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Abstract

Low energy metal ion implantation has been used to combine an easy “bottom-up” way of creating and tuning different topographic structures on submicron to micrometer scales with the embedding of a metallic element-rich functionalized layer at the surface for a variety of scientific and technological applications. The self-organizing and complex patterns of functionalized topographic structures are highly dependent on the implanted metal ion species, variations in the geometric confinement of the buckled areas on the larger unmodified elastomer film, and the boundary conditions of the buckled regions. Systematic investigations of these dependencies have been carried out via optical and atomic force microscopy, and confirmed with cross-sectional transmission electron microscopy.

Keywords

control, time, dependent, buckling, patterns, thin, confined, elastomer, film

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The control of time-dependent buckling patterns in thin confined elastomer film

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Low energy metal ion implantation has been used to combine an easy “bottom-up” way of creating and tuning different topographic structures on submicron to micrometer scales with the embedding of a metallic element-rich functionalized layer at the surface for a variety of scientific and technological applications. The self-organizing and complex patterns of functionalized topographic structures are highly dependent on the implanted metal ion species, variations in the geometric confinement of the buckled areas on the larger unmodified elastomer film, and the boundary conditions of the buckled regions. Systematic investigations of these dependencies have been carried out via optical and atomic force microscopy, and confirmed with cross-sectional transmission electron microscopy.

I. INTRODUCTION

Polydimethylsiloxane (PDMS) is a commonly used silicon-based, organic, cross-linkable elastomer. It is homogeneous, isotropic, and optically transparent down to 300 nm. In its cross-linked state, the elastomer does not permanently deform under stress or strain, and it is stable over a wide temperature range.¹ PDMS is chemically inert, and thus the material can be made biocompatible² with appropriate chemical and/or physical treatment to enable it to give the desired interfacial interactions. These properties make PDMS attractive for use in a variety of scientific and technological applications including microfluidics and lab-on-chip devices,^{3,4} memory storage devices,^{5,6} stretchable electronics, smart adhesives,⁷ optical diffraction gratings, optical microlenses,^{8,9} and biosensors.^{10,11} The ease with which dominant and complex patterns can be generated and controlled on the surface of an elastomer film makes self-organizing buckling an easy “bottom-up” way of creating and tuning different topographic structures on submicron to micrometer scales for such applications.

In addition to its usefulness in controlling the topographical regimes of buckling, metal ion implantation was chosen because it can also further functionalize the surface. Previous work has found that combining magnetic materials with wrinkling of PDMS can lead to magnetic correlations within the range of the buckling

features.¹² This has led to the creation of ferroscaffolds with unique topographical formations, which hold enormous potential as stimulus-responsive drug carriers and scaffolding materials for tissue engineering. Hu et al.¹³ found that the magnetic sensitivity of ferroscaffolds exhibited different degrees of magnetism, which could be further used to control growth factors for cells cultures. Similar behavior within the range of the buckling features can be expected when combining surface buckling with elemental functionalization through metal ion implantation.

Surface buckling or wrinkling of the elastomer PDMS can be created in a number of different ways. These include plasma treatment and oxidation,^{14–17} metal deposition,^{18–20} ion beam irradiation,^{4,21} and ionizing radiation.²² The control or tuning of the resultant buckling from these techniques has been achieved through controlling the properties used to induce buckling,^{23,24} prepatterning the elastomer film,^{14,18,25} the use of masks,^{15,21,26} or by selectively controlling the thickness of the film.¹⁶

In previous work, we have shown that modification of the surface of a thick PDMS film with implanted metal ions can induce complex buckling patterns, while also elementally functionalizing the surface features.²⁷ Briefly, Rutherford backscattering spectroscopy (RBS) and grazing angle x-ray diffraction (XRD) conducted earlier confirmed that films exposed to metal ion implantation all have a silicon- and oxygen-rich layer at the surface, resulting from decomposition of the elastomer, down to varying thicknesses, depending on the dose and

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the metal ion species. This leads to the surface becoming covered by stress-induced V-shaped cracks that penetrate deeply into the elastomer matrix. Over time, a wavelike regular pattern completely covers the surface of the film, filling in the space between the surface cracks. This leads to the advantageous situation of having element-rich, functionalized, tunable, three-dimensional (3D) surface features.

