

Nano-Scale Topographic Control of Polymer Surfaces via Buckling Instabilities

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ABSTRACT

We have used a plasma-mediated cross-linking process to generate the patterns on polydimethylsiloxane (PDMS) thin film surfaces. Exposure to an argon plasma leads to the formation of a siloxane network in the near-surface region. The silica-like surface layer is put into compressive stress when the sample cools after removing it from the plasma chamber due to differential thermal contraction, leading to a buckling instability to reduce the stress. The resulting surface waves exhibit wavelengths and amplitudes down to ~ 700 nm and 10 nm respectively. The wavelength and amplitude are controlled by modifying the plasma exposure time and the initial PDMS film thickness. Atomic force microscopy is used to study the topography as a function of these parameters. Comparison to a recent model of the buckling of compressively stressed films on viscous substrates is presented, where we observe consistent qualitative agreement with the model.

INTRODUCTION

Surface texturing can be used to control the wettability, biocompatibility, frictional, and optical characteristics of a material [1,2]. Surfaces with lateral features in the range of 100's of nm can be produced by lithographic means, although these methods are typically rather costly and require significant infrastructure. Features in the 1-10 nm range can be produced using molecular assembly techniques, but there is currently a gap in the ability to produce features in the 1-100 nm range. Yet this is precisely the range at which many biological mechanisms tend to function, for example. The ability to pattern surfaces from the nanometer to the micrometer scale is also important for technological applications such as the fabrication of microelectronic circuits and digital storage media [3]. As the trend for miniaturizing devices continues, so will the demand for thin polymer films with tailored surface properties. The aim of the present work is to create polymer thin films with nano-scale surface texture, and to control the pattern by varying the film thickness and plasma conditions. In this paper we present initial results demonstrating the formation of topographic patterns on polymer surfaces using plasma-mediated crosslinking.

Bulk samples of polydimethylsiloxane (PDMS) are known to form wavy, textured surface patterns under a variety of preparations, yet the mechanism(s) behind the formation of these patterns has not yet been deeply explored or utilized for any application. Two recent investigations using bulk PDMS samples as the substrate highlight the characteristics of these surface waves. Bowden *et al.* [4] exposed PDMS samples to an oxidizing plasma, producing waves with very short range periodic order, but long-range disorder, as the orientation of the wavevector meanders randomly every few wavelengths. The wavelength and amplitude are rather uniform. Oriented waves were produced by patterning bas relief structures into the substrates. Chua *et al.* [5] obtained similar results. Both groups found that longer plasma exposures led to larger surface features. They suggested that the patterns occur because the plasma oxidizes the PDMS to produce a silica-rich surface region. During the plasma process, the sample is thermally expanded due to the increased temperature during the plasma treatment. As it cools, the PDMS contracts much more than the silica surface region because of its far greater thermal expansion coefficient. This puts the silica region under compressive stress, producing a spontaneous surface buckling instability, as commonly observed in compressively-stressed thin films[6]. This method opens up the possibility of generating ordered periodic polymeric structures on flat substrates using non-lithographic techniques.

EXPERIMENTAL

Silicon wafers were cleaned with piranha [70:30 (% v/v) H₂SO₄: H₂O₂ (30wt%)] solution for 1 hr, then rinsed with deionized water and dried by clean dry N₂ gas. A thin film of hexamethyldisiloxane (HMDSO) was deposited using a plasma in order to form a uniform hydrophobic layer on the fresh silicon wafer to promote wettability of the hydrophobic PDMS.

