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## Design of Ordered Wrinkled Patterns with Dynamically Tuned Properties

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### Abstract

The formation of patterned surfaces is a common tool to engineer materials. The capability to design and reproduce detailed features is a key factor to fulfill requirements for functional surfaces. Generation of wrinkles via buckling of a stiff film on a compliant surface is an inexpensive, easy and reliable method to yield a patterned surface. The wrinkling method has been exploited in a wide variety of areas, including photovoltaics, microfluidics, adhesion, and anti-fouling systems. Here we show the ability to obtain deterministically ordered herringbone patterns. In a biaxially pre-stretched PDMS sample a thin film of a stiff coating is deposited by initiated chemical vapor deposition (iCVD). iCVD is a solvent-free technique that yields a conformal thin coating on virtually any substrate, giving a controllable thickness and tunable structural, mechanical, thermal, wetting, and swelling properties. Sequential release of the film-substrate system shows the transition from 1-D ripples to an ordered herringbone pattern. Wrinkle features can be controlled adjusting the film thickness, the initial load and the release process. Moreover, the surface topography can be dynamically tuned by applying a controlled mechanical stimulus. These properties make these materials excellent candidates for flexible applications.

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*Keywords:* iCVD; buckling; patterning.

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## 1. Introduction

Generation of patterned surfaces is a common tool to engineer materials. The capability to design and reproduce detailed features is a key factor to fulfill requirements for functional surfaces. Formation of wrinkles via buckling mechanism offers an inexpensive, cheap and reliable method to obtain these patterns. Wrinkled surfaces have found application in a wide variety of areas, including photovoltaics,(Kim et al., 2012) microfluidics,(Ohzono et al., 2009) adhesion,(Chung et al., 2007) and anti-fouling systems.(Efimenko et al., 2009) Sinusoidal shape wrinkles are obtained through buckling of a stiff coating on a compliant substrate. Generally, an elastic film is deposited on a pre-stretched substrate (e.g. polydimethylsiloxane, PDMS). When this strain is released, the mismatch between the strain equilibrium of both materials generates the wrinkle instability. The production and mechanism of formation of 1D wrinkles have been widely studied.(Basu et al., 2005; Bowden et al., 1998; Chung et al., 2009; Jiang et al., 2007) The generation of more complicated geometries via biaxial stretching, however, offers many alternative patterns to explore.(Cavicchi et al., 2009; Fu et al., 2009) Lin and Yang (Lin and Yang, 2007) reported the transition from 1D ripples to 2D herringbone structures with a jog angle of 90° through biaxial stretching of the sample. In addition, controlling the load and the release applied to the system enables the ability to deterministically yield ordered surface topologies.(Yin et al., 2012) Particularly significant is the possibility to reversibly switch from patterned to flat surfaces upon release or stretch of the substrate. Tuning the geometrical structure on the surface can result in new potential applications, with special interest in stretchable electronics, reflectivity, wettability, micro-fluidic flow and photovoltaic. This study shows the systematic design of ordered patterns through a wrinkling strategy. Adjusting the stretching and releasing processes enables to control the features of the wrinkled surface. Furthermore, the initial flat state and the final herringbone pattern can be reversibly obtained by applying a sequential release. A poly(ethylene glycol diacrylate) (pEGDA) film is deposited on pre-stretched PDMS by initiated chemical vapor deposition (iCVD), a solvent-free technique that yields conformal and functional polymer thin films. (Ozaydin-Ince et al., 2012; Yagüe et al., 2012) Then, sequential or simultaneous release of the x-axis and the y-axis were carried out to achieve the pattern. Finally, the x-axis and the y-axis were re-stretched sequentially or simultaneously to their initial positions. The surface topography is analyzed during the release and stretch process, comparing simulated results with experimental results.

## 2. Experimental part

### 2.1 iCVD polymerization

A layer of trichlorovinylsilane (97%, Sigma) was used to covalently bond the PDMS and the pEGDA film. First, the PDMS surface was activated in a plasma cleaner (Harrick Scientific PDC-32G) at 18 W for 30 s. Then, the biaxially stretched cross-shaped PDMS film was introduced in an oven at 40 °C under vacuum and exposed to trichlorovinylsilane vapors for 5 minutes. iCVD polymerizations were conducted in a custom-built cylindrical reactor (diameter 24.6 cm and height 3.8 cm). EGDA (98%, PolySciences) was heated to 60 °C and was introduced into the reactor at a flow rate of 0.5 sccm by using a regulated needle valve. Tert-butyl peroxide (TBPO) (98%, Aldrich) was fed into the chamber at a flow rate of 1.5 sccm through a mass flow controller (MKS Instruments). ChromAlloy O filaments (Goodfellow) were resistively heated to 230 °C. The temperature of the stage was set at 25 °C using a chiller/heater (Neslab RTE-7). Polymer thickness was monitored in situ by laser interferometry (JDS Uniphase).

