Area-selective atomic layer deposition using polymer growth inhibition layers: a case study for metal-oxides and noble metals

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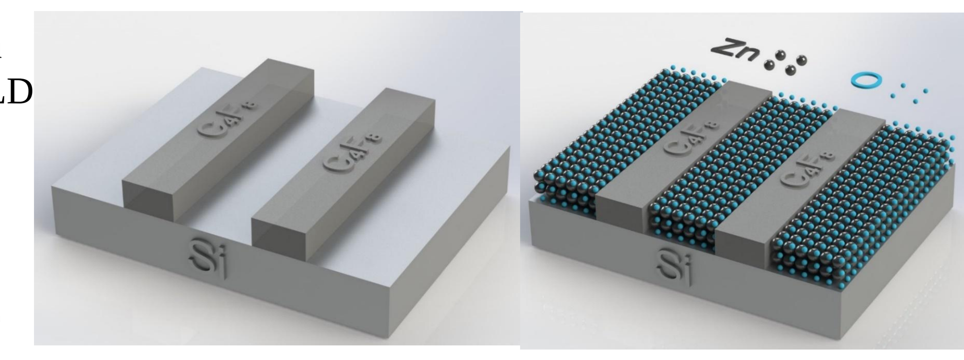
Area selective ALD (AS-ALD) of metal oxides using plasma polymerized CF_x growth inhibition layer: Motivation

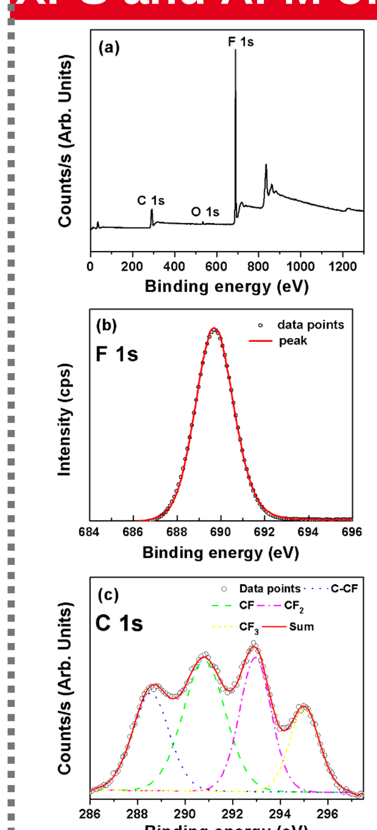
- Fast and conformal deposition of the CF_x layer (~30-35 nm of CF_x layer is grown within a minute)
- As the growth of CF_x blocking layer is performed in a vacuum reactor, it allows for easy integration with ALD reactors.
- A relative easy control over thickness of CF_x layer would possibly solve the issue of lateral broadening
- Possibility to achieve topographical selectivity due to relatively conformal growth of CF_x inorder to achieve patterning on 3d nanostructures
- CF_x layer can withstand ozone to a certain extent (possibility to demonstrate AS-ALD of materials grown via ozone based processes)



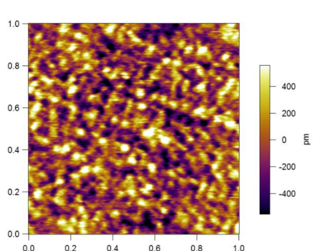
Experimental

- Deposition of fluorocarbon was performed for 70 s using C_4F_8 gas flow rate of 70 sccm in inductively couple plasma deep reactive ion etching reactor (plasma power = 400 W)
- Precursors: Et_2Zn and water, $Al(CH_3)_3$ and water, $Hf(NMe_2)_4$ and water, Tetrakis(dimethylamido)titanium (TDMAT) and H_2O, $MeCpPtMe_3$ and ozone precursors, Palladium(II)hexafluoroacetylacetonate (Pd hfaa) and Formaldehyde precursors

