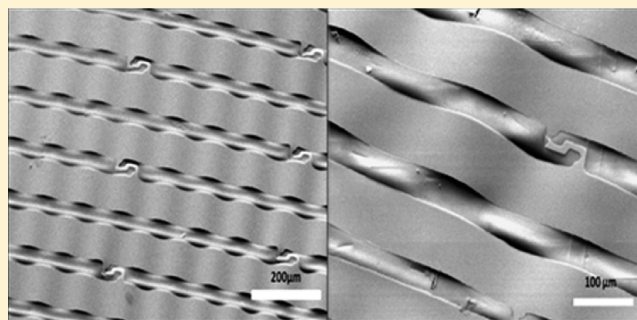


Controlled Morphology of Thin Film Silicon Integrated with Environmentally Responsive Hydrogels

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ABSTRACT: Environmentally responsive hydrogels hold multiple important applications. However, the functionality of these materials alone is often limited in comparison to other materials like silicon; thus, there is a need to integrate soft and hard materials for the advancement of environmentally sensitive materials. Here we demonstrate the capability of integrating a thermoresponsive hydrogel, poly(*N*-isopropylacrylamide), with thin film silicon ribbons, enabling the stiff silicon ribbons to become adaptive and drivable by the soft environmentally sensitive substrate. This integration provides a means of mechanical buckling of the thin silicon film due to changes in environmental stimuli (e.g., temperature, pH). We also investigate how advanced lithographic techniques can be used to generate patterned deformation on the aforementioned integrated structures. Furthermore, we explore multilayer hybrid hydrogel structures formed by the integration of different types of hydrogels that have tunable curvatures under the influence of different stimuli. Silicon thin film integration on such tunable curvature substrates reveal characteristic reversible buckling of the thin film in the presence of multiple stimuli. These results open new opportunities for developing stretchable and intelligent devices for multiple applications.



1. INTRODUCTION

Each individual material (soft or hard) possesses unique properties; it is often desirable to combine these materials to exploit complementary properties. One of the primary examples in the integration of soft and hard materials has been in the field of soft lithography, which allowed for printing of discrete features on hard materials. The integration of soft and hard materials, especially incorporating thin films, could have potential applications in the field of flexible electronics, which have garnered increasing attention in recent years. This is primarily accredited to the large quantity of applications that require systems to be highly conformable and able to withstand a significant amount of strain without compromising functionality.

Stretchable electronic materials could be achieved by two different ways, either by modifying conventional materials for being adaptable to withstand larger strains¹ or by incorporating new flexible materials (e.g., organic semiconductors^{2,3}). In the present work, the former option of conventional materials such as silicon has been studied; our approach is anticipated to enhance established silicon film technology, which is presently not adaptable to different substrates due to its planar and brittle nature. This fundamental limitation has prevented the growth of flexible materials with multifunctionality.

Silicon is essentially considered to be rigid; however, when the thickness is decreased to around 500 nm or less, it can be made flexible without damaging the properties of the material.^{4–6} This characteristic has enabled such thin materials to be integrated with elastomeric substrates to assume different shapes.^{7–10} However, the challenge with elastomeric substrates

is that there is always a mechanical force required to drive the desired change. Such limitation can be overcome by the use of “smart” materials, which have a stimulus responsive behavior. In this work, the approach of environmentally sensitive hydrogels as substrates is investigated.

Environmentally sensitive hydrogels have been at the forefront of many applications such as drug delivery,^{11–13} oil clean up,^{14,15} actuators,¹⁶ sensors,¹⁷ and novel devices. In spite of their potential usefulness, the idea of employing hydrogels in modern electronics is still a relatively new field. The main reason has been the lack of electrical properties of these materials in addition to integrating and packaging issues. One of the new methods of integrating stimuli sensitive hydrogels has been demonstrated by Yu et al.¹⁸ with combining silicon ribbons with a temperature-sensitive hydrogel, poly(*N*-isopropylacrylamide) (PNIPAAm). This integrated structure revealed that the silicon ribbons can be made responsive to an external stimulus, such as temperature, and more importantly, such responses are reversible without fracture of the thin film silicon. This work opens up a new approach of combining traditional semiconductor materials with environmentally responsive hydrogels.