To be useful for applications, however, the functionalized, self-organized, coherent, and semicoherent 3D surface features would need to be selectively induced onto the surface of the elastomer film. In this work, we have conducted a parameter study of this combined method of buckling and functionalization, to understand the influence of various metal ion species, the varying geometric confinement of buckled areas on a larger unmodified elastomer film, and the boundary conditions imposed by the said geometric confinement on the induced buckling regimes, thereby creating a simple nonphotolithographic means of patterning soft materials.

II. EXPERIMENTAL

To study the dependence of the complex buckling regimes on several parameters, such as metal ion species, geometric confinement, and mask boundary conditions, which are integral to the usefulness of metal ion implantation for the purposes of patterning soft materials, a series of identical high quality PDMS 4- μm -thick films was created. This was done by spinning a liquid silicone mixture with a base and catalyst ratio of 20:1 (Sylgard-184, Dow Corning, Kendallville, IN) onto a (111) single side polished silicon wafer (obtained from Solar Wafers, South Boston, MA) for 120 s at 8000 rpm. Before coating, the liquid silicone was allowed to degas for 10 min in a cool vacuum oven to eliminate the air bubbles introduced while mixing.

The resulting series of homogeneous, optically transparent films of PDMS on Si wafers were then ready for metal ion implantation, which was carried out at room temperature, using a metal vapor vacuum arc ion source. Fe, Co, Au, and Ta were chosen for their variety of atomic weights and oxidizing properties. For each sample produced, the ion acceleration voltage and the beam current were kept fixed at 45 kV and 8 mA, respectively, and several implantation times were used from 5 s to 20 min to determine the effects of controlling the dose on the sigmoidal-like buckling behavior. Eu, Mg, Ni, and Ti were also implanted at both high and low doses to further confirm universality in the behavior of implanted metal ion species.

Two aluminum masks with varying sized islands in varying proximity to each other were chosen. The first simply had a linear series of islands of different sizes at a set distance apart (measured from the edges of the islands). However, the second more complex mask had

different sized islands at varying distances from each other. This allowed the investigation of edge and proximity effects on buckling behavior.

The ion implantation parameters were monitored by He RBS, and the surface morphology was characterized by atomic force microscopy (AFM; Asylum MF-P3D, Asylum Research) in contact mode and by optical microscopy. Transmission electron microscopy (TEM) was conducted to establish a likely mechanism for the variation in buckling behavior.

III. RESULTS AND DISCUSSION

Immediately following the metal ion implantation of the surface, the PDMS surface became altered and covered by what appeared to be stress-induced V-shaped cracks, which penetrated deeply into the elastomer matrix. It is well known and has been demonstrated that V-shaped cracks tend to open up on the surface as a method of strain relief, and the frequency of these V-shaped cracks increases with the strain induced by increased implantation dose.²⁷ Over time, a wavelike regular pattern of undulations appears that is divided into complex coherent and semicoherent domains of various sizes and shapes. These different domains are due to the patterns established by the interference of the differing orientations of the waves that were formed [Fig. 1(a)]. These wrinkling domains completely cover the surface of the film and fill in the space between the surface cracks. A domain boundary was imaged by AFM and is shown in Fig. 1(b), supporting the cross-sectional TEM results in showing no evidence of delamination, simply the intersection of stress wave fronts, which produces an optical illusion of height changes. This becomes useful when designing or controlling discrete strain regions for use in technological and scientific applications, since it means that the stiff layer remains coupled to the underlying elastomer base, thereby retaining the bulk elastomer properties of PDMS.

The time required for this complex, coherent, and semicoherent buckling domain patterns to appear was governed by the implanted metal ion species and ranged from nearly instantaneous to a period of several hours. A qualitative analysis of the time dependence of wrinkle pattern formation for the metal ions implanted suggests the cause. When an energetic ion impacts the surface of the elastomer, the structure and composition are irreversibly changed, primarily through chain scission into lower molecular weight chains and the release of volatile species, to a depth that depends on the mass of the implanted metal ion and its energy. At the same implantation energy, the more massive an implanted ion is the less it will penetrate into the material and the narrower the Gaussian profile of implantation will be, due to the way in which the energetic ion loses energy in the solid

FIG. 1. AFM across the intersection of strain-induced buckling patterns: (a) optical microscope image showing the region of interest, (b) AFM scan across an intersection of strain wave fronts, in this case the corner of a polygon. This result is repeated across all intersections, and there is no evidence of delamination occurring.

