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Monatomic and Cluster Argon Ion XPS Depth Profiling of $SrTiO_3$ and HfO_2

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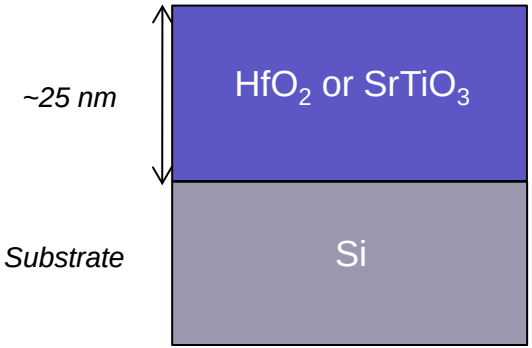
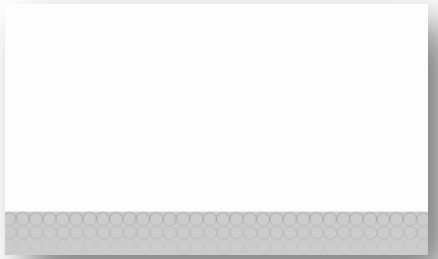
Introduction: Depth profiling of metal oxide layers



Sample structure

- HfO_2 or $SrTiO_3$ layer on Si substrate
- Problem
  - What is the stoichiometry of the film as a function of depth?
  - Traditional monatomic Ar+ sputtering causes changes in oxidation state when profiling metal oxides
  - How can we profile through the sample, keeping the chemistry intact?
  - Argon clusters with ≥2000 atoms are good for profiling through organic layers with minimal chemical damage
    - These large clusters etch too slowly with inorganic materials

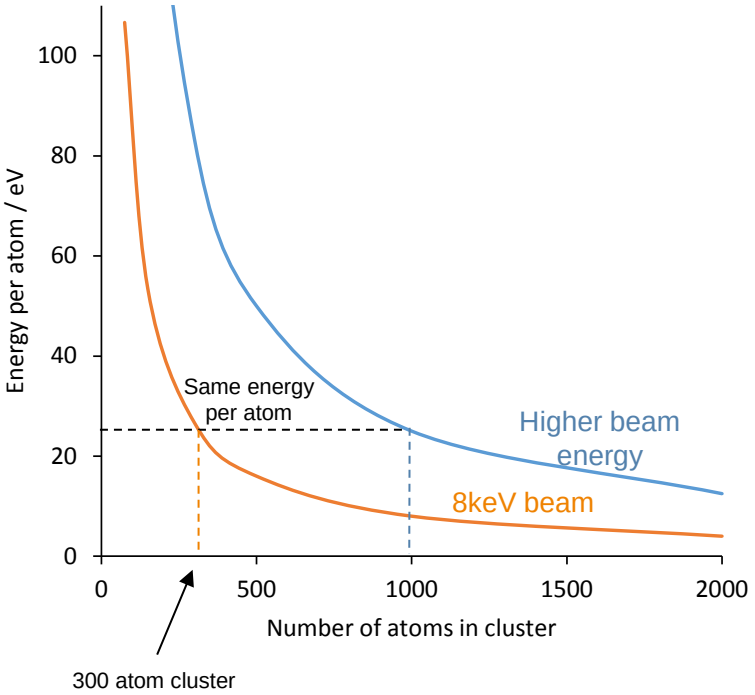
Introduction: Monatomic *versus* cluster profiling



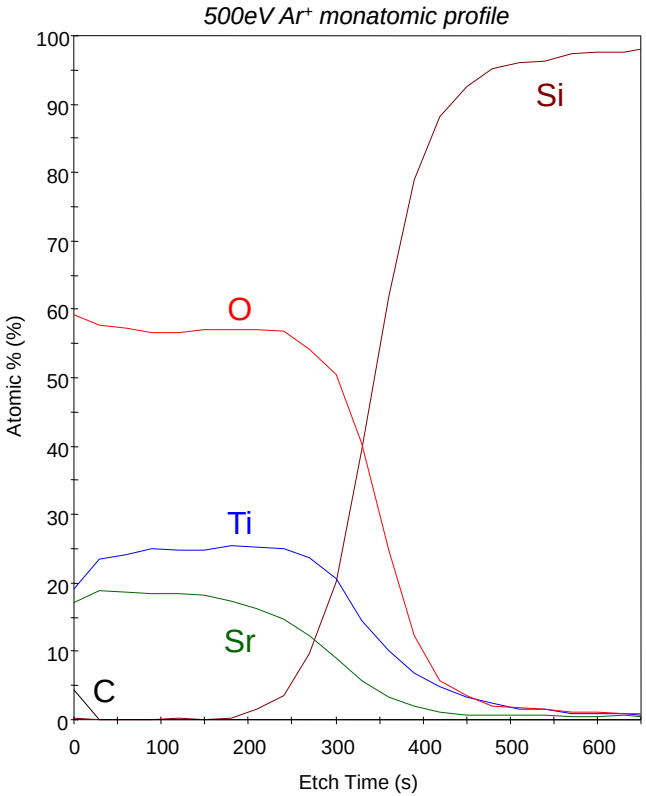
- Monatomic ions (Ar^+)
  - High energy per atom (200eV – 4keV)
  - High etch rate
  - Deep surface penetration
  - Can damage surface chemistry
  - Ideal for etching inorganic material
- Cluster ions (Ar^+_n)
  - Low energy per atom (1eV – 100eV)
  - Minimal surface penetration
  - Non-damaging to surface chemistry
  - Low etch rate for large clusters
  - Large clusters ideal for etching organic material