Although the work presented by Yu et al.¹⁸ contributed to the integration of soft and hard materials, one challenge that remains to be addressed is to enable integrated materials behave in a controlled manner so that the circuit would have certain active and inactive areas. In the present work this idea

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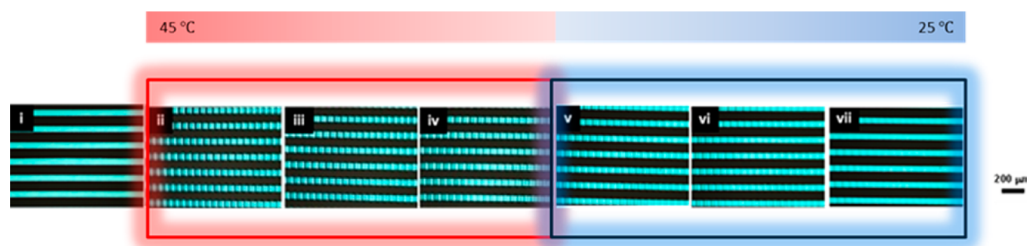


Figure 1. Buckling pattern on silicon ribbons integrated with thermoresponsive PNIPAAm hydrogels: (i) after transfer printing, (ii) 2 min after immersion into hot water (45 °C), (iii) 4 min, (iv) 6 min, (v) 8 min, (vi) 10 min, and (vii) 12 min.

has been investigated with silicon ribbons using a photolithographic method. The controlled morphology of the thin film would eventually enable tunable responses, with the active areas corresponding to the sensors or devices and the inactive areas corresponding to the interconnections between them. Furthermore, an environmentally responsive, integrated bilayer structure with two different types of hydrogel with tunable curvature has been integrated with thin silicon. The varying sensitivity led to a large discrepancy in the swelling ratio in a given solvent, thus resulting in the control of the curvature. Such controlled response, combined with precise silicon bonding to the gel surface, would lead to unique patterned buckling on the thin film when exposed to a given environmental stimulus.

2. METHODOLOGY

2.1. Materials. *N*-Isopropylacrylamide (NIPAAm) and acrylic acid (AA) from Sigma-Aldrich Chemicals were used without further purification. *N,N'*-Methylenebis(acrylamide) (MBAAm), ammonium persulfate (APS), *N,N,N',N'*-tetramethylethylenediamine (TEMED), and tetramethylsilane (TMS) were purchased from Sigma Chemical and used as supplied. A polydimethylsiloxane (PDMS) preparation kit was purchased from Dow Chemicals. Alexa Fluor 488 was purchased from Invitrogen and used for imaging purpose under a confocal microscope.

2.2. Synthesis of the PNIPAAm Hydrogel. The PNIPAAm-based hydrogel was prepared as described previously by Kim et al.²² The synthesis started with mixing 600 mg of NIPAAm with 12.6 mg of MBAAm in 5.354 g of deionized (DI) water and purged with nitrogen in a water bath maintained at 15 °C. Subsequently, 8.9 mg (23 μL) of TEMED and 104 mg (208 μL) of TMS were added and mixed well. After 10 min of degassing, 1084 μL of APS solution (1%) was added to the mixture. After waiting for 3 min, the polymeric solution was then cooled down to and maintained at −18 °C for 24 h. The frozen gel samples were then thawed and immersed in DI water to remove any unpolymerized monomers.

2.3. Preparation of PNIPAAm/PAA Bilayer Hydrogel. 600 mg of NIPAAm was initially mixed with 12.6 mg of MBAAm in 5.354 g of deionized (DI) water. A vortex mixer was used to mix the above solution for 10 min, after which 8.9 mg (23 μL) of the accelerator TEMED was added and mixed. Following 10 min of degassing, 1084 μL of 1% APS aqueous solution (initiator) was added in the mixture. An appropriate amount of the polymer solution was added in a cylindrical mold with dimensions of 16 mm diameter and 20 mm height and then followed with degassing with nitrogen for 15 min so that the polymerization can take place. For the pH-sensitive layer, 600 mg of NIPAAm, 375 μL of AA, and 12.6 mg of MBAAm were added to 5.354 g of DI water. The mixture was agitated well in a vortex mixer for 10 min, after which nitrogen gas was bubbled through it to degas for 20 min. 230 μL of TEMED and 1084 μL of 1% APS aqueous solution were then added to the above mixture. A specific amount of this mixture solution was added on top of the initial PNIPAAm layer which was partially polymerized, after which the mold was kept in an oven at 50 °C for 1 h to allow the polymerization process to complete.