FIG. 2. Cross-sectional TEM images of PDMS irradiated with Ni, Fe, and Au for 20 min, using an accelerating voltage of 50 kV and a beam current of ~ 1 mA. The black region is a metal coating grown on the surface as part of the focused ion beam lift-out process.

matrix, mostly through interaction with the electrons of the target. This leads to variations in the depth and thickness of the metal-rich layer implanted into the polymer matrix.

Cross-sectional TEM (Fig. 2) shows that, at the ion implantation potential used in this work, the range of implanted ions agrees with a TRIM calculation of a Gaussian depth distribution, with the peak at around 40 nm, and this was further confirmed by He RBS. However, from the TEM cross-sectional images shown in Fig. 2, it appears that there are varying and distinct compositional layers in the polymer as a result of the implantation, down to around 250 nm. This modification of the polymer matrix is deeper than the implantation depth of the metal ions. It has been speculated that this is due to further complex interactions between the polymer matrix

and the energetic ions.²⁸ This phenomenon requires further attention, and it is currently under investigation.

After the implantation process, the lower molecular weight molecules (LMW) will diffuse up to the surface from the elastomer bulk over time. The diffusion time is influenced by both the thickness of the surface layer; thinner layers lead to shorter diffusion times due to a smaller volume to serve as the LMW repository, and also the thickness of the metal-rich layer acting as a barrier to diffusion.²⁹ This explains why the gold implanted surface formed wrinkles within seconds, followed by iron, nickel, and cobalt, with titanium and magnesium taking the longest. Gold ions are more massive and therefore penetrate less deeply, creating a thinner stiff surface layer and also a thinner metal-rich layer to act as a barrier for the LMW molecules.

Geometric confinement also plays a role in controlling the wavelength of the sine-wavelike buckles within the islands. With the use of an Al mask, islands of buckling were induced onto a larger PDMS thick film confined on a Si wafer. There was an approximately constant 3 μm increase, for all metal ions tested, in the wavelength recorded between the buckling at the center of the island and that at the edge of the island. This suggests that there is a radial strain that increases linearly from the center of the island to the edge as a result of the use of a mask. This 3 μm increase in buckling wavelength was consistent for all island sizes tested; therefore, we can treat the implantation process as homogeneous across the islands, ruling out any gradient effect resulting from the metal ion implantation.

This persistence of the aligned radial buckling at the edge of the island is due to the azimuthal strain from the implanted ions, which is induced by circumferential pressurization at the boundary caused by the unmodified PDMS elastomer and the modulus mismatch.^{30,31} This leads to increases in the length of the aligned radial buckling at the edge of the island with dose, but decreases in the length with increased island size.

In the interior of the implanted islands, away from the geometrically confined, radially aligned buckling, random self-organized coherent and semicoherent buckling morphologies are seen to form. As the strain increases, the morphologies undergo a transition from radial and hooping zigzag patterns, to “telephone cord” buckling. This leads to a pattern of polygons in spots where random buckling intersects (Fig. 3). While the wavelength of the wrinkling is dependent on the metal ion species, as discussed, the wrinkling morphologies resulting from strain are similar in all cases.

So far, the possibility of using a shadowing effect from the ion implantation to create useful morphologies has not been mentioned. Through clever mask design,

the shadowing effect resulting from the distance of the mask from the film allows a small area immediately outside the island to receive a fraction of the dose of the exposed island. This allows the creation of specific strain minimization effects outside the buckled island, dependent on the dose and radius of curvature of the island boundary, which results in a buckling morphology that is significantly different from that inside the island.

Figure 4 shows boundary conditions resulting from two different radii of curvature, which have led to entirely different morphologies in islands implanted with identical doses of Fe. The edges of the islands with the two radii of curvature (Fig. 4) also highlight the evolution of the edge effect outside the boundary of the buckled island, with the first panel [Fig. 4(a)] showing a large radius of curvature, with an island size of 5 mm, giving the impression of an almost straight line at the given scale, and the second panel showing a smaller radius of curvature [Fig. 4(b)], with an island size of 1 mm, which at the same scale appears discontinuous.