## 2. 2 Pattern characterization

The final pattern and its dynamic evolution were imaged using a Hitachi TM-3000 tabletop SEM and a 3-D optical profilometer (Zeta-20™, Zeta Instruments).

## 3. Results and discussion

Fig. 1 shows the different topographies obtained applying a simultaneous or sequential release to equi-biaxially or non-equi-biaxially pre-stretched systems. Equi-biaxially pre-stretched samples lead to disordered patterns when the releasing is simultaneous. However, sequential release, first x-axis and second y-axis, results in the formation of a herringbone pattern. The characteristic zig-zag turning, known as jog angle ( $\alpha$ ), of these structures shows always a  $90^\circ$  angle. Furthermore, if instead of applying an equi-biaxial stretching is a non-equi-biaxial one is possible to tune the jog angle in the herringbone pattern. Being the pre-strain on x-axis  $\varepsilon_x = 10\%$  and on y-axis  $\varepsilon_y = 20\%$ , upon sequential release of first the larger pre-strain,  $\varepsilon_y$ , followed by the smaller pre-strain,  $\varepsilon_x$ , the jog angle obtained is higher than  $90^\circ$ , ( $\alpha=110^\circ$ ). Conversely, upon sequential release of first the smaller pre-strain,  $\varepsilon_x = 20\%$ , followed by the larger pre-strain,  $\varepsilon_y = 30\%$ , the jog angle obtained is smaller than  $90^\circ$  ( $\alpha=65^\circ$ ). It should be noted that this is the first time than herringbone patterns with a jog angle lower than  $90^\circ$  are created. Thus, these experiments demonstrates that adjusting initial experimental conditions it is possible to control the ordering of the wrinkled pattern and to tune its geometrical features.

