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Chemistry of Titanium Deposition Precursors for Area-Selective Deposition of Functionalized Silicon

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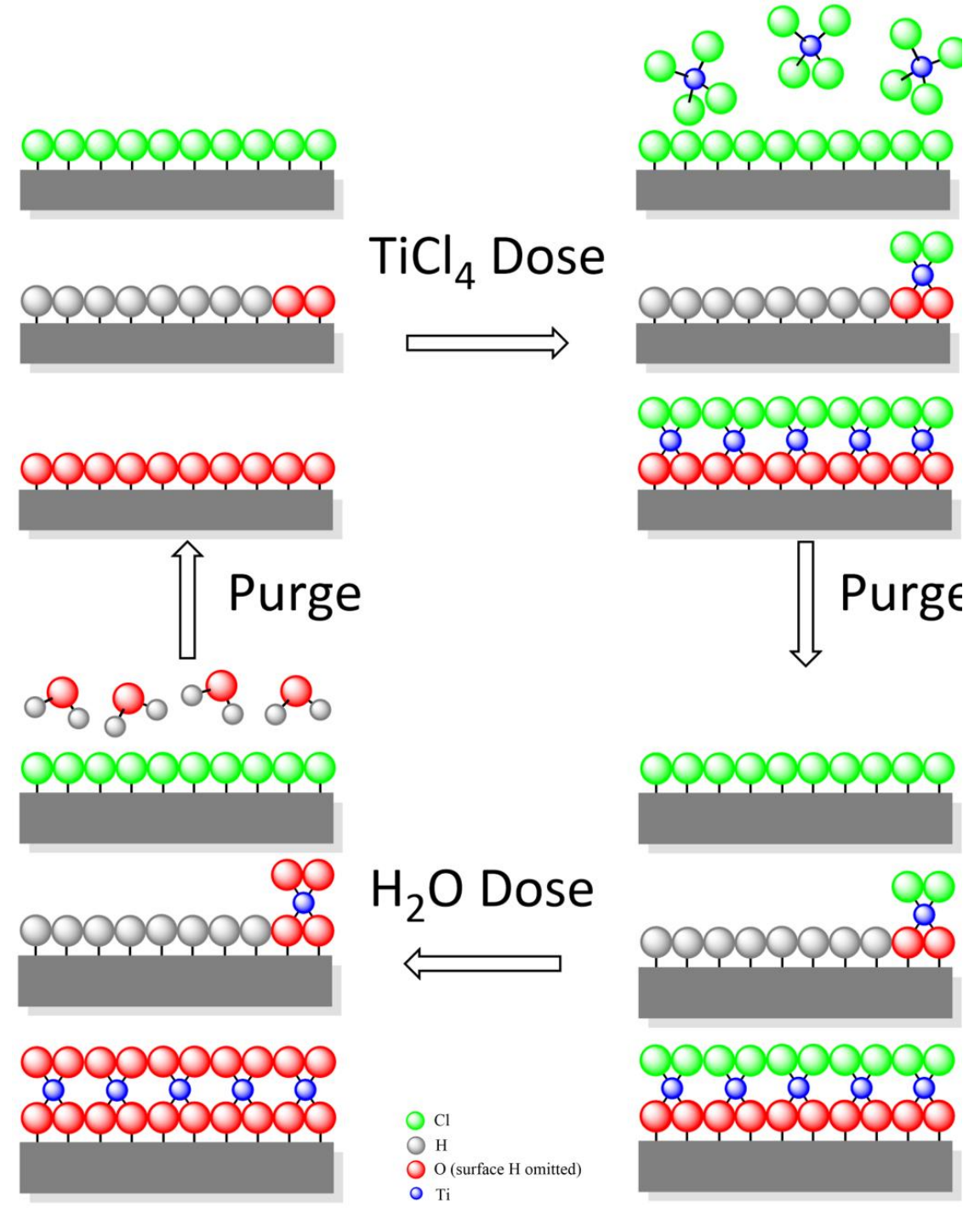
Introduction

Area-selective atomic layer deposition (AS-ALD) is an appealing bottom-up fabrication technique that can produce atomic-scale device features, overcoming challenges in current industrial techniques such as edge alignment errors[1] $TiCl_4$ is a common thermal ALD precursor for TiO_2 thin films, which are appealing candidates for DRAM capacitors due to their excellent dielectric constant[2].

