Surface wrinkling by chemical modification of poly(dimethylsiloxane)-based networks during sputtering

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Wrinkling is an important mechanical phenomenon that generates periodic topographical patterns across a surface. This paper presents experimental evidence that surface wrinkles, which form consequent to thin film magnetron sputtering of either indium tin oxide (ITO) or aluminum on poly(dimethylsiloxane) networks (PDMS-N) made from a commercial Sylgard-184 kit, result from chemical modification of the PDMS-N surface as opposed to extrinsic thermomechanical stresses originating from differential thermal expansion. X-ray photoelectron spectroscopy results reveal that the PDMS-N surface becomes depleted in carbon and concurrently enriched in oxygen relative to silicon due to sputtering. This silica-like surface layer possesses intrinsic compressive stress that leads to wrinkle formation during the first ≈5 seconds of sputtering. The wrinkles maintain their periodicity irrespective of the thickness of the ITO film formed during subsequent deposition. Furthermore, upon removal of the ITO layer, the wrinkles persist with their periodicity unchanged. A narrow sputtering pressure window between 2 and 12 mTorr generates wrinkles. Pressures below this range cannot sustain a radio frequency plasma, while pressures above this range provide sufficient thermalization of kinetic energy as to eliminate the energetic bombardment that modifies the PDMS-N. This study provides a new understanding of the origins of wrinkling in sputtered films on polymeric substrates and creates opportunities to manipulate the topography produced by spontaneous surface wrinkling.

Introduction

Electronic and photonic materials rely routinely on topographically patterned micro- and nano-structures to endow functionality and/or enhance performance.1 In systems composed of hard and soft multi-layers, spontaneous surface wrinkling can be transformed from an unwanted mechanical instability to a naturally occurring opportunity that produces corrugated surfaces. Wrinkling occurs by subjecting a bilayer comprising a stiff skin resting on and adhering strongly to a deformable substrate to stress. This stress can be released through the bending and deformation of the layers to form regularly spaced corrugations. By controlling the directionality of the compressive stress, wrinkling can be used to produce different types of periodic surfaces, ranging from randomly-oriented to well-aligned wrinkles, as a consequence of the relaxation of isotropic and anisotropic stresses, respectively.2,3 In the case of uniaxial stress, both compressive stress as well as stress in elongation can lead to wrinkling.

In many cases, wrinkled surfaces are formed by depositing a rigid film (e.g., vapor deposited metal or metal oxides) onto a compliant polymeric substrate, such as a poly(dimethylsiloxane) network (PDMS-N).2,4–11 Alternatively, the rigid film may be generated by chemically modifying the surface of a PDMS-N substrate (e.g., oxidation via exposure to oxygen plasma).10,12–18 Ultimately, the wrinkling instability occurs by subjecting the bilayer system to some form of extrinsic or intrinsic stress, i.e., thermal expansion mismatch strain due to heating or mechanical stretching, or swelling of the substrate by exposure to a solvent.19–21 While the stress can result from a variety of sources, the common requirement is surface compression.

Here we report a study of surface wrinkling in a system consisting of an indium thin oxide (ITO) film deposited on a PDMS-N substrate. This system forms wrinkles (1) in situ during the first 5–10 seconds of sputter deposition, (2) with characteristic wavelengths independent of film thickness, and (3) with topography that perseveres after removing the deposited ITO film. These results are in contrast to multiple studies that attribute wrinkles formed by physical vapor deposition of rigid films on elastomeric substrates to the stresses arising from...
thermal expansion mismatch due to local heating. The present results illustrate that chemical modification of the substrate is sufficient to cause in situ buckling of PDMS-N. We explore buckling in the ITO/PDMS-N system because of opportunities to create transparent conductive surfaces featuring topography, although the results appear to extend to other sputtered systems such as Al/PDMS-N.