XPS and AFM of CF_x layer

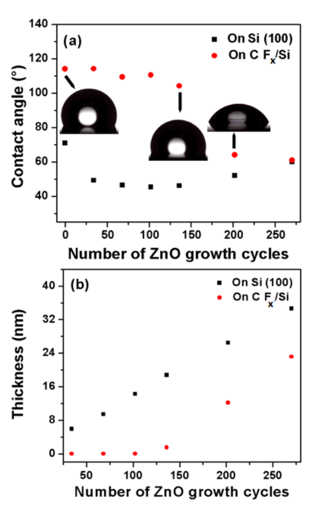


(a) XPS survey scan obtained from a ~32 nm thick plasma polymerized fluorocarbon thin film deposited on Si(100). High resolution XPS scans of (b) F 1s and (c) C 1s obtained from the same film.

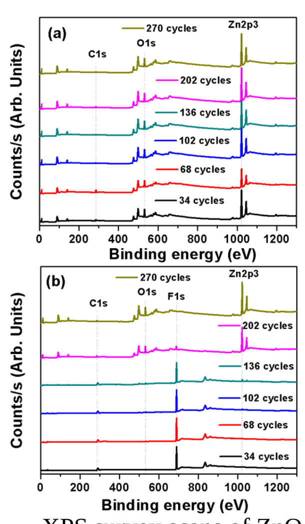


AFM image obtained from ~32 nm thick plasma polymerized fluorocarbon thin film

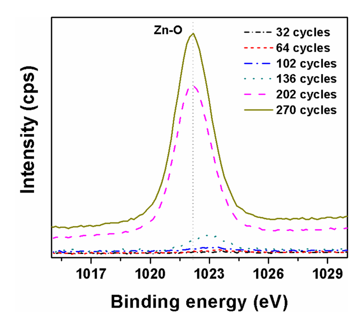
ZnO growth selectivity on CF_x surfaces



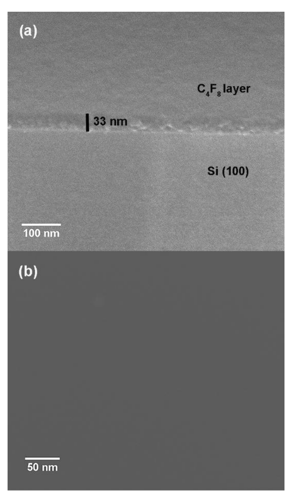
Variation in contact angle (a) and thickness (b) of ZnO with the increase in number of growth cycles on Si (100) and CF_x/Si.



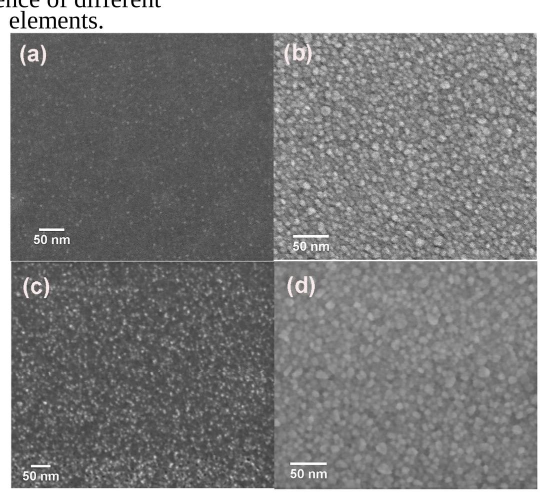
XPS survey scans of ZnO grown with different number of ALD cycles on (a) Si(100) and (b) CF_x/Si(100) revealing presence of different elements.



HR-XPS scans of Zn $2p_{3/2}$ obtained from ZnO grown on fluorocarbon/Si as a function of ALD growth cycles.