Hydrogen and chlorine termination passivate the Si surface, allowing for selective deposition of $TiCl_4$ onto HO-terminated areas. However, selectivity loss occurs after several ALD cycles. Ti oxide nucleates onto surface defects on Cl- and H-Si resists. Previously, the use of H-Si as an ALD resist has been studied extensively[3], but less work has focused on chemical forces driving nucleation, especially for Cl-Si[4].

Here, formation of defect nuclei was investigated with selectivity loss during TiO_2 ALD with $TiCl_4$ and water on the (100) and (111) crystal surfaces of hydrogenated, chlorinated, and oxidized Si.



Experimental

ALD was performed on solution-prepared H-, HO-, and Cl-Si(100) and Si(111) samples for 5 and 10 cycles. Alternating doses of $TiCl_4$ and H_2O were delivered at ~100 °C in medium vacuum.

Si_xH_y clusters representing two dimers of Si(100) with each surface termination were used to model $TiCl_{4/3}$ adsorption and surface reaction on local surface structures using DFT*. Results on simplistic clusters were largely consistent with ongoing investigations of adsorption on larger structures. Adsorption energy was calculated

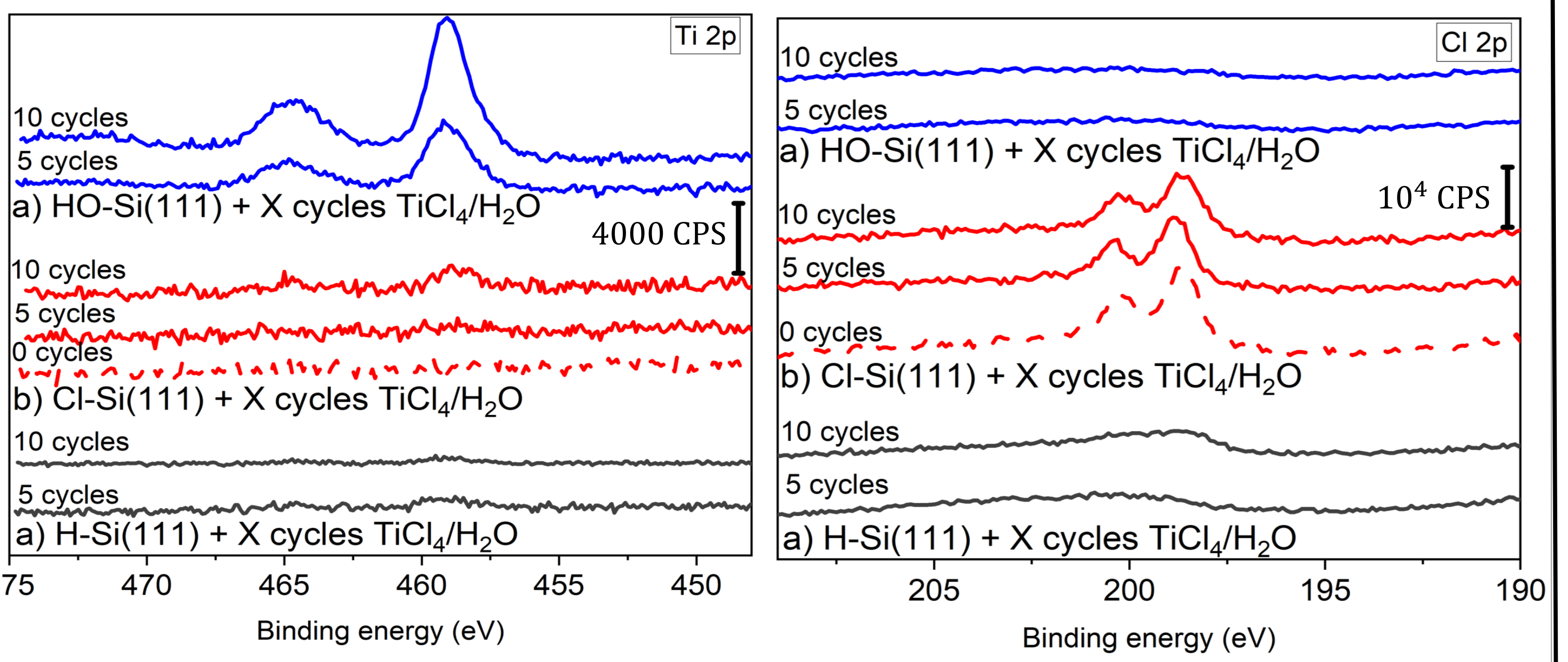
$$\Delta E_{ads} = E(TiCl_x) + (4-x)*E(byproduct) - E(TiCl_4) - E(Cluster)$$