Finally, a bilayer gel structure was obtained with a PNIPAAm top layer and poly(NIPAAm-co-AA) bottom layer.

2.4. Characterization. **2.4.1. Confocal Microscopy.** The structure of the hydrogels was investigated using a Leica SP5-X confocal microscope. Alexa Fluor 488 fluorescent dyes were absorbed by the hydrogels to differentiate between the polymeric network and intermittent pores. An argon laser (488 nm) was used to image these materials.

2.4.2. Environmental Scanning Electron Microscopy. An environmental scanning electron microscope (Philips XL-30 ESEM) was utilized to study the patterned deformation of silicon on the surface of the thermoresponsive gels. The gels were initially immersed in hot water until they shrunk completely and then quenched in liquid nitrogen. The latter procedure was performed to slow the reswelling of the gels and facilitate the imaging under the ESEM.

2.4.3. Rheometry. A rheometer (TA Instruments AR-G2) was employed to perform a strain sweep on the pH-responsive hydrogel and a temperature sweep on the temperature-responsive gel. The pH-sensitive gel samples were first equilibrated in different pH solutions (2, 7, and 11) and then subjected to a strain sweep from 0.001 to 1 at the frequency of 1 Hz.

2.4.4. Differential Scanning Calorimetry. A differential scanning calorimeter (TA Instruments Q-20) was used to characterize the lower critical solution temperature (LCST) of the thermoresponsive hydrogels. First, the dry gels were equilibrated with HPLC water and then analyzed with respect to water as reference. The samples were subjected to cyclic heating and cooling from 10 to 70 °C at 3.00 °C/min.

3. RESULTS AND DISCUSSION

3.1. Controlled Buckling of Silicon Integrated with Thermally Sensitive Hydrogels. As previously reported by Yu et al.,¹⁸ thin silicon ribbons can be successfully integrated with thermoresponsive PNIPAAm hydrogels and respond to temperature (Figure 1). However, the control over the pattern of their response and buckling had not been explored. In order to implement such a control, a photolithography method was employed; such a method had previously shown exciting results using flat elastomeric substrates such as PDMS.^{20,21}

In order to incorporate the aforementioned methodology, the gels had to be further processed with an intermediate PDMS layer. The PDMS and PNIPAAm bulk gel were bonded using TMS via a condensation reaction which has been earlier reported.^{18,19,22} The PDMS served two important purposes. First, it offers a smoother surface for the silicon layer transfer, and second, it provides a waterproof boundary which is essential for the silicon transferring. Subsequently, to generate patterned active and inactive bonding areas, a mask was used and exposed to an UV environment. Upon contact with silicon, the exposed sites would form strong siloxane linkages between silicon and PDMS, while the rest of the parts would only have weak van der Waals interactions.²⁰ Thus, the silicon ribbon would then have intermittent bonding and weak bonding areas

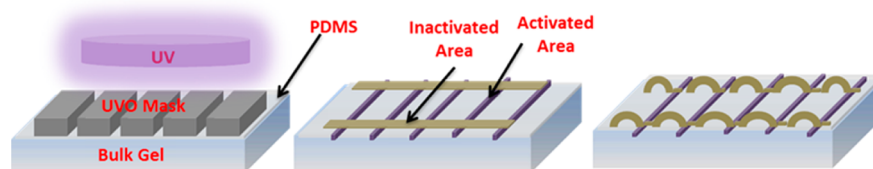


Figure 2. Schematic illustration of the process of integrating thin silicon ribbon (300 nm thick) with PNIPAAm gel: a UVO mask was used to control the buckling pattern.