We present a self-consistent set of data, which shows that (1) magnetron sputtering plasmas can rapidly and substantially modify the chemical composition of PDMS-N surfaces in very short times, (2) intrinsic compressive stresses accompany this modification, and (3) the initial formation of this layer regulates wrinkling onset and ultimate wavelength. We determine the chemical changes that occur during surface modification and establish the window of sputtering conditions in which it occurs by pressure-dependent energetic bombardment of the PDMS-N surface and the growing ITO film.

**Experimental procedure**

**Preparation of poly(dimethylsiloxane) network substrates**

Poly(dimethylsiloxane) networks (PDMS-N) were prepared from a commercially available elastomer kit. Specifically, Dow Corning’s Sylgard-184. Sylgard-184A and Sylgard-184B were mixed in a 10 : 1 ratio by mass, according to the recipe suggested by the manufacturer. Gentle vacuum (≈ 100 Pa) removed the trapped air bubbles prior to casting the mixture into a flat polystyrene dish. An oven cured the PDMS at 60 °C for at least 120 min. A scalpel cut the crosslinked, yet flexible PDMS-N substrates (≈ 1 mm thick) into 2.5 cm × 2.5 cm pieces. The substrates were placed on a quartz plate and heated under high vacuum (2 × 10^{-6} Torr) at 120 °C for 3 hours to aid in outgassing any low-molecular mass components from the network. Substrates were stored in a covered Petri dish at ambient conditions until use. A 3.75 cm × 3.75 cm glass slide supported the PDMS-N during ITO deposition.

An additional set of thinner PDMS-N samples was prepared by spin coating uncured PDMS-N onto 2.5 cm × 2.5 cm pieces of silicon wafers. Varying the spin coating speed from 5000 to 7000 rpm and the spin coating duration from 1 to 10 min produced samples with thicknesses spanning 1 to 35 μm. An oven cured these films at 65 °C for at least 120 minutes. A profilometer (Veeco Dektak 150 Surface Profilometer) measured the thickness of the films.

**Deposition of indium tin oxide top films**

A radio frequency (RF) magnetron sputtering chamber prepared ITO films using a commercially available sputtering target of indium tin oxide (In_{2}O_{3}/SnO_{2}, 90/10 wt%, 99.999% purity, 2 inch diameter, Kurt J. Lesker Company). We deposited the films at room temperature in a load-locked instrument with a base pressure of 2.0 × 10^{-8} Torr, a sputter power of 30 W, a target-to-substrate distance of 8.5 cm, and a pure Ar sputtering ambient. These conditions resulted in a deposition rate of ≈ 5 nm min^{-1} such that a 40 nm thick ITO film could be prepared in ≈ 8 minutes of deposition. The ITO target was not exposed to atmosphere between depositions and ITO was pre-sputtered prior to film growth to ensure consistent films. A 40 nm thick ITO film was used initially because it provided a sheet resistance that was suitable for a number of photovoltaic and light-emitting applications.

**Results and discussion**

Fig. 1 depicts an optical microscope image of a representative wrinkled surface of ITO on PDMS-N (40 nm ITO on 1 mm thick PDMS-N). The surface is populated by regularly spaced, but randomly oriented wrinkles exhibiting a characteristic wavelength of ≈ 1.2 μm, which was determined through fast Fourier transforms (FFT) of optical microscope images.

The formation of random wrinkles necessitates a compressively stressed ITO/PDMS-N laminate. A routine way to generate compression is to stretch an elastomeric substrate prior to deposition and subsequently release the strain. The PDMS-N in Fig. 1, however, was not stretched. In the absence of externally applied strain, a compressive stress may arise due to thermal expansion mismatch between the ITO film and the PDMS-N substrate. For example, metal layers deposited on PDMS-N at elevated temperatures will wrinkle upon cooling to minimize compressive surface forces that evolve because PDMS-N has a much larger coefficient of thermal expansion (CTE) than the metal. The PDMS-N in Fig. 1, however, was not intentionally heated.