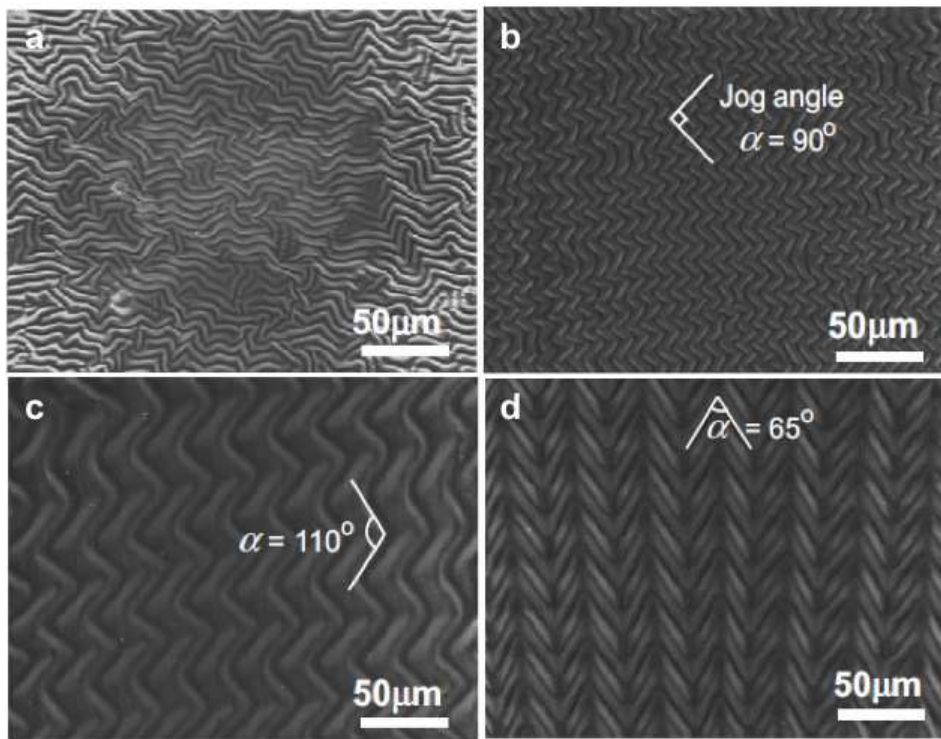


Fig. 1 SEM images of pEGDA coatings deposited by iCVD on pre-stretched PDMS substrates upon simultaneous release of equi-biaxial strain of 10% with a coating thickness of 100 nm (a). Upon sequential release of equi-biaxial strain of 10% with coating thickness of 100 nm (b). Upon sequential release of non-equi-biaxial strain, first larger pre-strain  $\varepsilon_y = 20\%$  and then smaller pre-strain  $\varepsilon_x = 10\%$  with a coating thickness of 300 nm (c). Upon sequential release of non-equi-biaxial strain, first smaller pre-strain  $\varepsilon_y = 20\%$  and then larger pre-strain  $\varepsilon_x = 30\%$  with a coating thickness of 300 nm (d).

Next, the reversibility of the process was tested by conducting several stretch/release cycles. Fig. 2 shows the dynamic evolution of the sequential release process of a non-equibiaxial pre-stretched,  $\epsilon_x = 10\%$  and  $\epsilon_y = 25\%$ , PDMS coated with a 400 nm layer of pEGDA. Upper images present the surface topography during the release process of the strain on the x-axis. Here, the coating-substrate system buckles up due to the mismatch in the equilibrium state of both components resulting in the typical 1-D sinusoidal shape pattern. The wavelength of the wrinkle pattern remains steady but the amplitude of the wave increases along the release process. Lower images show the release of the larger strain,  $\epsilon_y = 25\%$ . The release of the y-axis generates a compressive strain that buckles the sinusoidal columns creating the herringbone structure. Since the axis with the lower strain was released first and then the axis with the higher strain, the herringbone pattern shows a jog angle lower than  $90^\circ$  as it was expected.

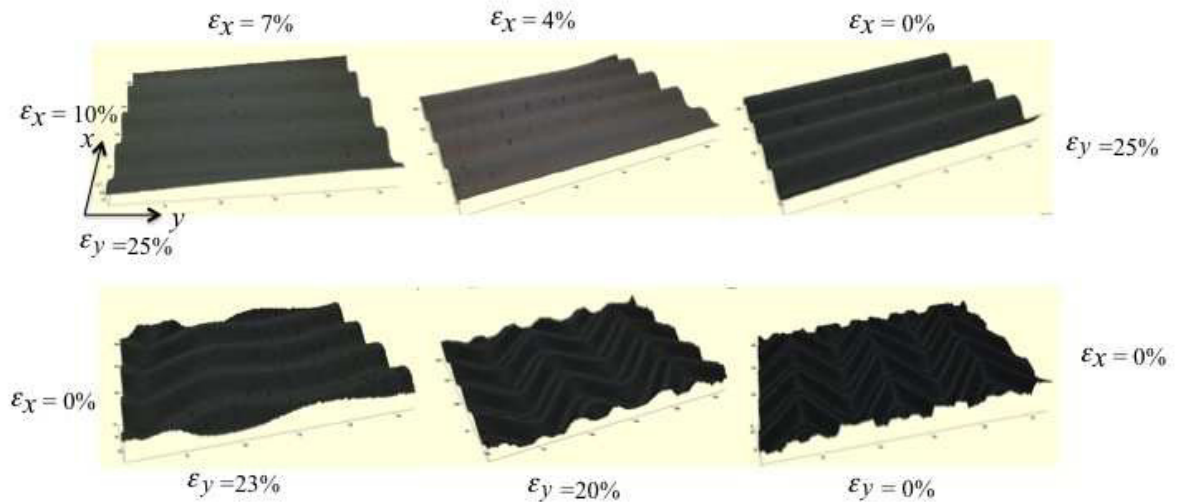


Fig.2 Wrinkling patterns of EGDA coating on PDMS substrates upon sequential release of bi-axial strains with a pre-strain of 10% along x-axis and a pre-strain of 25% along y-axis. Upper figures correspond to strain release along the x-axis, and lower, to strain release along the y-axis. The total area of the images shown is  $200\ \mu\text{m}$  in the x-axis and  $275\ \mu\text{m}$  in the y-axis.