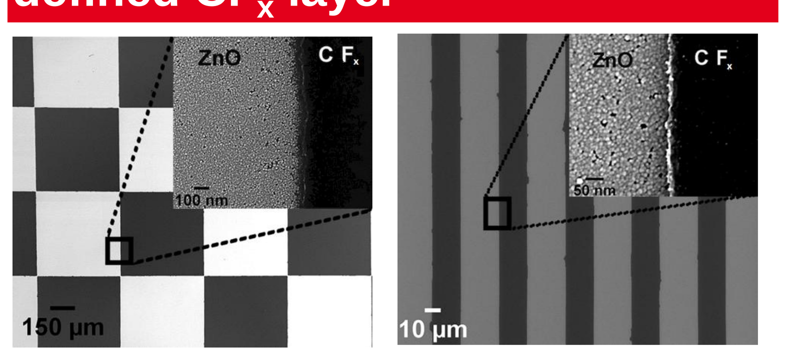
SEM images of (a) bare CF_x/Si sample, (b) ZnO coated on CF_x/Si sample with 68 number of growth cycles



Plane view SEM images of 102 cycles ALD grown ZnO on (a) CF_x/Si and (b) Si (100); 136 cycles ALD grown ZnO on (c) CF_x/Si and (d) Si (100).

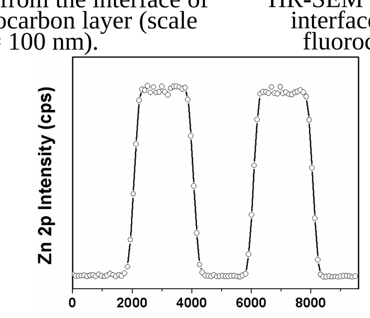
XPS, SEM, contact angle, and ellipsometer measurement's cumulatively confirm that ZnO growth is inhibited on CF_x surfaces upto 136 growth cycles which corresponds to a thickness of 20 nm on Si surfaces.

ZnO patterning on lithography defined CF_x layer



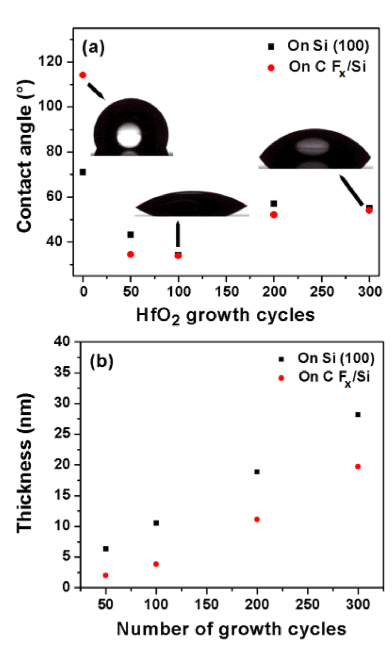
Plan-view SEM image of 102 cycle ZnO ALD grown on fluorocarbon checker board patterns (inset) HRSEM image from the interface of ZnO and fluorocarbon layer (scale bar = 100 nm).

Plan-view SEM image of 102 cycle ZnO ALD grown on fluorocarbon line patterns (inset) HR-SEM image from the interface of ZnO and fluorocarbon layer

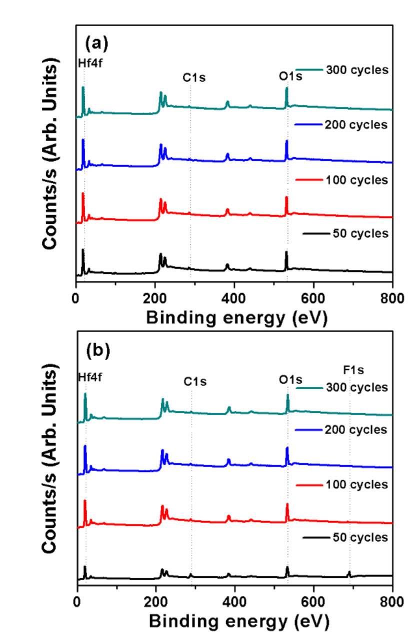


XPS line scan obtained from patterned ZnO substrate.