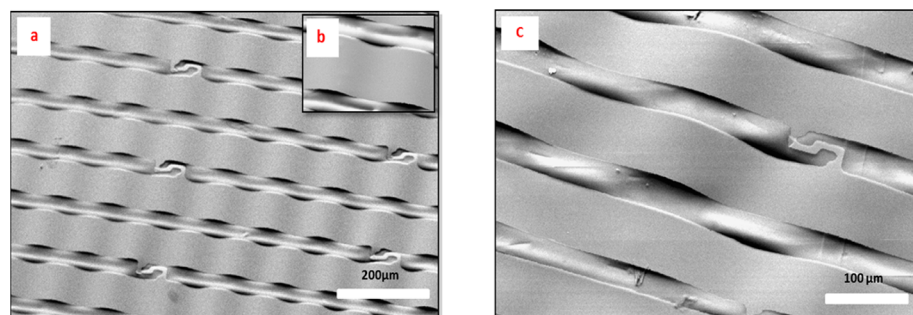


Figure 3. Environmental scanning electron microscopy images of controlled buckling pattern of the integrated silicon on PNIPAAm hydrogel: (a) (mask: 30 μm active–90 μm inactive) wavelength $68.5 \pm 6.3 \mu\text{m}$; (b) close-up image of the pop-up structure; (c) (mask: 30 μm active–190 μm inactive) wavelength $142.6 \pm 6.8 \mu\text{m}$.

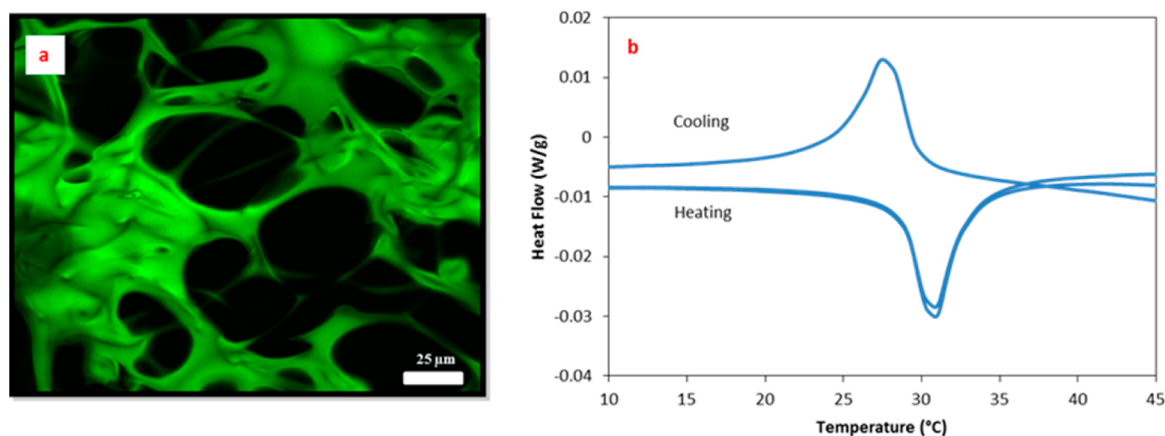


Figure 4. Material characterization of PNIPAAm hydrogel. (a) Confocal image of PNIPAAm gel depicting the macroporous nature with average pore size of 50 μm . (b) DSC capturing LCST behavior of gels and quantifying heat absorption during transition.

with the PDMS surface. Figure 2 describes the process of integrating silicon on hydrogels.

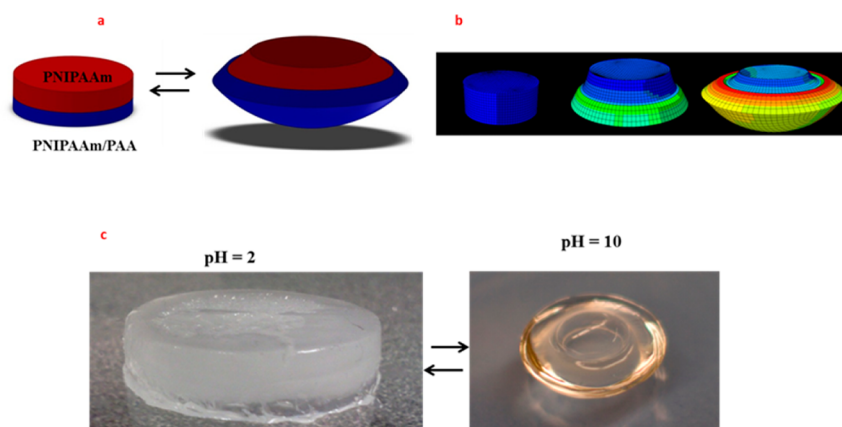
The integrated soft and hard material was then studied under an optical microscope followed by an environmental scanning electron microscope (ESEM). In order to facilitate ESEM imaging, the materials had to be quenched at low temperature using liquid nitrogen after the sample was heated above the lower critical solution temperature (LCST). This was done to maintain the integrity of the silicon pattern formed due to the shrinkage of the gel. The images depicted that under an influence of a thermal stimulus the integrated material can be used to generate different patterns of buckled response. The images were then analyzed using ImageJ, an image analysis software, for measuring the wavelength of the silicon wavelike patterns (Figure 3a–c). Such analysis suggested that the wavelength of the silicon buckles agrees with the equation developed previously in prestrained elastomeric substrates integrated with silicon ribbons, where wavelength = $W_{\text{inactive}} / (1 + \epsilon)$.⁵ Here W_{inactive} is the width of inactive region of the