Fig. 3 presents the recovery process of the initial strains applied. Upper images show the re-stretch of the y-axis up to strain of 25%, and lower images show the re-stretch of the x-axis up to the initial value of 10%. The transition from 2-D to 1-D wrinkled pattern is observed during re-stretching on the y-axis. The features of the pattern obtained upon total re-stretch of the y-axis are identical to the features observed upon total release of x-axis in Fig. 2. Lower images in Fig. 3 correspond to the re-stretch on the y-axis and present the evolution from 1-D wrinkles to the original flat state. After several stretch/release cycles, the initial flat surface and the herringbone pattern were obtained alternatively. The same procedure was carried out applying a simultaneous release. Here, release of the strain results in a disordered pattern. However, a residual zig-zag pattern was found exhibiting a small out-of-plane amplitude when loading again the sample. Thus, simultaneous release does not result in a reversible process. We hypothesize that reversibility in the wrinkling process is due to achieving a quasi equilibrium state on the surface. When loading and releasing the sample, wrinkles follow an energetically reversible path that allows for switching the topology back and forth. Thus, this favorable path is the responsible for the dynamic control of the pattern.

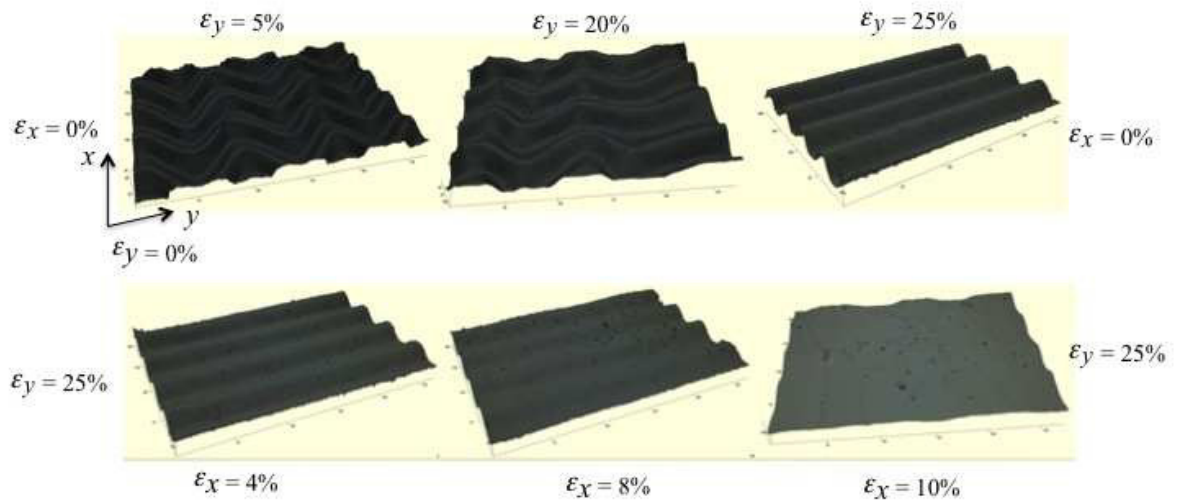


Fig.3 Evolution of wrinkling patterns through sequential re-stretching of wrinkled pEGDA coating on PDMS substrates along two directions to the original stretching strain of 10% along the x-axis and 25% along the y-axis. Upper images correspond to re-stretch in the y-axis, and lower images correspond to the x-axis. The total area of the images shown is 200  $\mu\text{m}$  in the x-axis and 275  $\mu\text{m}$  in the y-axis.

#### 4. Conclusions

This study shows the possibility to design patterns on demand using a wrinkling strategy. Simultaneous release of equi-biaxially pre-stretched PDMS samples coated with pEGDA by iCVD results in disordered patterns. Conversely, applying a sequential release leads to an ordered herringbone pattern. Furthermore, the jog angle in this herringbone pattern can be tuned depending on the experimental conditions applied to the system. Also, we show the ability to dynamically tune the surface micro-topography of these 2-D deterministic herringbone patterns. In situ optical profilometry revealed the sequential wrinkling mechanism responsible for the formation of herringbone patterns. The same herringbone pattern and the initial flat state can be obtained applying a sequential release and a posterior re-stretch, demonstrating the repeatability of the process. In contrast, simultaneous release results in disordered and non-reproducible patterns. These patterns with a reversible topography can provide a means to yield surfaces with tunable functionality.

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