PDMS (Mw=116,500) was then spin coated from a solution on to the silicon with HMDSO layer. The solvent used was ether with polymer concentrations ranging from 2wt% to 5wt% in order to vary the PDMS film thickness. The substrate was rotated at 2000 rpm for 30 s as the polymer solution was directly deposited. After spin coating the samples were placed in the plasma reactor described below, which was evacuated

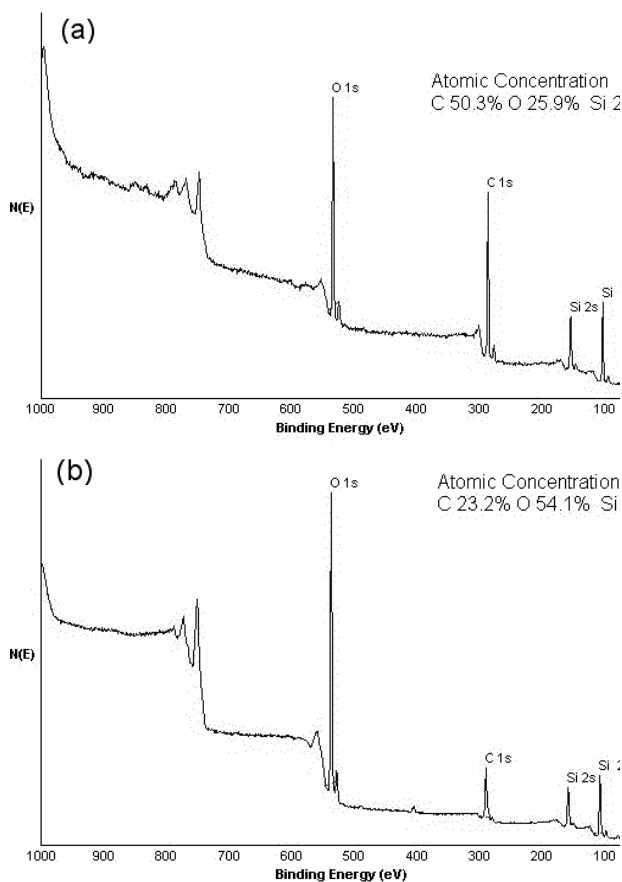


Fig. 1 XPS survey spectrum for PDMS (a) before Ar plasma treatment (b) after Ar plasma treatment. Note the increase in O and decrease in C.

to a base pressure 20 mtorr. The plasma reactor is a cylindrical, capacitively coupled, parallel plate RF reactor chamber made of stainless steel. Samples were heated to 125°C for 20 to 30 minutes prior to plasma exposure to evaporate the remaining solvent and promote spreading of the viscous PDMS film on the substrate. The film was then subjected to varying exposure times of a 400 W argon plasma with the gas flow rate 6.5 sccm (gas pressure 200 mtorr). The substrate was held at 125°C during plasma exposure to reduce thermal inhomogeneity.

Spin-coated specimens were analyzed by X-ray photoelectron spectroscopy (XPS) before and after argon plasma exposure. The XPS spectra were obtained using a Perkin-Elmer 5400 ESCA photoelectron spectrometer with a Mg K α source ($E=1235.6\text{eV}$, 300W) with an incident beam angle of 45°. Under these conditions, the sample chemical composition is probed to a depth of approximately 10 nm. The surface structures after plasma exposure were studied with an atomic force microscope. A Digital Instruments Nanoscope IV AFM with a silicon nitride cantilever was used to study the film topography. Conventional optical microscopy was also used for this purpose. Film thicknesses were determined using ellipsometry measurements made on a Rudolf

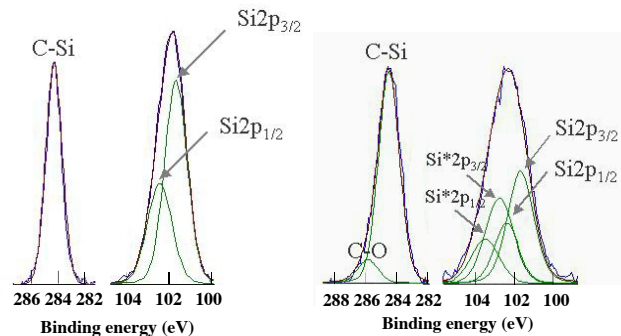


Fig. 2 High resolution XPS spectrum of C1s and Si2p for PDMS (a) before Ar plasma treatment and (b) after Ar plasma treatment. Shown are peak fits

Research/Auto EL II ellipsometer using a He-Ne laser (632.8nm) at an incident angle of 70° relative to the surface normal of the substrates.