mask or the part of the silicon not strongly bonded to the PDMS. The ϵ is calculated using $\Delta L/L$, where L is the original one-dimensional length of the hydrogel and ΔL is the linear dimension change resulting from the volume shrinkage under the influence of thermal stimulus. The strain generated was 0.29, which theoretically produced a wavelength of 69.8 μm for the 90 μm inactive mask; this matched very well with the measured mean wavelength of 68.5 μm . Similar results were also obtained for the mask with 190 μm as the inactive region. Thus, the silicon buckling wavelength can be finely tuned by changing different UV masks with different active and inactive regions. This degree of control is desired for effective strain mitigation due to the hydrogel shrinkage without comprising the active sites.

For the above structures to respond to temperature stimulus effectively, it becomes imperative to understand the structure–property relationship. The LCST–volume change phenomenon has been leveraged in the present case; as the dimension changed dramatically during LCST, it resulted in a great

Table 1. Comparison of LCST and Heat Absorption of the Macroporous and Microporous Thermoresponsive PNIPAAm Gels during Heating and Cooling Cycles

macroporous PNIPAAm			microporous PNIPAAm		
LCST	heat absorbed (heating cycle)	heat released (cooling cycle)	LCST	heat absorbed (heating cycle)	heat released (cooling cycle)
31.4 ± 0.42 °C	1.38 ± 0.29 J/g	1.32 ± 0.32 J/g	31.7 ± 0.21 °C	2.29 ± 0.12 J/g	2.19 ± 0.42 J/g

**Figure 5.** Bilayer hydrogels with tunable curvature: (a) pictorial representation of a bilayer hydrogel; (b) finite element modeling of bilayer gels depicting the various stages of swelling; (c) pH responsiveness of the bilayer hydrogel: top layer is the PNIPAAm hydrogel (temperature sensitive), and bottom layer is copolymer of acrylic acid and PNIPAAm hydrogel (pH sensitive).

amount of strain in the system, which was then successfully utilized to drive the onboard silicon ribbons to form distinct patterns. The strain generated would have to be sufficiently large for the silicon to respond and also have a quick reversible nature. When introduced to stimuli, the response time and volume shrinkage of the PNIPAAm gels are largely dependent on the mechanism of uptake and release of solvents by these gels. As previously estimated,²³ the gels with larger than 1 μm pore size would have a faster capillary action dominated solvent uptake and release mechanism. The gels having pore size below this value would have generally a slower uptake mechanism.^{24–28}

In the present case, the thermal response of PNIPAAm is hypothesized as a function of pore size because this would most likely dictate the rate of uptake and release of water. In order to increase the pore size and decrease the response time of the gels, cryogel-type synthesis was implemented.²⁹ In this type of synthesis, the polymeric solution was frozen just after addition of the initiator (APS) to the system. Such rapid cooling produced large crystals of ice inside the polymeric solution, which then served as the backbone for the formation of the polymeric chain. After the process was completed and the gels were thawed, the polymers would intrinsically have a large pore size due to vacancy left by the melted ice which leads to macroporous gels. In order to observe the morphology of the PNIPAAm gels, we incorporated Alexa Fluor 488 dyes and studied using confocal microscopy (Figure 4a). The gels observed had an average pore size of 50 μm (ranging from 10 to 80 μm), determined using ImageJ. This pore size supported the initial hypothesis which suggests that by adopting a polymerization temperature below the freezing point of the solution, the pore size can be modified and made significantly larger than other comparable synthesis techniques.^{30–33}

The thermal response of the hydrogels was quantified using a differential scanning calorimeter (DSC). The DSC results suggested the LCST of the gel to be around 32 °C (Figure 4b). The DSC curves also revealed the reversible nature of the

