First principles modelling of the silicon-hafnia interface

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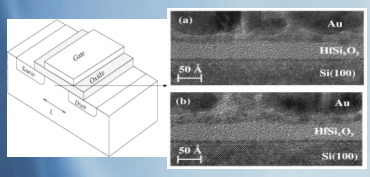
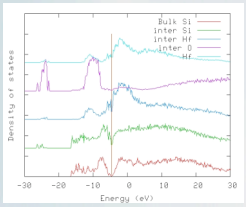
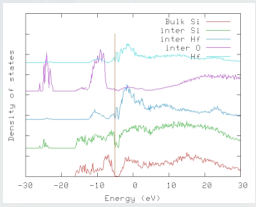
Introduction

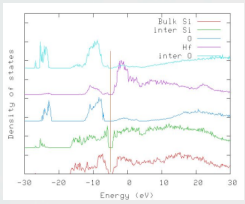
If the rapid increases in computing power witnessed over the past decades is to be maintained, then significant developments must be made in basic microelectronics technology. Assuming that MOSFETs will still play a dominant role, then a replacement for silica (SiO_2) must be found. Hafnia (HfO_2) is currently the most promising replacement candidate.



Understanding the properties of the silicon-hafnia interface are crucial in deciding whether hafnia is suitable for the task.







① Non-stoichiometric

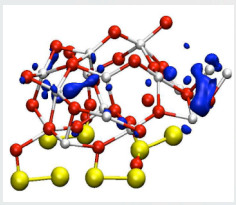
Consider first an interface built from layers of HfO, such that Hf is under-coordinated:

- Large reconstruction at the interface as Hf seeks bonds
- Forms several silicide bonds
- Results in a metallic interface, with continuous Hf-Si states through the gap

② Stoichiometric

In the second interface, the oxide layer is stoichiometric HfO_2, such that Hf should be fully coordinated:

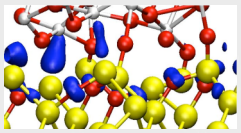
- Much less relaxation at the interface
- Oxide tends more to bulk-like structure
- DOS shows a clear state in the gap - LDOS analysis shows that it results from Hf-Si bonds



③ Saturated

In the third interface, bonds saturating oxide layer is deposited over the second structure:

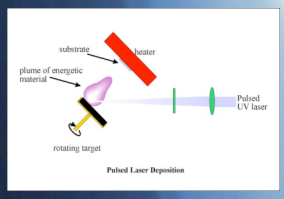
- Structure remains similar to the second one
- Metallic Hf-bonds now saturated
- DOS shows no obvious state in the gap, but gives zero band offsets with silicon



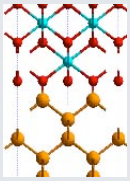
- density analysis shows that Hf-Si bonds are still present

Interface growth

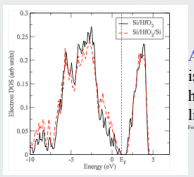
The nature of the interface is directly influenced by the growth method used to prepare the oxide film on silicon. Method considered here is closest to PLD, as we model the deposition of very reactive O and Hf directly on the substrate.



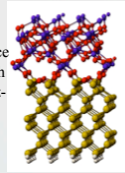
In Pulsed Laser Deposition (PLD) a UV laser excites a plume of material from a solid target, which is then directed onto a heated surface.



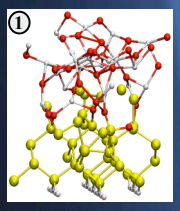
Interfaces built by hand and constrained by full periodicity avoid silicide formation despite being chemically similar.



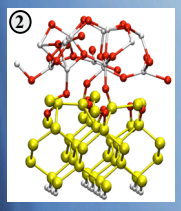
ALD simulated interface is much less dense, with hafnia forming a quartz-like structure.



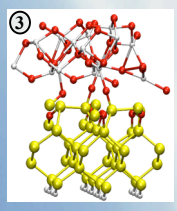
Simulated structures



Si(100)-HfO structure

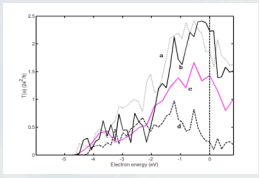


Si(100)-HfO2 structure



Si(100)-HfO2-O structure

Transport



Tunneling probability through
(a) nonstoichiometric interface,
(b) stoichiometric interface,
(c) saturated interface and
(d) benchmark interface.

- Transport high in all the systems
- Tunneling in (c) much larger compared to (d) due to smaller thickness of the interface

Methods

- Density Functional Theory - PBE
- Localized basis set - SIESTA
- Initial Si(100) surface terminated by oxygen
- Interfaces generated by cycles of simulated annealing from 600K.
- Finite element based Green's functions method for electron transport

Summary

- As expected, the electronic structure of the interface is very sensitive to the stoichiometry of the oxide - metallic Hf-Si bonds will form if Hf is under-coordinated.
- Even for a fully stoichiometric metal oxide layer, the propensity of a silica layer to form still results in silicide bonds, and states in the gap.
- For fully saturated interface there are no states in the gap, but weak Hf-Si bonds result zero offsets between hafnia and silicide.
- Even a small number of metallic bonds lead to a significant tunneling.
- In terms of real growth these results implicate that the interface must be stabilized to prevent Hf and O diffusion:
  - Hf could be deposited over silica in a significant ambient oxygen pressure
  - Hf dangling bonds could be saturated by some other species during the growth to prevent the metallization