Where x ≡ number Cl ligands removed *Byproduct* ≡ HCl or Cl_2 formed by Cl ligand on $TiCl_4$ and surface-bound H or Cl

*Clusters optimized at B3LYP/6-311G+dp with Grimme D3 dispersion correction, subsurface atomic positions fixed

X-ray Photoelectron Spectroscopy (XPS)

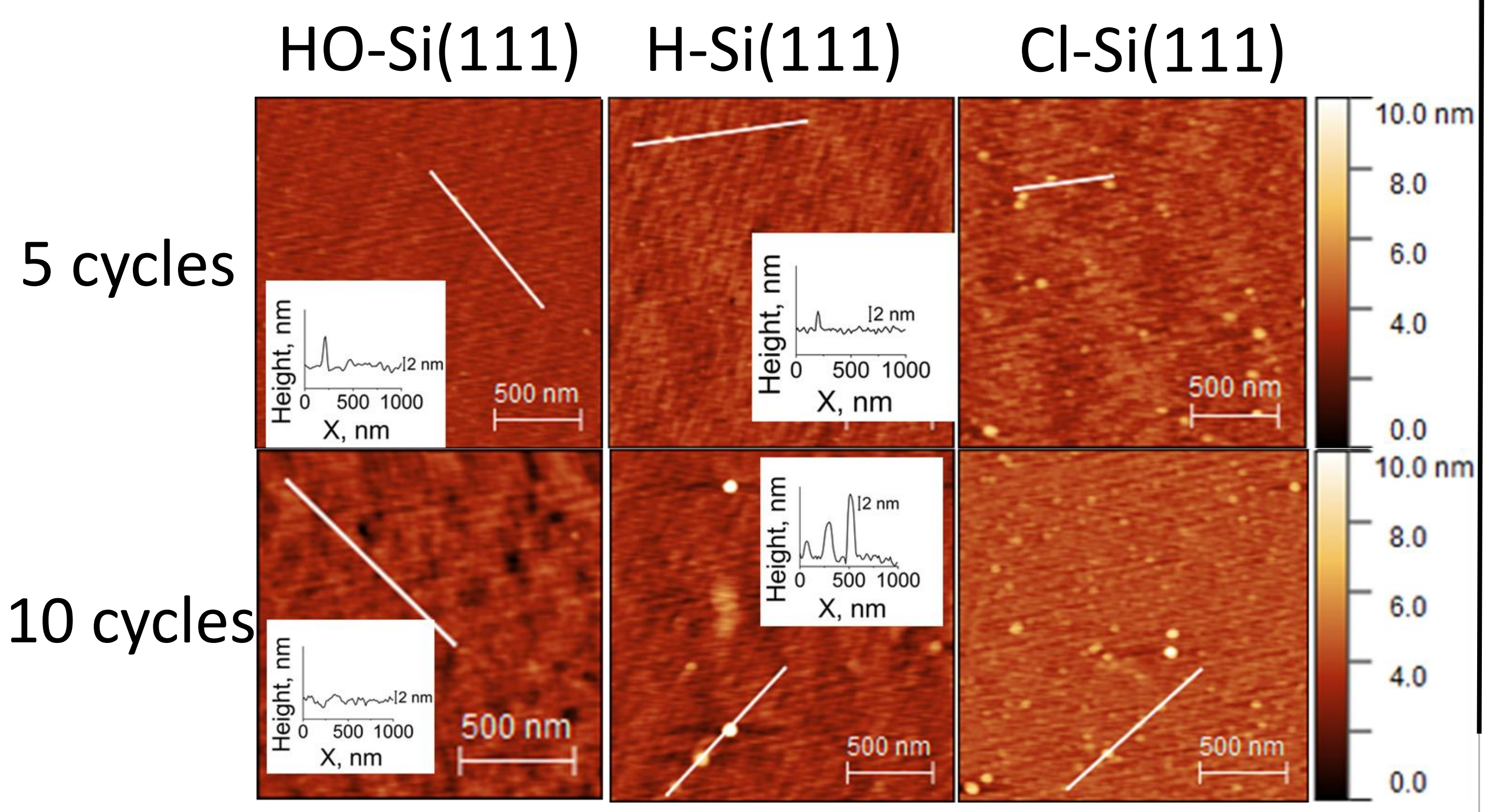
After 5 cycles, $TiCl_4$ deposits readily onto HO-Si, minimally on H-Si, and not at all on Cl-Si, showing high selectivity.