HfO_2 growth selectivity on CF_x surfaces



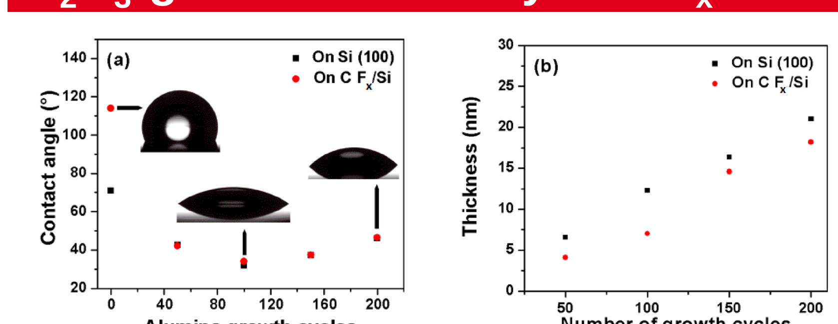
Variation in (a) contact angle and (b) thickness of HfO_2 as a function of ALD growth cycles on Si(100) and CF_x/Si.



XPS survey scans of HfO_2 grown with different number of growth cycles on (a) Si (100) and (b) CF_x/Si revealing presence of different elements.

XPS, contact angle, and ellipsometer measurement's reveal that HfO_2 nucleation is relatively slow on CF_x surface during initial growth cycles.

Al_2O_3 growth selectivity on CF_x surfaces



Variation in (a) contact angle and (b) thickness of Al_2O_3 with the increase in number of growth cycles on Si(100) and CF_x/Si.

Contact angle, and ellipsometer measurement's reveal that CF_x surface is ineffective in blocking Al_2O_3 growth.

Summary

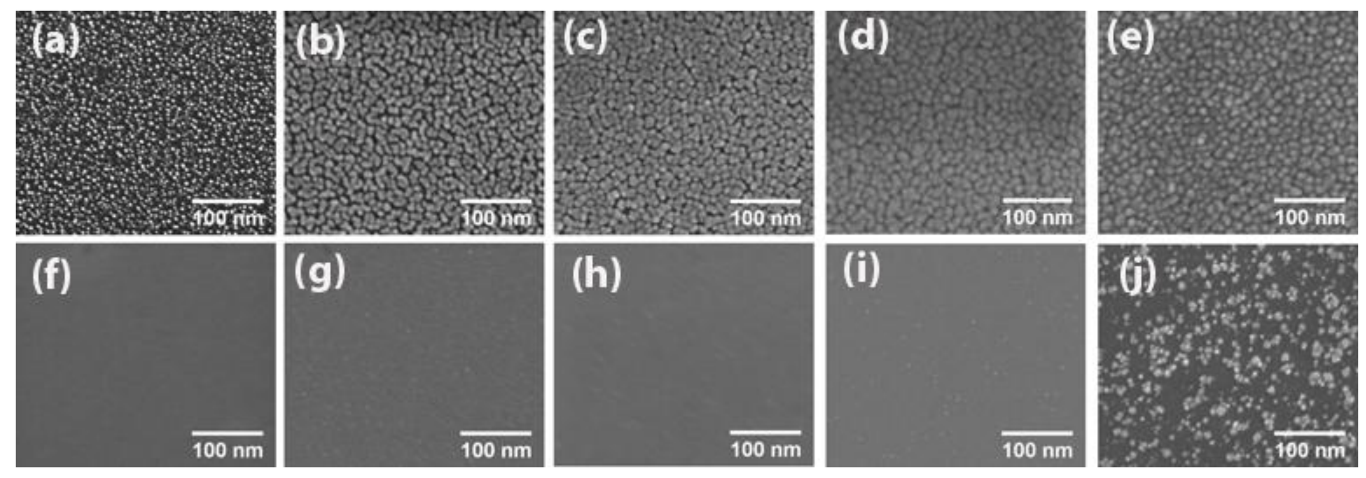
- Investigation of area selective ALD (AS-ALD) of metal oxides using inductively couple plasma grown CF_x polymer film as a model hydrophobic growth inhibition layer.
- ZnO patterning using AS-ALD on lithography defined CF_x patterned Si.
- Use of polymers including poly(methyl methacrylate) (PMMA), polyvinylpyrrolidone (PVP), and octafluorocyclobutane (C_4F_8) for area selective atomic layer deposition (AS-ALD) of TiO_2.
- Patterning of TiO_2 using a PMMA masking layer that has been patterned using e-beam lithography.
- AS-ALD of Pt and Pd metals using inductively couple plasma grown CF_x polymer growth inhibition layer
- Pd patterning using AS-ALD on lithography defined CF_x patterned Si.