Wrinkles are known to form during plasma oxidation of PDMS-N. A common explanation is based on the surface of PDMS-N heating during deposition, and upon cooling (i.e., when the plasma process ends) wrinkles evolve to minimize stress due to the CTE mismatch between the film and the substrate. It is important to note that this explanation does not account for all observations of wrinkling transitions in thin film/elastomer stacks. In an attempt to elucidate the operative mechanism, we performed a series of experiments aimed at determining the onset of wrinkling.
Kinetics of wrinkle formation

If wrinkles are generated by a thermal mechanism, they should form at the end of the sputtering process (i.e., when the substrate begins to cool). We observed the onset of wrinkle formation by visually inspecting the substrate through a window in the sputtering chamber in real time, and by exposing PDMS-N surfaces to the magnetron plasma at 5 second intervals. Interestingly, wrinkles form at ITO deposition times between 5 and 10 seconds, causing the surface to appear hazy. At a growth rate of \( \approx 5 \text{ nm min}^{-1} \) this time interval will provide between 0.4 and 0.8 nm of material. ITO layers will not coalesce at these thicknesses, thus eliminating their ability to apply a biaxial stress and to participate in buckle formation. We have also seen similar behavior during deposition of aluminium. In addition, because wrinkling occurs rapidly during sputtering, the temperature of the surface is modest and is heating gradually rather than cooling. These observations suggest that the wrinkling mechanism is not due to thermal expansion mismatch of the ITO and PDMS-N. It also suggests the film itself (i.e., ITO or Al) is not important, but rather, there is some chemical modification of the substrate during the first few moments of sputtering that induces wrinkles.

Effect of ITO film thickness

Because wrinkles appear during the first few seconds of sputtering, we sought to understand whether additional deposition would change the periodicity or, instead, if the wavelength is set during the initial sputtering stage. We deposited ITO films 40–300 nm thick (8 to 60 minutes of deposition at 30 W RF power) onto 1 mm thick PDMS-N substrates on silicon wafers. The data in Fig. 2 show that the wavelength does not vary with the thickness of the ITO top film. We also deposited ITO (100 nm thick) on PDMS-N (1 mm thick) at various sputtering powers of 30, 70, and 90 W RF and 4 mTorr Ar. Because the deposition rate varies with sputter power, we varied the sputtering times to maintain a constant thickness of the ITO top film. In all cases, the sample surfaces exhibited random buckles with a characteristic wavelength of \( \approx 1 \text{ \mu m} \), similar to Fig. 1.

At first consideration, the results in Fig. 2 seemingly disagree with established theoretical models and experimental reports that predict the wavelength to depend strongly on top film thickness. In systems where the substrate is heated before top film deposition, the top film thickness is established prior to cooling and wrinkling; thus its entire thickness contributes to the mechanical response. Similarly, if the substrate is heated prior to exposing its surface to oxygen plasma, then the thickness of the oxidized surface of the substrate will affect wrinkle wavelength as stress develops upon cooling.

However, if we consider the hypothesis that wrinkles result solely from initial PDMS-N modification at modest temperatures while the system is gradually warming, this result is self-consistent: additional ITO simply deposits on top of pre-existing wrinkles. If this hypothesis is true, not only should the wrinkles form very early during the sputtering process, but they should persist after removing the ITO, provided the modified surface remains stable.

Wrinkles after removing ITO

We removed the ITO top film by etching for 5 minutes with hydrochloric acid (HCl, Fisher Scientific, trace metal grade). Brief HCl exposure does not alter PDMS-N yet it etches away ITO. Films were then rinsed in deionized water and dried with nitrogen gas. Resistivity measurements confirmed the removal of the ITO, and AFM shows the wrinkles remain present on the sample and maintain their original characteristic wavelength, regardless of sputtering power (Fig. 3). This result further supports the conclusion that wrinkles result from surface modification of the PDMS-N substrate during the first few seconds of sputtering, and that the ITO coating adopts the pre-existing buckle texture.

Chemical modification by sputtering

The persistence of wrinkles in the absence of the top film with no change in wavelength suggests the sputtering process

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**Fig. 2** Characteristic buckle wavelength as a function of ITO top film thickness with a constant substrate thickness. Estimated error is within the symbol size.