Introduction: Small clusters for inorganic profiling

Energy per atom versus cluster size for different beam energies



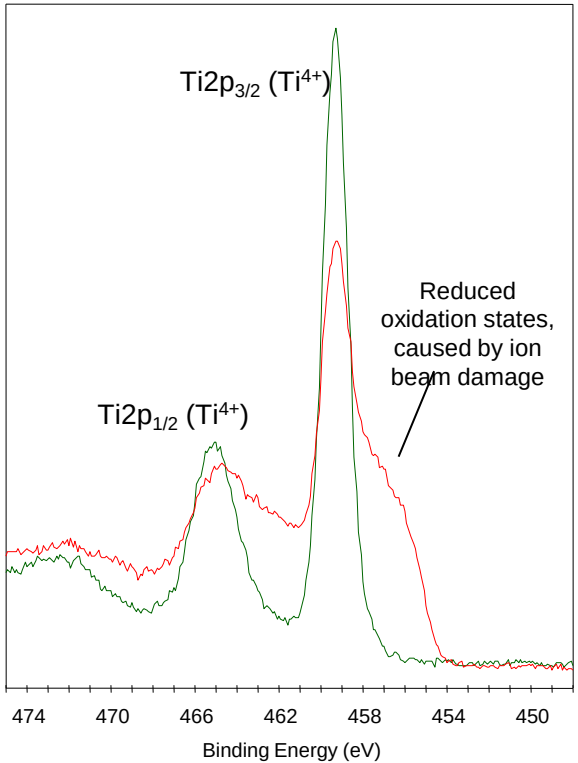
Monatomic Argon profile - $SrTiO_3$ film on Si



- Monatomic Argon profile
  - 500eV beam energy
  - Sr:Ti ratio is expected to be 1:1 throughout film but ~0.75:1 observed instead
  - Monatomic Argon beam is modifying the stoichiometry of the film

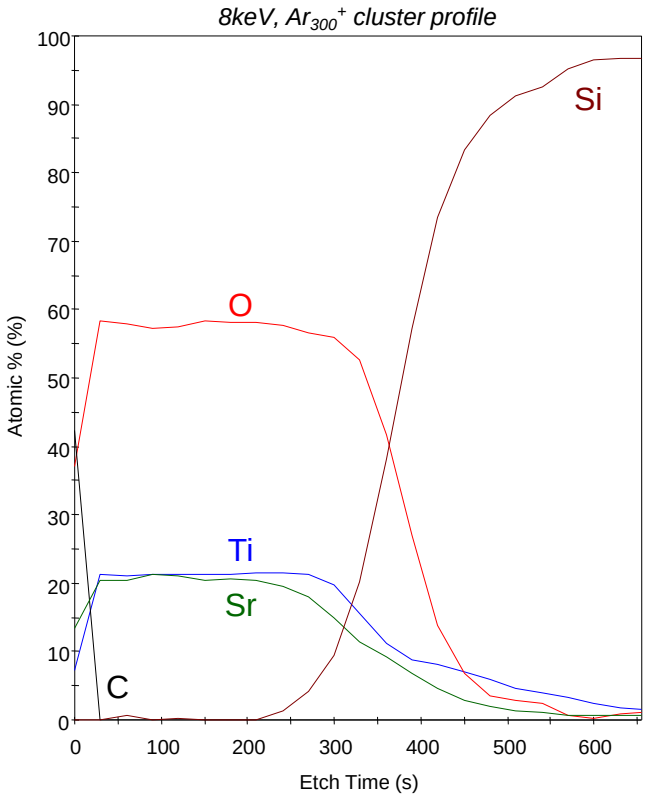
Monatomic Argon profile – Titanium chemistry $SrTiO_3$ film on Si

*Ti2p spectra **as received** and during **500eV Ar^+ sputter profile***



- Monatomic Argon profile
  - Ti2p spectrum from as received surface shows only peaks due to $Ti4^+$ chemical state (as expected for $SrTiO_3$)
  - After only 90s of 500eV Ar^+ profiling, a significant intensity of lower oxidation states (Ti^{3+}, Ti^{2+}) are observed in the spectrum
  - ~45% of the Ti2p spectrum is due to these damaged states after 500eV sputtering