References

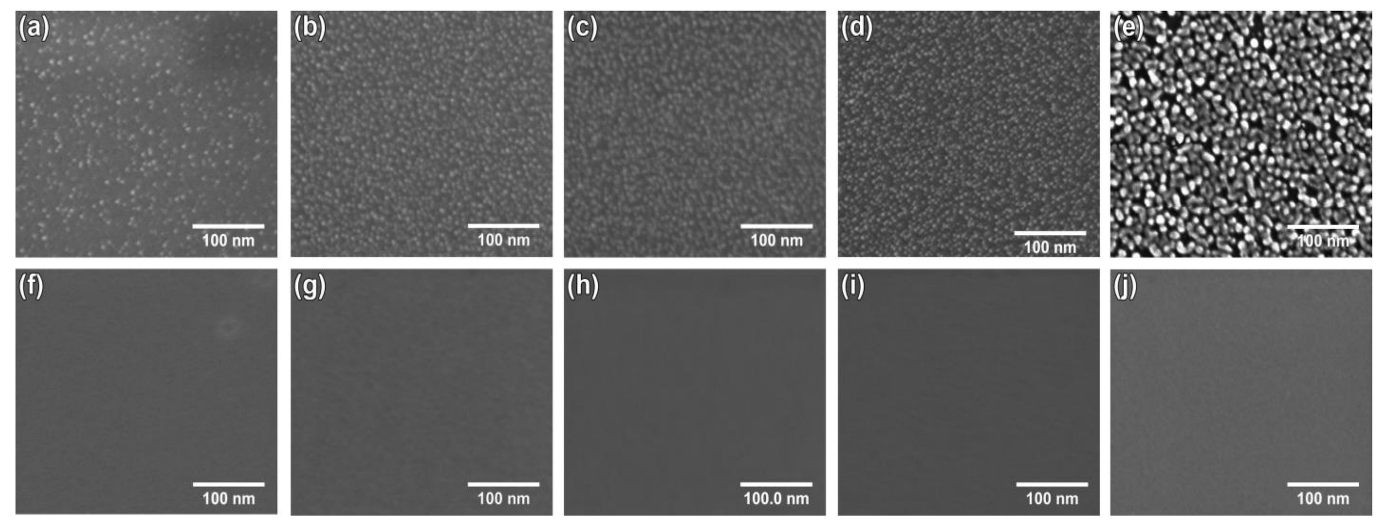
Haider et al, Journal of physical chemistry ©, 120, 26393 (2016).

Haider et al, RSC advances, 6, 106109 (2016).

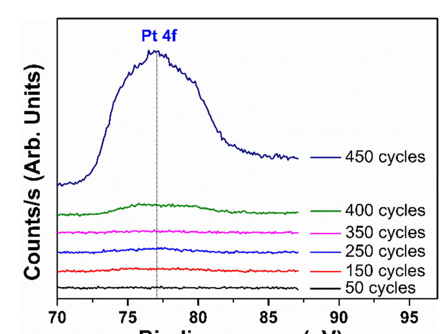
Area selective ALD of Pt (Ozone based process) and Pd using plasma polymerized CF_x growth inhibition layer