RESULTS

XPS analysis indicated that the surface before the argon plasma treatment contains carbon, oxygen and silicon. The atomic composition was ~50% carbon, ~26% oxygen and ~24% silicon as shown in Fig. 1 (a), which is nearly identical to the constituent elemental percentages of PDMS. After the plasma treatment, we found that a thin silica-like layer on the PDMS surface had formed. Fig. 1 (b) shows that the O:C ratio has increased substantially, with the relative proportion of Si remaining nearly constant.

High resolution XPS spectra (Fig. 2) show that the main C and Si peaks, centered at 284.4 eV and 101.8 eV respectively exhibit significant broadening which indicate the presence of new bonding species, discussed below.

The AFM and optical microscopy techniques revealed that these films exhibit surface waves very similar to those found using bulk PDMS as a substrate [4,5]. Fig. 3 illustrates the results obtained from a range of film thicknesses and the plasma exposure times. The wavelength and amplitude increases with increasing plasma exposure time (Fig. 3 a-c). As well, initially thicker PDMS films also lead to larger wavelengths and amplitudes (Fig. 3 e, f). Fig. 3d is a two-dimensional Fourier transform of the data in Fig. 3a. The bright ring indicates the relatively uniform periodicity and nearly completely isotropic nature of the patterns.

DISCUSSION

Before crosslinking, the high resolution XPS spectra (Fig. 2a) are completely consistent with the known XPS signatures of PDMS. However, after crosslinking, the spectra indicate the presence of C-O bonds in the crosslinked surface layer. For example, after crosslinking, the main C peak at 284.4 eV shows a new shoulder at 286.5 eV, consistent with C-O linkages. As well, after crosslinking, the Si peak is broadened, which is consistent with a new pair of higher energy peaks which may represent Si-O-C linkages or Si bonded to more than two O atoms. Finally, the O peak at 532 eV (not shown)