Figure 4 also serves to highlight the evolution of buckling with increasing strain. There are three regions of strain clearly delineated, and this behavior is similar for all island sizes and metal ion species: the first 20 μm closest to the edge, followed by a different alignment for another 80 μm out, followed by random buckling. Using these relationships, and by regulating the dose and the curvature of the boundary through island size, different buckling regimes of determinable length, both with and without the island, can be manufactured as part of a larger scale buckled system, where a variety of buckling regimes are needed within a single system. Usefully, the shadowing effect can be further controlled when two shadowing effects are placed in proximity. An $\sim 50\text{-}\mu\text{m}$ -wide field of 2- μm buckles has been established that is an order of magnitude smaller than the buckling seen in the exposed island region.

Initially, wrinkling was induced onto an unstrained, unconfined PDMS film to demonstrate the effects of low energy implantation of various metal ions at different doses. All of the implanted ions behaved similarly with dose, with the wavelength of the wrinkles rapidly increasing with increasing dose until a critical dose at which the increases in wavelength started leveling off in a sigmoidal-like behavior, as seen in Fig. 5. The various ions start buckling at dramatically different wavelengths, which leads to a leveling off with time at different ranges, whereas with constant dose the wavelength of the sinelike buckling pattern was found to be dependent on the metal ion species implanted. Since all implanted metal ions behave similarly in inducing wrinkling, although with different wavelengths, results for iron implanted PDMS are shown hereafter for consistency.

FIG. 3. Optical microscope image of a geometrically confined region of buckling. Exposure time is 30 s. (color online)

FIG. 4. Optical microscope images of two different radius of curvature boundary conditions, for identical dose of Fe implantation, resulting in different strain buckling: (a) large radius of curvature (island radius 5 mm) leading to three distinct regions of strain at the outside of the implanted island; (b) small radius of curvature (island radius 1 mm) with lower strain, showing the beginning of the buckling edge effects; (c, d) AFM results from across the edge of the larger and smaller metal ion implanted islands, respectively.

FIG. 5. Dependence of wrinkle wavelength on the implanted metal ion; Ni, Ti, Eu, and Mg were also implanted at specific exposure times and found to follow the above sigmoidal trends.

While it has already been shown that low energy ion implantation acts to decompose the surface of the elastomer to a silicon- and oxygen-rich stiff layer, thereby causing the wrinkling behavior due to strain mismatch,²⁷ this does not explain the difference in the sigmoidal-like behavior shown when different metal ions are implanted. It is speculated that the dependence of the PDMS wrinkle wavelength on the metal ion species is due to a metal-rich layer implanted into the elastomer matrix. Once implanted, the metal ions act to form either a homogeneous metal-rich oxide composite layer or a layer of metallic clusters suspended within the elastomer matrix beneath the decomposed stiff layer. The thickness and depth of this metal-rich layer is dependent on the dose and penetration depth of the metal ions implanted. This conclusion is supported by previous work done on metal ion implantation in polyethylene terephthalate.^{32,33} Earlier glancing angle XRD results, which showed that different ion species introduced different amounts of strain into the surface layer, along with initial cross-sectional TEM of Ni, Fe, and Au implanted PDMS, demonstrate that various depths and thicknesses of metallic-rich layers could affect the wavelength. Unlike Fe, Co, and Ta, Au only has three data points, therefore it is possible that the trend may be dissimilar, although the authors think this unlikely.

Since all of these parameters are fairly easy to control, a combination of geometric confinement through the clever selection of masks, dose, and metal ion species would allow the engineering of several different buckling regimes, with different elemental functionalization of 3D features within a global buckling system. This constitutes a large advantage of this method of buckling for easy “bottom-up” creation and tuning of different topological structures on submicron to micrometer scales for use in a variety of scientific and technological applications.

IV. CONCLUSION

We have successfully shown that low energy metal ion implantation can be used to modify the surface of PDMS into different functionalized buckling morphologies, within a global system of buckling, by inducing and directing discrete regions of strain without the effort of pre patterning the substrate. This is done through the control of the metal ion species, the dose, and the geometric confinement of the buckled area and control of the boundary conditions by the use of masks. This allows for a rapid and versatile “bottom-up” way in which to create discrete topological morphologies for use in the selective modification and control of the surface topology of elastomers for future applications such as degradable biomedical devices, including surgical dressings,

vascular grafts, tissue engineering scaffolds, sutures, and structures for guided tissue regeneration.

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