LCST phenomenon and quantified the energy required during transition. An endothermic peak was observed when the PNIPAAm was heated and an exothermic peak occurred during the cooling cycle. The endothermic peak here corresponds to the amount of energy required for the dissociation of the phases, while the release of energy corresponds to the bond formation during the cooling cycle. Table 1 shows that the macroporous PNIPAAm gel has nearly identical energy during the heating and cooling cycle and confirms the completely reversibility. The glass transition temperature of the dried gel was also measured to be 143.7 ± 2.1 °C by the DSC, which revealed that these materials can be used at high temperature with minimal structural deformation.

3.2. Controlled Environmental Sensitivity of a Bilayer Hydrogel with Tunable Curvature. One of our focuses is to create controlled response of thin film silicon; here we adopt two different hydrogels with distinct properties, for example, with dissimilar swelling ratios and stimulus sensitivity, to design a three-dimensional curved structure. The gels were then integrated with thin silicon ribbons with the assistance of a PDMS intermediate film as discussed in the previous section. However, due to the complexity of the substrate shape, intermediate bonding and nonbonding regions with silicon were not attempted; only simple bonding with silicon was performed as reported previously.¹⁸

In the present work, a copolymer of NIPAAm and acrylic acid was chosen for the bottom layer and a thermosensitive PNIPAAm was chosen for the top layer. The diverse swelling ratio is attributed to the higher hydrophilic nature of acrylic acid, which results in a more drastic swelling ratio in water. In addition, unlike the PNIPAAm hydrogel discussed previously, the PNIPAAm hydrogel here was less sensitive to thermal stimulus and deswelled considerably much less with temperature increase ($\sim 11\%$) compared to thermoresponsive gels in the previous section ($\sim 29\%$). This was done intentionally to prevent delamination of such an integrated bilayer structure due to the high amount of strain created at the gel interface.

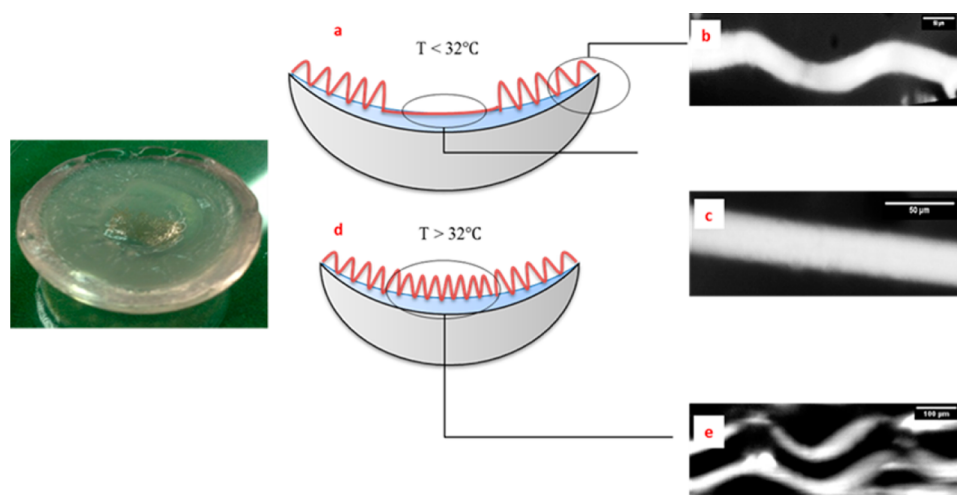


Figure 6. Responsiveness of silicon thin film integrated with bilayer hydrogel: (a) effect of pH (pH = 10); (b) buckling of silicon ribbons at the edges (scale bar 50 μm); (c) flat silicon at the center (scale bar 50 μm); (d) pictorial representation of buckling under influence of temperature; (e) horizontal view of buckling under influence of temperature $>32^\circ\text{C}$ and pH = 10 (scale bar 100 μm).