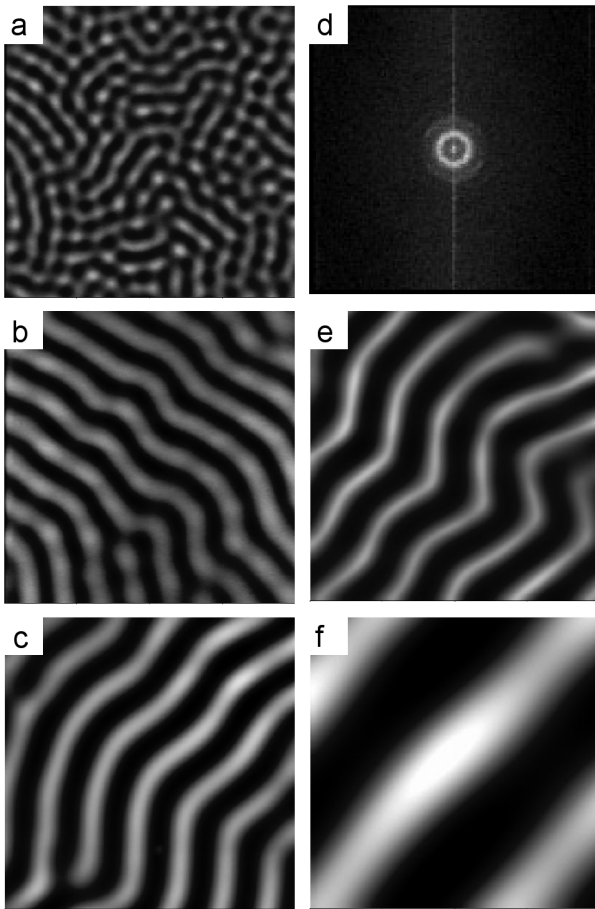


Fig.3. Surface topography images, $10 \times 10 \mu\text{m}^2$ in lateral size, obtained with AFM for varying plasma treatments times and initial PDMS thicknesses. (a)-(c) Exposure time dependence. The initial thickness of the PDMS was 580 ± 3 nm (this is the standard deviation of three measurements of sample thickness using ellipsometry; the systematic error may be substantially larger). The plasma power, exposure time, and height scale of the images are as follows: (a) 400 W, 1 min, z scale: 25nm; (b) 400 W, 2 min, z scale: 40nm; (c) 400 W, 5 min, z scale: 100 nm; (d) two-dimensional spatial Fourier transform of the image (a); (e)-(f) Film thickness dependence. The plasma power is 400 W and the exposure time is 2min. The film thickness and height scale of the images are as follows: (e) film thickness 876 ± 1 nm, z scale: 70 nm; (f) film thickness 1431 ± 6 nm, z scale: 250 nm.

also broadens, consistent with O bonded to both Si and C, or to two C atoms. All the peaks are then consistent with the notion that Si-C bonds have been cleaved, and the resulting free radicals form additional C-O and Si-O linkages by bonding to O atoms that remain in the vacuum chamber, whose base pressure is only 20 mTorr. This leads to the formation of an altered surface layer which we refer to as the “crosslinked” layer or a silica-like layer although it is certainly not pure silica given the extensive amount of C still present in it. Compressive stress is produced in the crosslinked layer once the plasma

treatment ceases due to the rapid cooling of the sample. This is simply due to the large thermal expansion mismatch between the crosslinked layer and the PDMS film, since the thermal expansion coefficient of PDMS is approximately 100 times larger than that of pure silica [7].

The buckling patterns generated in this process are fundamentally governed by the balance of bending and stretching stresses of each layer in the film [8]. Bowden *et al.* [4] used a two-component model to relate the wavelength to the elastic properties of the crosslinked layer and the PDMS, which were both assumed to be elastic solids. This was probably appropriate to their case, since their PDMS had been chemically crosslinked prior to plasma exposure. However, this model does not apply well to our system since our underlying PDMS is not crosslinked and therefore viscous.

Sridhar *et al.* [9] considered the misfit strain between a viscous layer and an elastic surface layer which is more appropriate for our system. Here, the viscous layer thickness, elastic layer thickness, and compressive stress are the factors which govern the instability condition and the resulting wavelength and amplitude. There is a critical value for the onset of this buckling instability. When the bending energy in the film is just smaller than the energy for the expansion of the film, the wavelength is large. The wavelength decreases with increase of the misfit strain between the layers. As well, the wavelength decreases as the viscous layer thickness decreases. Interestingly, the viscosity of the underlying film has no effect on the stability criterion or the resulting wavelength and amplitude, however it does affect the *rate* at which the patterns form, with higher viscosity causing slower pattern formation.

Our experimental results qualitatively support the main predictions from this theoretical analysis. It can be seen from Figs. 3 (a), (b), (c) and 4 that the wavelength and amplitude of the waves increase with the plasma exposure time. The longer the exposure time, the thicker the crosslinked layer. Correspondingly, the energy needed to bend is larger and the compressive stress in the surface layer is smaller. Therefore a

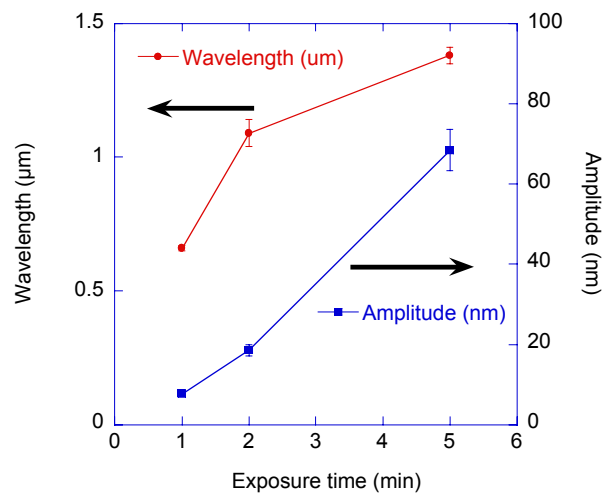


Fig. 4. The wavelength and amplitude of the waves increase with the exposure time. The plasma power is 400W and the initial PDMS thickness is 580 ± 3 nm.