**Fig. 3** AFM image of the PDMS-N surface clearly demonstrating the presence of buckles after the removal of 40 nm ITO by etching.
chemically modifies the PDMS-N surface during the initial stages of sputtering and creates compressive stresses that result in buckles. The stability of polymers in oxidizing environments has been investigated previously; it is well established that argon ion (Ar⁺) bombardment, oxygen plasma treatment, and ultraviolet (UV) or ultraviolet/ozone (UVO) exposure lead to modification of the surface of PDMS. For example, oxygen plasma treatment removes preferentially methyl groups, leading to the formation of additional Si–O–Si cross-links in PMDS and hydroxylation of the PDMS surface, while Ar⁺ bombardment creates crosslinks between silicon atoms. During sputtering of ITO, the plasma that is generated comprises a partially ionized gas consisting of ions such as Ar⁺, O₂−, O₂−, and UV photons.

When exposed to such environments PDMS forms a silica-like surface layer. For example, one study utilizing oxygen plasma exposure reports the formation of a 130–160 nm thick smooth, oxidized SiO₂-rich surface layer after 80–180 seconds exposure, in which silicon bonds to three or four oxygen atoms. Similarly, argon plasma exposure forms a 30 nm thick oxygen rich layer. In the case of UVO exposure, PDMS-N surface modification (chain scission, recombination and densification) extends 5–10 nm below the surface, while for longer exposure a silica-like surface layer formed with a density approaching 50% of the theoretical silica value. These reports determined that active oxygen species are integral to the modification process, as UV treatments alone did not yield extensive chemical modification.

Consequently, there are important implications for sputtering oxides on PDMS-N given the presence of energetic species in all sputter plasmas, particularly at the initial stages of film deposition. A modified or silica-like layer formed in situ must impact wrinkle formation.

To explore this possibility, we used X-ray photoelectron spectroscopy (XPS, Riber LAS-3000 with MgKα excitation of 1254 eV) to compare the surfaces of (1) PDMS-N stripped of 40 nm ITO that was sputtered at 30, 70 and 90 W RF, (2) virgin PDMS-N, and (3) virgin PDMS-N exposed only to the HCl etchant. We established an energy calibration for the XPS measurements by referencing to adventitious carbon (C-1s line at a binding energy of 285 eV). During measurements, the background pressure within the analysis chamber was ≈10−10 Torr, the take-off angle was ≈75° from the surface, the X-ray incidence angle was ≈20°, and the X-ray source to analyzer angle was ≈55°. With this setup, the XPS probing depth is approximately 8.7 nm.

Fig. 4 displays XPS survey scans of each sample across the binding energy range of 0 to 1200 eV, revealing prominent signals that are attributed to O-1s, O-2s, C-1s, Si-2s, and Si-2p binding energies. In some cases, minor peaks were also observed and correspond to In-3d, In-3p, and Sn-3d. Table 1 summarizes the atomic percents determined from these survey scans.

Both control samples (PDMS-N and PDMS-N exposed briefly only to HCl) show surface compositions that are similar to what is theoretically expected based on the chemical formula of PDMS (50 at% C, 25 at% O, and 25 at% Si). The deviations from pure PDMS are similar to several literature reports (47.1 at% C, 25.1 at% O, and 27.7 at% Si) and can be understood considering that Sylgard-184 is not pure PDMS, rather it is a composite containing a substantial fraction of silica fillers (30–60 wt%), resins, and other components. The entire set of surface compositions is represented graphically in Fig. 5 for clarity. Though not shown, the plasma-exposed samples exhibited Si 2p and O 1s peak shifts of approximately +0.3 and 0.4 eV, respectively. The increase in binding energy is consistent with the increased electronegativity of higher oxygen coordination and a more SiO₂-like chemical environment. Similar peak shifts have been reported as a consequence of plasma exposure.