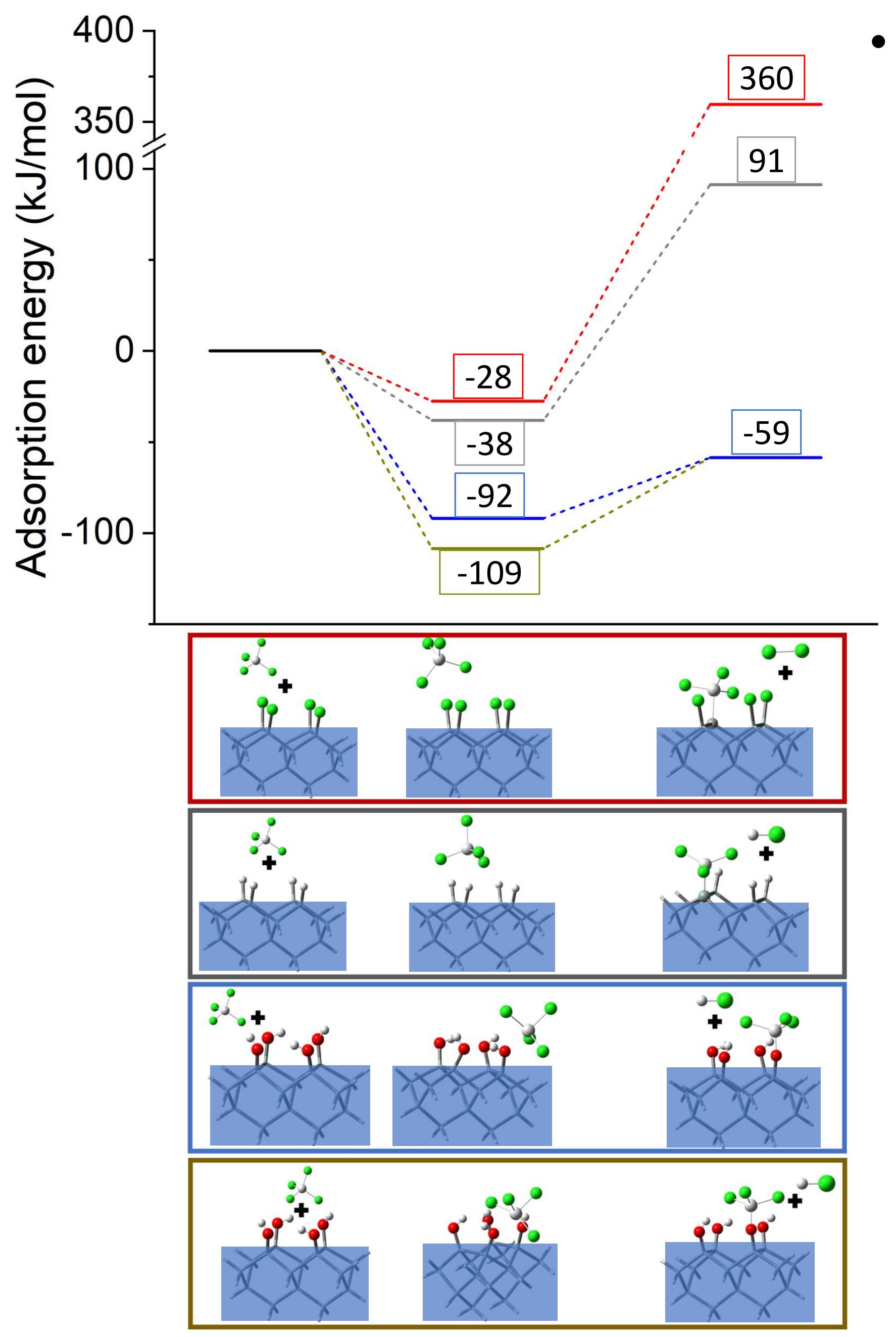
After 10 cycles, some selectivity is lost on H- and Cl-Si resists. Nucleation is likely due to oxidation-induced defects. Current work is focused on angle-resolved XPS to compare morphology of TiO_2 deposited on HO-Si(111) and on defects in H- and Cl-(111).