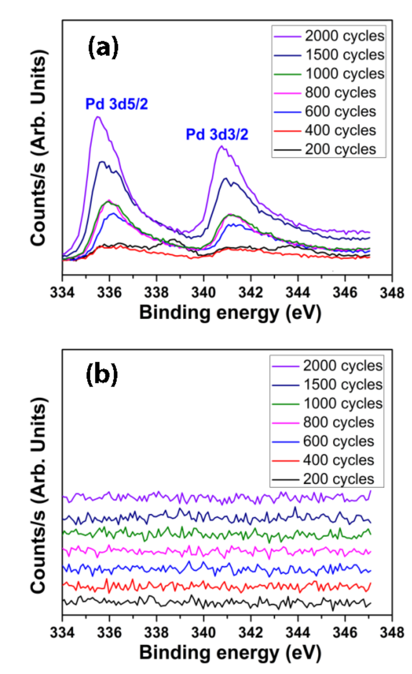
SEM images of Pt nanoparticles on Si (a-e) and flourocarbons (f-j) substrates with different Pt ALD cycles (a, f) 50 cycles (b, g) 150 cycles (c, h) 250 cycles (d, i) 350 cycles and (e, j) 450 cycles.



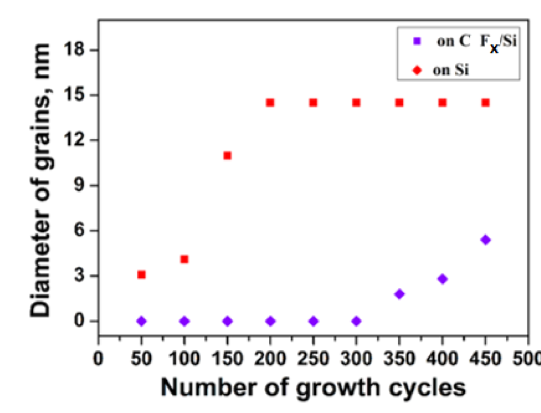
SEM images of Pd nanoparticles on Si (a-e) and flourocarbons (f-j) substrates with different Pd ALD cycles (a, f) 200 cycles (b, g) 600 cycles (c, h) 1000 cycles (d, i) 1500 cycles and (e, j) 2000 cycles.



XPS high resolution scans of Pt grown with different number of ALD cycles on CF_x surfaces, confirming effective inhibition/blocking of Pt on CF_x surface up to 350 growth cycles.

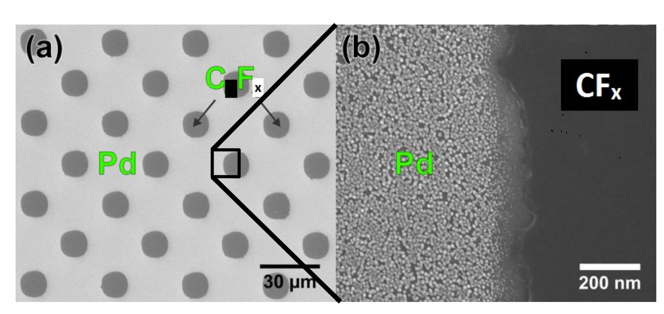


HR-XPS survey scans of Pd 3d obtained from Pd at different stages of ALD-growth on (a) Si(100) and (b) CF_x/Si(100).

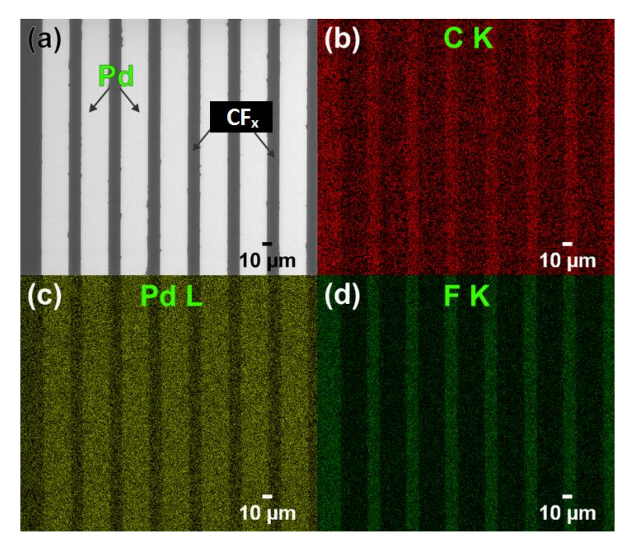


Variation in grain size of Pt with increase in number of growth cycles on Si and CF_x surfaces