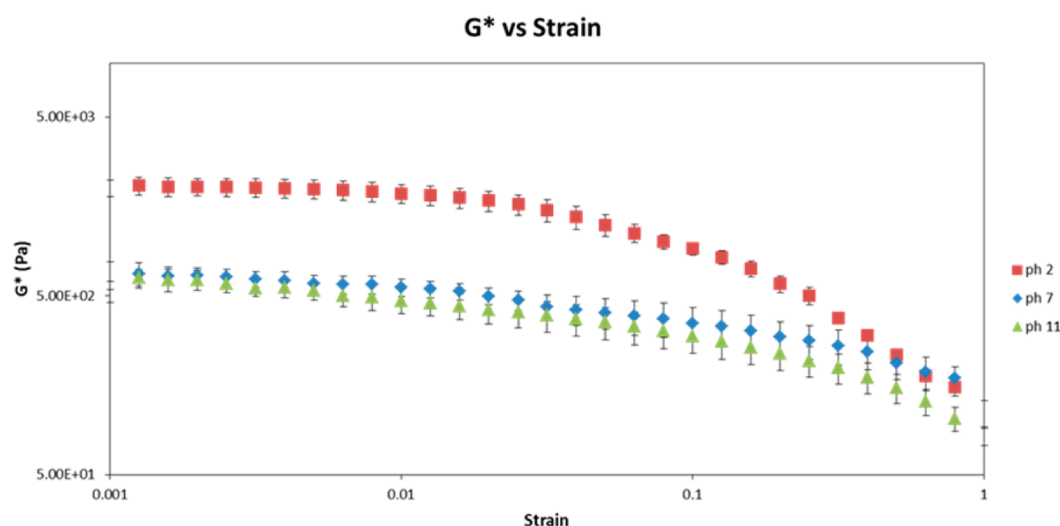


Figure 7. Rheological characterization of bottom layer (pH sensitive): G^* as a function of strain at constant frequency of 1 Hz under different pH conditions.

More importantly, the functionality of the top layer was to provide an appropriate constraint on the higher swelling bottom layer to create a three-dimensional curved structure (Figure 5a,b). Figure 5b is an Abaqus finite element model describing the curvature change of the bilayer substrates in swelled and deswelled states. The model was especially useful for adjusting proportions of layer thickness in order to obtain the desired overall curvature.

The bottom layer behaves as a pH-sensitive hydrogel due to the presence of acrylic acid and can essentially accept and/or donate protons in response to a pH change.^{34–36} At a low pH, the poly(acrylic acid)-*co*-NIPA hydrogels are relatively unswollen since the acidic groups ($-\text{COOH}$) on the gel are protonated and hence neutralized. When the environmental pH is above the pK_a of the ionizable moiety, the pendant acidic groups are deprotonated. As ionization increases, fixed charges are developed on the polymer network, and there is a resultant increase in electrostatic repulsions between the ionized polymer chains, further increasing the swelling. Other than electrostatic

repulsions, a large osmotic swelling force from the presence of ions also increases the uptake of solvent in the network.^{34–37}

The important factor in such an integrated system is that the shrinkage of the bottom layer in acidic pH and the nonresponsiveness of the top layer produce a curved integrated structure to become a function of external stimulus, acidity, or basicity. As the bottom layer shrinks, there is a release of strain, which makes the bilayer structure flatten out (Figure 5c). The above behavior is reversed when the basicity of the surrounding media is increased. Also, the thermoresponsive characteristics of the top layer make the structure responsive to the temperature as well. Interestingly, the bottom layer, a copolymer of PNIPAAm, does not demonstrate any significant thermal responsive behavior. This is because the ionized acrylic acid components convey sufficient solubility to offset the aggregation of the hydrophobic temperature-sensitive components above a specific concentration of acrylic acid.³⁸ This fact ensures that the stimulus response of both the top and the bottom layer remains mutually exclusive, and thus a multifunctional material is obtained.