Atomic Force Microscopy (AFM)

- No emergence of new features on HO-Si(111) suggests $TiCl_4$ reacted over entire surface, forming a continuous film
- Reaction Cl- and H-Si occurred only on small number of nanoparticles
  - Likely due to $TiCl_4$ reaction on hydroxyl defect sites
  - Deposition on H-Si clustered on fewer, already existing nuclei, forming taller particles
  - Deposition on Cl-Si is more widely distributed, introducing new defects
  - Difference in nucleation possibly due to different types of defects present on Cl-Si and H-Si



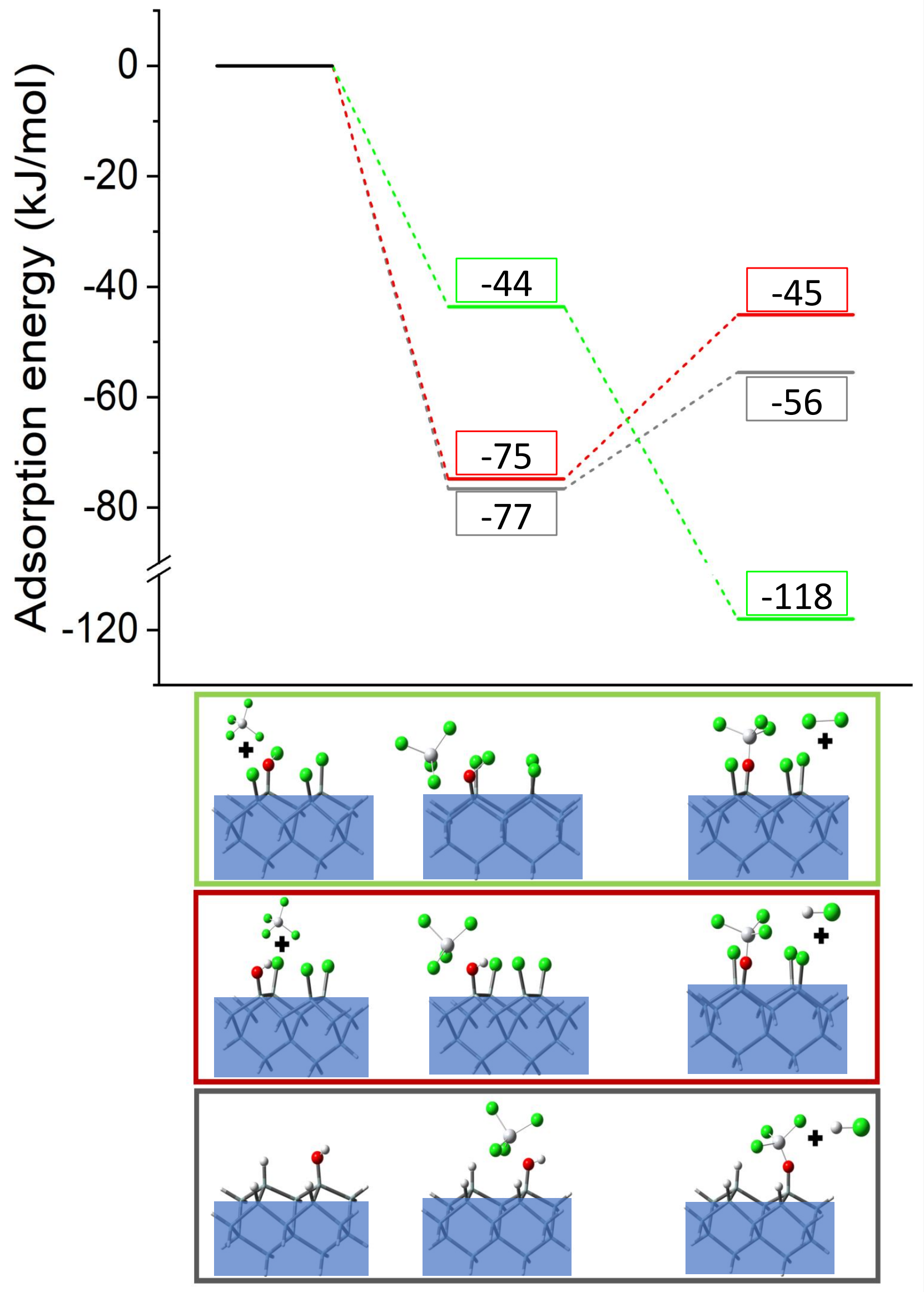
Density Functional Theory (DFT)



- $TiCl_4$ adsorbs strongly to HO-Si(100) clusters, weakly on Cl-Si, H-Si
- Surface reactions producing surface-bound $TiCl_3$ consistent with CRC bond dissociation energies[4], following the reaction

$$(\mathrm{Ti-Cl}) + (\mathrm{Cl-Si}) \rightarrow (\mathrm{Ti-Si}) + (\mathrm{Cl-Cl})$$

- Distorted $TiCl_4$ geometry on HO sites suggests reactivity due to strong O-Ti interaction
  - May adsorb in trigonal bipyramidal geometry on single HO site or octahedral between to HO sites
- HO/OCl defects increase adsorption exothermicity on Cl-Si and H-Si.
  - Multiple HO defects results in additional stabilization
- Larger computations show hydroxyl defect is unstable on dichloride-terminated Si(100),
  - Ongoing computations investigating reactivity of more likely OCl defects on dichloride structures



Conclusions

$TiCl_4$ was shown by XPS to selectively deposit onto HO-Si, with minimal deposition on chlorinated or hydrogenated resists after 5 $TiCl_4$ ALD cycles. Some selectivity loss occurred by 10 cycles. AFM showed selectivity loss was due to formation of defect nanoparticles - clustered on fewer, higher particles for H-Si and dispersed among shorter, more numerous particles for Cl-Si.

DFT modeling of Si clusters identified hydroxide and chloroxide sites as drivers of adsorption on hydroxylated Si(100) surfaces and on chlorinated and hydrogenated Si(100) defects.

Ongoing work is focused on investigating adsorption on larger representative models, with dichloride and dihydride sites, with chloroxide defect sites, and with multiple hydroxide sites.

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