Pd patterning on lithography defined CF_x layer

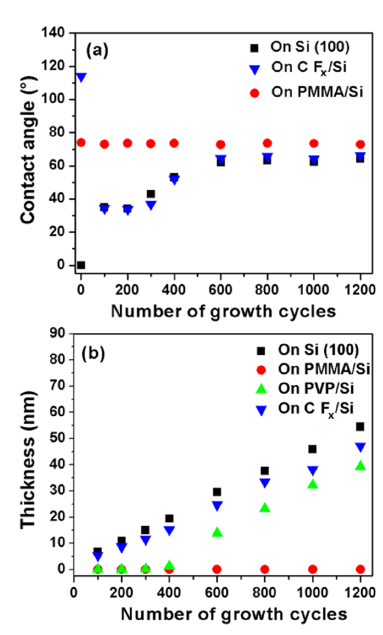


SEM and HR-SEM images after 2000 cycles of Pd ALD obtained from the coated and uncoated CF_x regions. Patterned CF_x-Pd interfaces at microscale (a) and nanoscale (b).

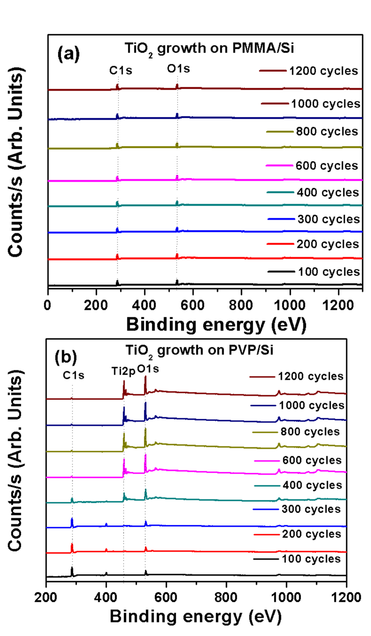


(a) SEM image of Pd pattern, (b) C K EDX elemental map, (c) Pd L EDX elemental map (d) F K EDX elemental map.

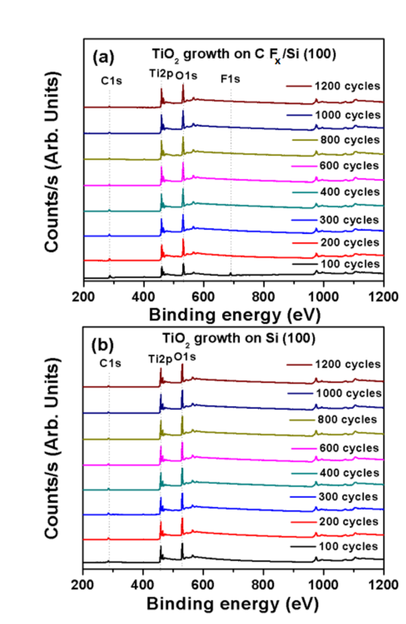
AS-ALD of TiO_2 using e-beam patterned growth inhibition polymers



Variation in contact angle (a) and thickness (b) of TiO_2 with the increase in number of growth cycles on Si (100), PMMA, PVP, and CF_x/Si.