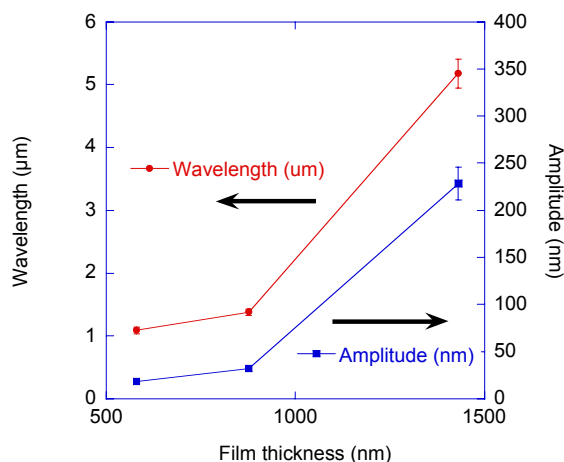


Fig. 5. The wavelength and amplitude of the waves increase with the initial PDMS film thickness. The plasma power is 400W and the exposure time is 2 min.

longer wavelength occurs. We found that the wavelength and amplitude also increases with the initial PDMS film thickness, as shown in Fig. 5, and in Fig. 3 (a), (e) and (f), also in agreement with the model.

The model thus provides guidelines for achieving yet smaller patterns. To drive the wavelength to regimes less than 100 nm, we should impart higher compressive stresses (using higher temperatures during plasma processing), deposit thinner PDMS films initially using lower solution concentrations, and produce thinner crosslinked layers using shorter plasma exposure times. Work is currently underway to produce such smaller patterns. To perform a fully quantitative comparison with the model we would need to know the effective thickness of the crosslinked layer. So far this has not been determined although we are currently investigating methods to accurately perform this measurement.

There are a number of improvements to the model which would be useful. First, our crosslinked layer is still somewhat polymeric in nature and therefore significantly viscoelastic. This should be taken into account. In addition, our system is not actually composed of two discrete layers but rather of a continuously varying mixture of crosslinked and non-crosslinked regions. This may affect the instability condition and predicted wavelengths and amplitudes. Finally, the model does not make any prediction regarding the *in-plane* buckling or “kinking” that is clearly evident in Figs. 3(b), (c) and (e) and is consistently observed in these systems. As well, at small wavelengths, the pattern apparently makes a transition from waves to bumps as seen in Fig. 3(a). These two effects are likely additional stress relief mechanisms that require further study.

Future work will involve extending the range of PDMS and crosslinked layer thicknesses, and varying the compressive stress in the film through *in-situ* heating of the sample during plasma exposure. In addition, we need to determine the effective thickness of the crosslinked “layer” and the corresponding composition profile as a function of depth. This may be accomplished using

multicomponent modeling of ellipsometry measurements as well as by nanoindentation techniques. In combination, these experiments will allow a more quantitative study of the dependence of pattern characteristics and more detailed testing of the model. In addition, further development of the model will be pursued in order to apply it more directly to the system under study.

CONCLUSION

Spin-coated films of PDMS were exposed to an argon plasma for different periods of time. XPS showed that the plasma treatment led to the formation of an oxidized surface layer. The layer is put into compressive stress upon cooling due to differential thermal contraction of the crosslinked and underlying PDMS, producing a buckling instability. The wavelength and amplitude of the waves on the surface are smaller for shorter plasma exposure times and for thinner PDMS films, qualitatively consistent with a model recently proposed by Sridhar *et al* [9].

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