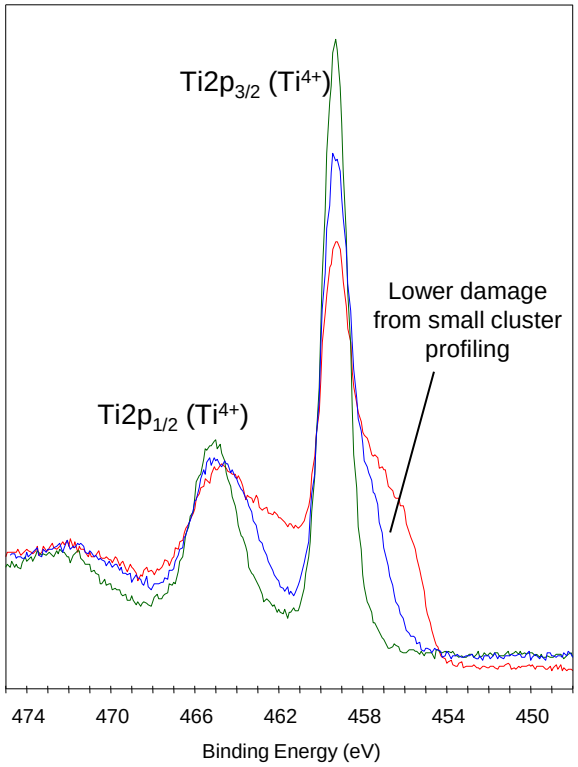
Argon small cluster profile - $SrTiO_3$ film on Si



- Argon small cluster profile
  - 8keV, $Ar300^+$ small cluster beam
  - Etch rate is comparable to the 500eV monatomic profile (0.07 nm/s)
  - With small cluster profiling, the Sr:Ti ratio is much closer to the expected 1:1 value
  - Small cluster beam is much better at preserving the elemental composition of the $SrTiO_3$ film, compared to the 500eV monatomic beam

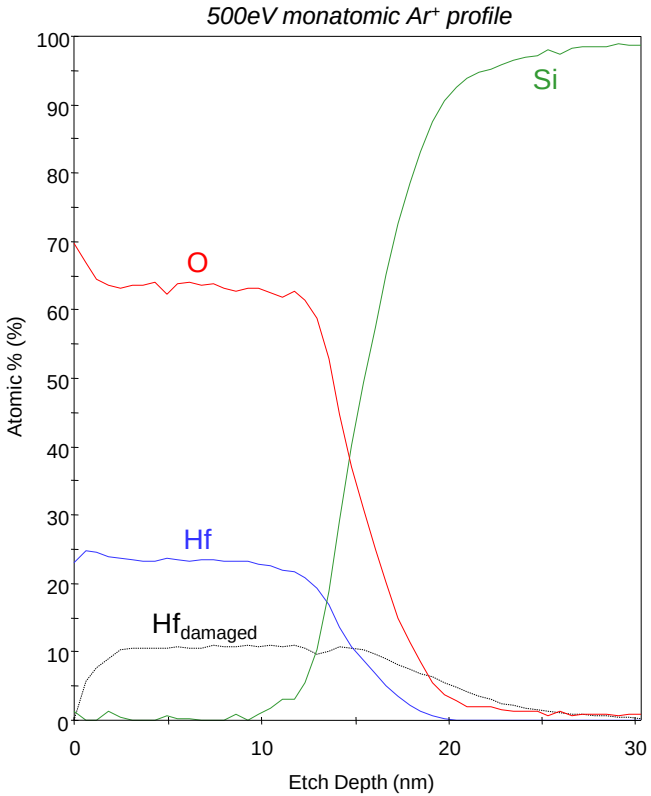
Argon small cluster profile – Titanium chemistry - $SrTiO_3$ film on Si

*Ti2p spectra **as received**, during **8keV Ar_{300}^+ sputter profile** and **500eV monatomic profile***