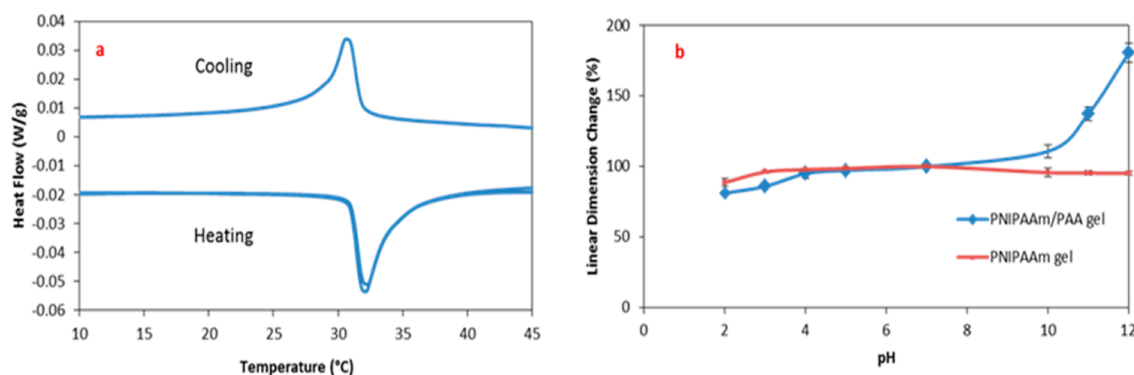


Figure 8. Environmental response of the bilayer hydrogel: (a) DSC capturing LCST behavior of top layer and measuring heat absorption during transition; (b) linear dimension change of bottom and top layer of gels with pH.

These responses generated an interesting pattern, including heterogeneity, with a thin film of silicon integrated on the top of the bilayer hydrogel. As demonstrated in Figure 6a, such an integration would lead to buckled features on the thin film. The temperature and the pH both would cause the silicon to buckle on account of the strain developed; the independent response of both the above stimuli on the integrated structure was studied using an optical microscope. The study revealed that regions at the center of the ribbon did not buckle in presence of basic pH because of the low strain in these regions (Figure 6b,c). However, in response to temperature there was more buckled regions due to the upper layer contracting; this increases the strain on the silicon ribbon and causes more buckled features (Figure 6d,e).

For such integrated structures to respond effectively to an environmental stimulus, we need to understand the material characteristics in detail, especially the thermal and the rheological characteristics. The rheological studies revealed that, under an acidic environment, pH-sensitive gels had a relatively higher storage modulus (G'); the G' decreased with increasing pH while the viscous modulus (G'') increased with increasing pH. Figure 7 demonstrates the complex modulus G^* ($(G'^2 + G''^2)^{1/2}$) decreased with increasing pH over the entire strain range, suggesting that the storage modulus (G') is the more dominant factor in the hydrogel which implies a more solidlike behavior of these gels. The above results are in agreement with the visual observations which suggest that the gels shrink (high complex modulus) in acidic environment and expand (low complex modulus) in a basic environment. Additionally, the G^* revealed the linear viscoelastic region followed by a shear thinning like behavior at higher strain.

As mentioned before, the thermal characterization was performed using a DSC to validate and quantify the transition energy requirement. The PNIPAAm gel here (refer to as microporous gel) demonstrated a similar LCST transition point (Figure 8) as before; however, the heat flow curve of the gel when compared to the previous section was quite different. The macroporous PNIPAAm gels in the first section exhibited much lower heat absorption at the LCST in comparison to the present PNIPAAm gels (Table 1). This may be attributed due to an easier passage of water from the polymeric network gel due to the larger pore size. However, the pore size in the present top layer of PNIPAAm is consciously made low to avoid large swelling ratio at the top which might lead to delamination between the bilayer hydrogels. Glass transition temperatures of the top and bottom layer were measured as 59.8 ± 1.7 and 91.4 ± 0.9 °C, respectively. The glass transition

analysis proved that the gels could be used at moderately high temperatures above room temperature, which would be the desired operating temperature for such materials.

4. CONCLUSION

The present study has demonstrated that environmentally sensitive hydrogels can be successfully integrated with thin-film silicon to obtain responsive, intricately patterned flexible structures using photolithographic methods. The integration provides a means of controlled mechanical buckling of the thin silicon film due to changes in environmental stimuli such as temperature. An approach to create substrates with tunable curvatures was also developed. The bowl-like shape was obtained from a bilayer structure comprising of PNIPAAm hydrogel and a copolymer hydrogel made from *N*-isopropylacrylamide (NIPA) and acrylic acid (AA). Such substrates were integrated with thin-film silicon, and their buckling phenomenon was studied, which revealed the reversible nature of both the gels and the buckling pattern of the silicon on the top layer. In addition to their mechanical properties, the stimuli response of the system in both temperature and pH was also investigated. The use of diverse environmentally responsive substrates could have broader impacts on numerous applications, especially in the field of adaptable electronics (e.g., flexible sensors, high-performance bioinspired systems, etc.).

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Notes

The authors declare no competing financial interest.

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