

Claims:

1. A method comprising:

providing to a chamber a high aspect ratio (HAR) structure having a stimulus responsive polymer (SRP) in a high aspect ratio gap formed between features of the HAR structure, the high aspect ratio gap having a total thickness T_{total} ; and

performing one or more cycles of removing the SRP from the gap comprising, each cycle comprising:
 - (a) pulsing a first reactant to the chamber such that the first reactant diffuses into the gap only to a depth less than T_{total} ;
 - (b) after (a), purging the chamber,
 - (c) after (b), pulsing a second reactant to the chamber such that the second reactant diffuses into the gap only to a depth less than T_{total} ;
 - (d) reacting the first reactant and the second reactant to form a compound that degrades the SRP;
 - (e) degrading a thickness of SRP that is less than T_{total} ; and
 - (f) removing the degraded SRP.
2. The method of claim 1, wherein the SRP comprises a poly(phthalaldehyde) or a derivative thereof as a homopolymer or as one of the polymers of a copolymer.
3. The method of claim 1, wherein the SRP comprises a poly(aldehyde) or a derivative thereof as a homopolymer or as one of the polymers of a copolymer.
4. The method of any of the above claims, wherein the first or second reactant is water vapor.
5. The method of claim 4, wherein the other of the first or second reactant is a gaseous oxide that reacts with the water vapor to an acidic or basic species.
6. The method of claim 5, wherein the gaseous oxide is nitrogen dioxide.
7. The method of claim 5, wherein the gaseous oxide is sulfur dioxide.
8. The method of claim 5, wherein the gaseous oxide is carbon dioxide.

9. The method of claim 4, wherein the other of the first or second reactant is ammonia.
10. The method of any of the above claims, wherein a target diffusion depth in (a) and (c) is the same.
11. The method of any of claims 1-9, wherein a target diffusion depth in (a) and (c) is different.
- 5 12. The method of any of the above claims, wherein the reaction in (d) is uncatalyzed.
13. The method of any of claims 1-3, wherein the compound is an acid or base.
14. A method comprising:
 - providing to a chamber a high aspect ratio (HAR) structure having a stimulus responsive polymer (SRP) in a high aspect ratio gap formed between features of the HAR structure, the SRP film having a
 - 10 total thickness T_{total} ; and
 - performing one or more cycles of removing the SRP from the gap comprising, each cycle comprising:
 - (a) pulsing first reactant to the chamber such that the first reactant diffuses into the gap to a depth $D_{\text{first reactant}}$,
 - 15 (b) after (a), purging the chamber,
 - (c) after (b), pulsing a second reactant to the chamber such that the second reactant diffuses into the gap only to a depth $D_{\text{second reactant}}$, wherein $D_{\text{second reactant}}$ is less than $D_{\text{first reactant}}$,
 - (d) reacting the first reactant and the second reactant to form a compound that degrades the SRP;
 - 20 (e) degrading the SRP to a depth $D_{\text{second reactant}}$; and
 - (f) removing the degraded SRP.
15. The method of claim 13, wherein the SRP comprises a poly(phthalaldehyde) or a derivative thereof as a homopolymer or as one of the polymers of a copolymer.
16. The method of claim 13, wherein the SRP comprises a poly(aldehyde) or a derivative thereof as
 - 25 a homopolymer or as one of the polymers of a copolymer.
17. The method of any of claims 13-15, wherein the first or second reactant is water vapor.

18. The method of claim 16, the other of the first or second reactant is a gaseous oxide that reacts with the water vapor to an acidic or basic species.
19. The method of claim 17, wherein the gaseous oxide is nitrogen dioxide.
20. The method of claim 17, wherein the gaseous oxide is sulfur dioxide.
- 5 21. The method of claim 17, wherein the gaseous oxide is carbon dioxide.
22. The method of claim 17, wherein the other of the first or second reactant is ammonia.
23. The method of any of claims 13–21, wherein $D_{\text{first reactant}}$ is equal to T_{total} such that the first reactant is diffused through the total thickness of the SRP film in a single cycle.
24. The method of any of claims 13–21, $D_{\text{first reactant}}$ is less than T_{total} and multiple cycles are
10 performed.
25. The method of any of claims 13–23, wherein the reaction in (d) is uncatalyzed.
26. The method of any of claims 13–15, wherein the compound is one of sulfurous acid, nitric acid, carbonic acid, and ammonium hydroxide.
27. A method comprising:
- 15 providing a substrate having a stimulus responsive polymer (SRP) thereon;
performing multiple removal cycles, each cycle comprising:
exposing only a top portion of the SRP to a compound capable of degrading the SRP to thereby degrade the top portion of the SRP; and
removing only the top portion of the SRP.
- 20 28. The method of claim 26, wherein the SRP is provided without a catalyst.
29. The method of claim 26 or 27, wherein exposing the top portion of the SRP to a compound comprises pulsing the compound in vapor phase into a chamber housing the substrate.
30. The method of claim 28, wherein the compound is one of hydrogen bromide (HBr), hydrogen chloride (HCl), hydrogen fluoride (HF), hydrogen iodide (HI), nitric acid (HNO₃), formic acid (CH₂O₂),
25 acetic acid (CH₃COOH), formonitrile (HCN), or ammonia (NH₃), and an alkyl amine gas.

31. The method of any of claims 26–29, wherein exposing the top portion of the SRP comprises sequential pulsing of a first reactant and a second reactant, wherein the first reactant and the second reactant react to form the compound.
32. The method of claim 30, wherein the first reactant and second reactant react in the top portion
5 of the SRP film.
33. The method of any of claims 26 and 27, wherein exposing the top portion of the SRP comprises a first pulse of a first reactant followed by multiple sequential pulses of a second reactant, wherein the first reactant and the second reactant react to form the compound.
34. The method of any of claims 30–32 wherein sequential pulses are separated by inert gas purges.
- 10 35. The method of any of claims 26–33, wherein the SRP comprises a poly(phthalaldehyde) or a derivative thereof as a homopolymer or as one of the polymers of a copolymer.
36. The method of any of claims 26–34, wherein the SRP comprises a poly(aldehyde) or a derivative thereof as a homopolymer or as one of the polymers of a copolymer.
37. The method of any of claims 26–35, wherein the SRP is provided between features of high
15 aspect ratio (HAR) structures.
38. The method of any of claims 26–35, wherein the SRP is provided as a protective coating on substrate.