-layer film can endow mechanical durability not only on hard coatings but also on other hard materials such as organic transistors, without thinning the substrates. We fabricated organic thin film transistors (OTFTs) on four types of polymer substrates: the single-layer PET films (125, 188, and 250 \(\mu\)m thicknesses) as well as the triple-layer film (200 \(\mu\)m thickness) as shown in Figure 4f. Our recent reports\(^{[41-43]}\) and Figure S11 (Supporting Information) detail fabrication process. The transfer and output curves of the OTFTs did not show any injection limitations and any contact resistance, indicating that the devices performed well (Figure S12, Supporting Information). The increased curvature of the OTFTs decreased the drain current (Figure S13, Supporting Information). The decreasing trends were clearly different; the decrease in the drain current of the OTFT on the 200 \(\mu\)m thick triple-layer film was the smallest, whereas that of the OTFT on the single-layer 250 \(\mu\)m thick PET film was the largest. The mobilities, extracted at gate voltage of \(-20\) V in the saturation regime, further distinguished the recorded differences (Figure 4g). The mobility of the OTFT on the triple-layer substrate registered a remarkably small change compared to those of OTFTs on the other substrates, which is rationalized by the fact that mobility is proportional to surface bending strain in a substrate (Figure S14, Supporting Information). These demonstrate the importance of the strategic design of flexible substrates and the analysis of surface bending strain in them to further enhance the mechanical and electrical properties of flexible devices (Figure 1 right).

In summary, the surface bending strains in various flexible materials were quantitatively analyzed by the surface-labeled grating method with a single-nanometer resolution. The real-time strain analysis we achieved has multiple benefits: high resolution, precision, and a wide range of measurable materials, which is superior to the other available method. The reliability of the measurements was confirmed using the modified Elastica theory. This method revealed that the cracking of hard coatings on the surface of PET films occurred at surface strains exceeding 1.45%, regardless of the film thickness and curvature. As a proof-of-concept, the multilayering of two PET layers with a soft PDMS layer between them reduced the surface bending strain by 50% compared with that of a single-layer film with the same thickness, thereby achieving the surface bending strain of 1.0% at the radius of curvature of 4 mm. This triple-layer film successfully suppressed the cracking of the hard coating and the breakdown of the OTFT. Although only transparent materials were tested using the transmissive diffraction system in this study, the development of a reflective diffraction system will expand the applicability of this method to non-transparent materials. The surface-labeled grating method, therefore, is a practical tool that allows the analysis of surface bending strain in the elaborately designed materials such as programmable materials, hybrid composites, and multi-layered structures, and contributes to the development of advanced flexible electronic devices and soft robots.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by a Grant-in Aid for Scientific Research on Innovative Areas "Molecular Engine" (JSPS KAKENHI Grant Number JP18H05422). This work was supported by JSPS KAKENHI Grant Numbers JP18K14297, JP20K15339. This work was supported by JST CREST Grant Number JPMJCR1814, Japan. This work was performed under the Cooperative Research Program of “Network Joint Research Center for Materials and Devices. This work was performed under the Research Program of “Dynamic Alliance for Open Innovation Bridging Human, Environment and Materials” in “Network Joint Research Center for Materials and Devices”. The authors thank Koji Usui (Tokyo Tech), Dr. Kyoei Hisano (Ritsumeikan University), Dr. Masaki Ishizu (Tokyo Tech), Motoyuki Fukuhara (Tokyo Tech), Kohei Yamada (Tokyo Tech), Dr. Miho Aizawa (AIST), Kohsuke Matsumoto (Tokyo Tech), Yurina Kanehara (Tokyo Tech), and Prof. Christopher J. Barrett (McGill University and Tokyo Tech) for fruitful discussions.
Conflict of Interest

The authors declare no conflict of interest.

Keywords

bending, flexible electronics, polymer films, soft robotics, surface strain

Received: September 22, 2020
Revised: November 30, 2020
Published online: January 25, 2021

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