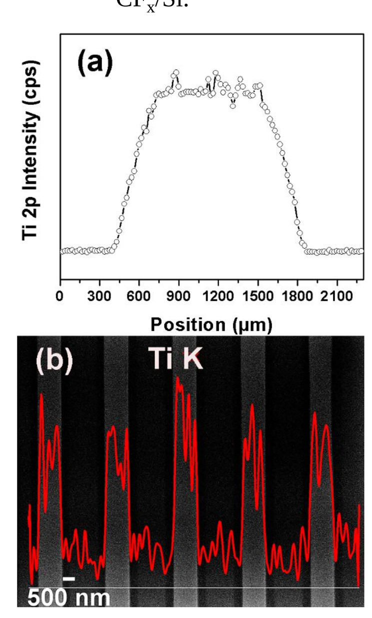


XPS survey scans of TiO_2 grown with different number of growth cycles on (a) PMMA and (b) PVP surface revealing presence of different elements.

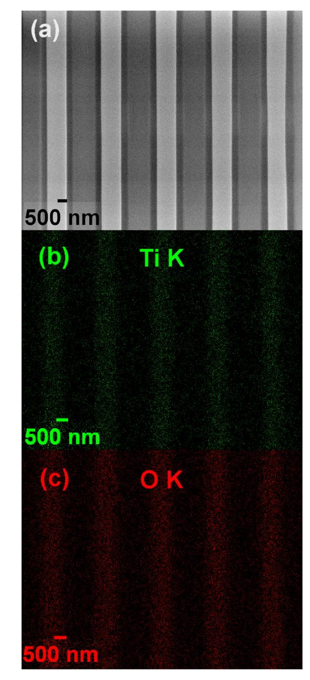


XPS survey scans of TiO_2 grown with different number of growth cycles on (a) CF_x/Siand (b) Si (100) revealing presence of different elements.

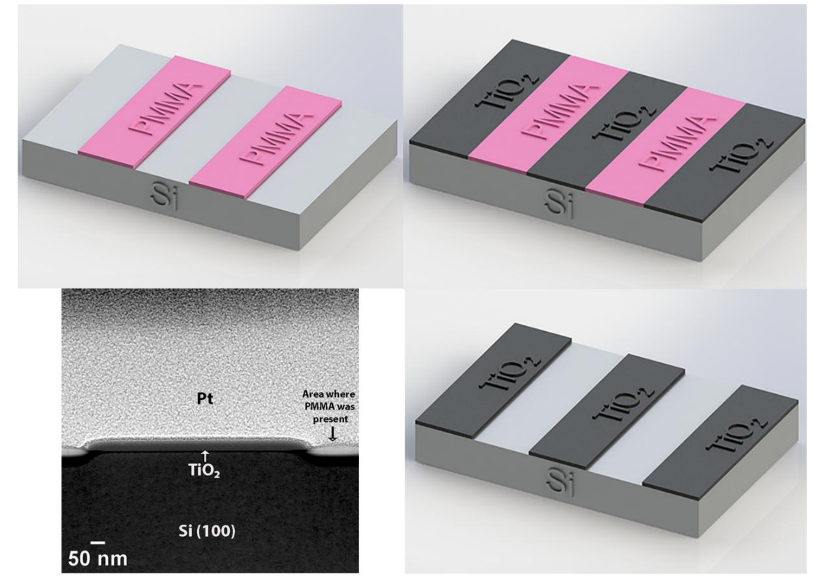
(i) PMMA successfully blocks/inhibits the TiO_2 deposition for at least 1200 growth cycles, which is equivalent to a blocking film thickness of 55 nm
(ii) PVP blocks TiO_2 growth up to 300 ALD cycles and further increase in growth cycles eventually leads to nucleation of TiO_2 on PVP,
(iii) CF_x is unable to inhibit TiO_2 nucleation and growth, despite its higher initial contact angle.



(a) XPS Ti2p line scan obtained from mm big TiO_2 pattern placed on Si (100), (b) EDX Ti K line scan obtained from nm scale TiO_2 line features.



(a) SEM image of TiO_2 pattern, (b) Ti K EDX elemental map, (c) O K EDX elemental map.



Self aligned nano patterning of TiO_2 using area selective atomic layer deposition