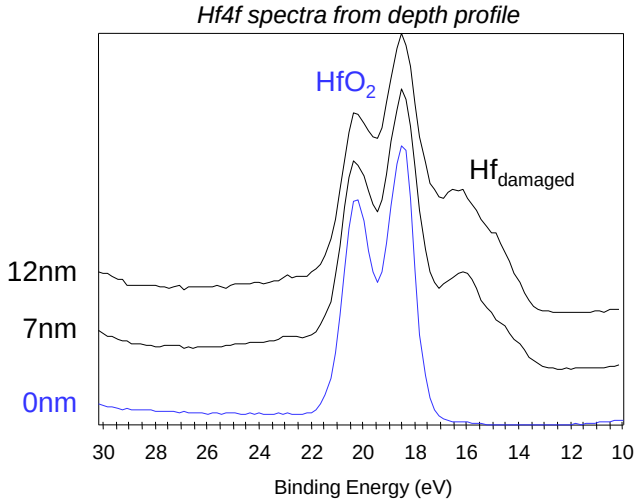


- Argon small cluster profile
  - Ti2p spectrum from as received surface shows only peaks due to Ti^{4+} chemical state (as expected for $SrTiO_3$)
  - After 90s of 8keV Ar_{300}^+ profiling, the damage to the titanium is considerably lower than was observed for the 500eV monatomic beam
  - Small cluster profiling only caused the production of Ti^{3+} states, whereas monatomic profiling generated Ti^{3+} and the more reduced Ti^{2+} state in similar quantities

Low energy (500eV) monatomic Argon profile - HfO_2 film on Si



- Significant change in [Hf]/[O] ratio in top few nm, caused by preferential sputtering of oxygen
- Damage to Hf chemistry, as observed in Hf4f spectra (almost 50% on total Hf concentration in film)
- Prolonged tailing of Hf damaged into Si substrate



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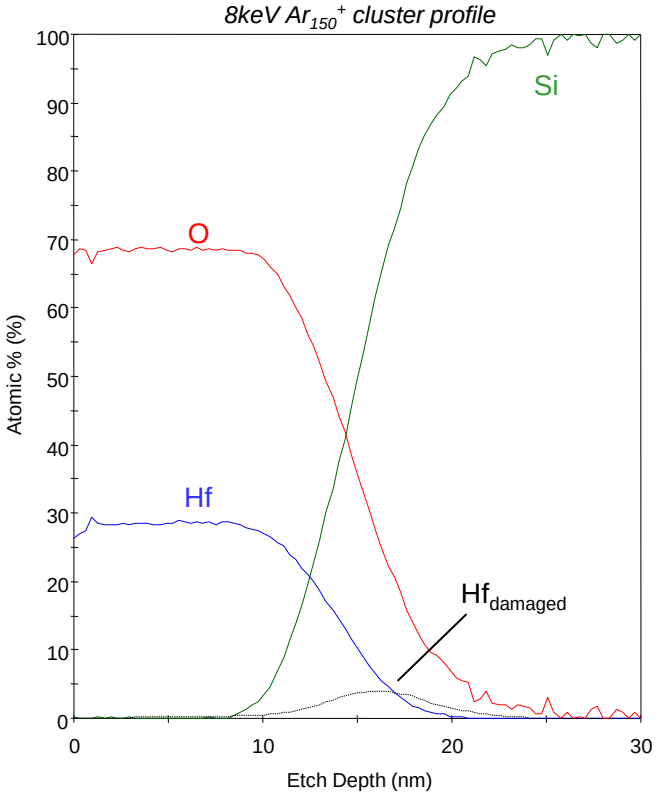
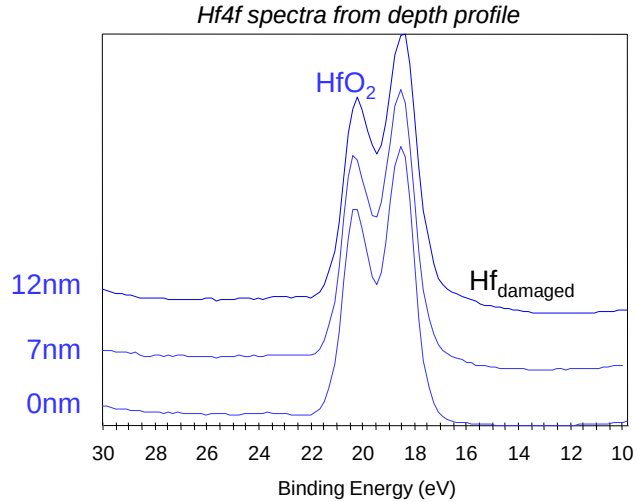
Small Argon cluster (8keV, Ar^{+}_{150}) sputter profile - HfO_2 film on Si



- Sample tilted to give more glancing ion incidence during sputtering
- Constant [Hf]/[O] ratio throughout film (minimal preferential sputtering of oxygen)
- No significant damage to Hf chemistry, until well into interface region (much less damage compared to 500eV monatomic mode)



Conclusion - HfO_2 film on Si

Thermo Scientific Monatomic and Gas Cluster Ion Source (MAGCIS)

- Small cluster profiling of HfO_2 and $SrTiO_3$ films
- Monatomic and Gas Cluster Ion Source
  - Comprehensive XPS profiling with small Argon clusters (75-300 atoms) enables HfO_2 films to be analysed with lower chemical damage than monatomic Argon