The surface composition of the PDMS-N substrates, when considered relative to Si (which will not change since it is not volatile and it is not a component of the ITO plasma), shows an average 24% decrease in C and an average 35% increase in O, which can be determined from the values shown in Table 1. These data show that more oxygen was added than carbon removed. In addition, traces of In and Sn were found after etching. We propose that in addition to the surface modification by oxidation, the PDMS-N surface was implanted by In, and Sn from the plasma during sputtering. We further hypothesize that the additional ≈10 atomic% of material observed after deposition results in surface swelling, and thus compressive stress. This newly formed surface/substrate stack

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**Table 1** Atomic percent as determined by XPS

<table>
<thead>
<tr>
<th></th>
<th>C (%)</th>
<th>O (%)</th>
<th>Si (%)</th>
<th>In (%)</th>
<th>Sn (%)</th>
<th>Ca (%)</th>
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</thead>
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<tr>
<td>PDMS-N</td>
<td>45.43</td>
<td>30.08</td>
<td>24.48</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>30 W</td>
<td>33.85</td>
<td>40.78</td>
<td>24.89</td>
<td>0.23</td>
<td>0.08</td>
<td>0.17</td>
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<tr>
<td>70 W</td>
<td>36.71</td>
<td>37.99</td>
<td>24.60</td>
<td>0.41</td>
<td>0.08</td>
<td>0.21</td>
</tr>
<tr>
<td>90 W</td>
<td>33.23</td>
<td>42.34</td>
<td>24.35</td>
<td>0</td>
<td>0.08</td>
<td>0</td>
</tr>
</tbody>
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accommodates subsequently this volume expansion by a buckling transition.  

The formation of a silica-like surface has been reported previously upon exposure of PDMS to UVO, argon plasma, Ar⁺ bombardment, or oxygen plasma, but the formation of wrinkles was attributed to stresses arising from thermal expansion. Our report is the first to describe such modification and wrinkling in situ to thin film deposition and relate its importance to the mechanism of wrinkling.  

Modeling wrinkle periodicity  
We sought to model the characteristic wavelength of the wrinkles with the understanding that they originate from a silica layer on the surface of the PDMS-N. We evaluated the wavelength (λ) in the context of the classic model that describes wavelength as a function of thickness (t):

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\lambda = t \left( \frac{2\pi}{\lambda} \right) \left( \frac{E_{\text{film}}(1 - \nu_{\text{substrate}}^2)}{E_{\text{substrate}}(1 - \nu_{\text{film}}^2)} \right)^{\frac{1}{3}}
\]

where \( \lambda \) is the wrinkle wavelength, \( t \) is the thickness, \( \nu \) is Poisson’s ratio, and \( E \) is Young’s modulus.  

We employed the model to predict separately the wavelength assuming properties for ITO and silica overlayers. Fig. 6 summarizes the results for constant thickness ITO films (10 and 40 nm) on a variable thickness PDMS-N substrate assuming \( E_{\text{film}} = 118 \) GPa, \( t_{\text{film}} = 10 \) nm or 40 nm, \( \nu_{\text{film}} = 0.35 \), and \( E_{\text{substrate}} = 1.5 \) MPa. The model significantly overestimates the wavelength at all ITO thicknesses. This result is consistent with the understanding that the ITO film is a minor participant to the wrinkling.  

In addition, a more complex model that minimizes the total free energy of the top film bending and substrate deformation with respect to characteristic buckle wavelength was used to predict wavelength and gave nearly identical results.  

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\text{Intrinsic stress from sputtering}
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The studies presented thus far suggest that the compressive surface stress originates from the modified surface layer of the PDMS-N. However, the stress in a sputtered film is known to depend strongly on deposition pressure, and the potential contributions from as-deposited, intrinsic stresses must be considered. To tune the as-deposited stress, we investigated a spectrum of deposition energetics by varying the argon pressure during sputtering. This technique is effective in regulating the landing energy of sputtered ions by controlling the number of gas-phase collisions, and thus the degree to which kinetic energy of the plasma species is thermalized in the gas phase. To do so, we prepared 40 nm thick ITO layers on 1 mm thick slabs of PDMS-N at pressures between 2 mTorr and 12 mTorr argon, while maintaining constant power (30 W RF) and argon flow rate (9 sccm Ar). Fig. 7 displays characteristic buckle wavelengths as a function of Ar deposition pressure. Randomly oriented wrinkles form only at pressures between 2 and 12 mTorr, and there is no significant relationship between wavelength and pressure. However, at deposition pressures greater than 12 mTorr, the surface forms cracks without buckling, while at pressures below 2 mTorr, the plasma cannot be sustained, and ITO cannot be sputtered.
While we have proposed a mechanism for buckle formation via bombardment, it is necessary to understand this pressure window of buckling and film cracking within the same context. By considering how the plasma interacts with the growing film after PDMS-N modification, we can establish a self-consistent explanation. At low pressures, gas phase scattering is limited, and energetic impingement results in forward sputtering (or atom peening) of the growing film. Peening contains enough energy for implantation into a growing film and for dislodging already deposited atoms to higher energy positions that are strained with respect to the equilibrium lattice. This effect produces densification and in many cases compressive stress, which can generally be supported without catastrophic mechanical failure. We propose that these energetic species are responsible for modifying the surface of PDMS-N. As pressures are increased beyond 10 mTorr, the kinetic energy of plasma species is thermalized prior to deposition. The surface damage to PDMS-N is reduced, and adatoms have less overall mobility after landing. Under such conditions surface modifications that produce buckling no longer occur, and tensile stresses are expected to evolve following the grain boundary relaxation model. In brittle oxides, i.e., ITO, such stresses lead to cracking at modest levels, particularly for depositions on substrates like PDMS-N, which offer limited structural support. The transition from compressive to tensile stress can be quite sharp. In one well-documented example, a nearly 4 GPa swing from compressive to tensile film stress occurred over a 5 mTorr pressure range in sputtered molybdenum and other metals. It is important to note that intrinsic stress in thermally evaporated films is usually tensile, and thus wrinkling in thermally evaporated systems typically occurs from external compressive stress. This behavior is reported for metal evaporation on PDMS-N at elevated temperatures, and wrinkle formation upon post-deposition cooling.

These pressure-dependent bombardment-based mechanisms can also explain film cracking, because deposition pressures that mitigate energetic bombardment should reduce adatom mobility to levels that allow tensile stress to accumulate, simultaneously eliminating substrate damage that chemically alters the PDMS-N to instigate a wrinkle transition. Finally, it is necessary to consider the role of intrinsic compressive film stresses on wrinkle formation, as in principle, these can provide a contributing influence. To do so, we return to experiments measuring the deposition time required to form wrinkles. As discussed previously, these measurements show buckle formation at times between 5 seconds and 10 seconds. At a growth rate of $\approx 5$ nm min$^{-1}$ this time interval will provide between 0.4 and 0.8 nm of material. ITO layers will not coalesce at these thicknesses, thus eliminating their ability to apply a biaxial stress and to participate in buckle formation.

Conclusions

We present evidence that buckles formed by sputter deposition form due to stress arising from chemical modification of the PDMS-N substrate rather than thermal stress. Buckles are typically attributed to the compressive forces that result when a film deposited on an elastomeric substrate cools from elevated to room temperature. Here, a number of factors suggest a new mechanism: (1) the buckles form in the first 5–10 seconds of deposition at which time the temperature of the surface should be modest and heating gradually rather than cooling and (2) the wavelength of the buckles is independent of the thickness of the ITO layer and persists when acid chemically removes the ITO film. XPS analysis shows that the modified surface of PDMS-N has lower carbon content and higher oxygen content relative to the parent material. Taken in entirety, these results suggest that the chemical modification of the surface of the PDMS-N creates compressive stresses that induce wrinkles. These wrinkles establish the final wavelength, and subsequent ITO deposition only increases the film thickness without changing the wavelength.

These results demonstrate the important effects of sputtering on controlling intrinsic top film stress such that spontaneous wrinkling can occur. Furthermore, this work leads to a clearer understanding of the origins of wrinkling in sputtered top films on polymeric substrates, which is promising as a strategy for controlled texturing and patterning of surfaces by wrinkling.

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Notes and references
