Defects and Disorders in Hafnium Oxide and at Hafnium Oxide/Silicon Interface

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Outline

1. ***Introduction, disorders and defects***
2. ***Intrinsic oxygen vacancies***
3. ***Oxygen Interstitials***
4. ***Grain boundary states***
5. ***Extrinsic defects (water-related defects)***
6. ***Interface traps***
7. ***Conclusions***

1. Disorders and defects

- are often localized states which can trap electrons or holes and are often termed as trapping centers or simply "traps";
- give rise to various reliability issues, such as V_T shift, gate leakage, NBTI, PBTI and dielectric breakdown.

They are quite clear in silicon oxide, but still not be fully explored in most high-k materials!

1. Defects and disorders

- *Bonding:* Hf atom has 4 valence electrons given by $5d^2 6s^2$, each Hf atom in the HfO_2 is coordinated to four O atoms. An O atom has 6 valence electrons ($s^2 p^4$), thus each O atom bridges with two Hf atoms in HfO_2.

- *Crystal structure:* amorphous/unique form of crystal modification.

- *Impurities:* In the form of as network sites or interstitials.

➔ *Perfect material:* all atoms in the material did not deviate from their regular coordination numbers.

1. Disorders and defects

- In stoichiometric oxides, the atomic disorders always exist.
- Disorders can be due to *cation* or *anion* vacancies (Schottky disorders), or *interstitial* atoms (Frenkel disorders).

- *Oxygen Vacancies* (V_O): most metal oxides are often found to be (slightly) non-stoichiometric and are oxygen deficient.
  - Formation energy of V_O and oxygen interstitial are smaller than that for the defects at the metal sites.
  - V_O is primary source of intrinsic defects.

- *Grain boundary states:* localized states near the E_C associated with the grain boundaries TM/RE oxides with anocrystallites.

- *Impurities:* the impurities from the deposition precursors result in the formation of structural imperfections or interstitial trapping centers.

2. *Intrinsic oxygen vacancies*

Why ?

- Large chance for incomplete oxidation and leads to a higher amount V_O because of the low oxidation temperatures for metals (< 700 °C).
- High-k oxides are more ionic and less stable. Annealing of the TM/RE oxide in inert gases or in vacuum would result in the decomposition of M-O bonds and would give rise to more V_O.

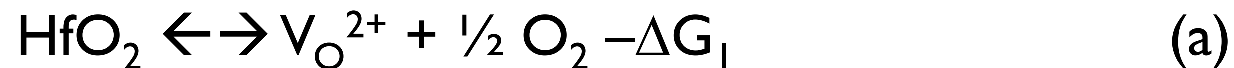
How?

- High-k V_O centers have a strong localization effect because of the ionic bonding and the strong localization of the defect wavefunctions on the neighboring metal ions.
- The localized states may be either near the band edges or can be deep states.
- HfO_2 V_O is in the upper mid-gap of Si. It can trap electrons and induce instability of MOS device operation.

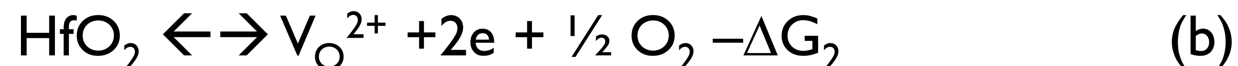
2. *Intrinsic oxygen vacancies*

Formation

- The formation energy required to form an V_O in an O_2 ambient in a TM/RE oxide is generally much smaller than the covalent dielectrics because of the higher energy level of O vacancies in the ionic oxide.
- V_O formation may also result in the generation of excess electrons in the conduction band.
- V_O in HfO_2 film may be formed through the following two reactions:



$$HfO_2 \leftrightarrow V_O^{2+} + \tfrac{1}{2} O_2 - \Delta G_1 \qquad \text{(a)}$$

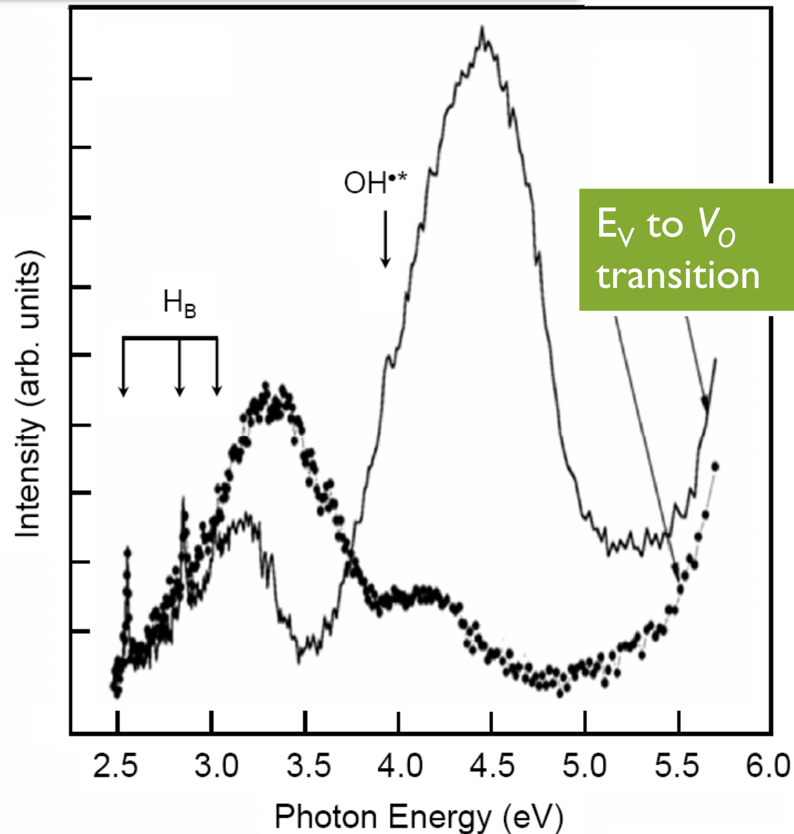


$$HfO_2 \leftrightarrow V_O^{2+} + 2e + \tfrac{1}{2} O_2 - \Delta G_2 \qquad \text{(b)}$$

- For the energy point of view, reaction (b) is more favorable.

2. *Intrinsic oxygen vacancies*

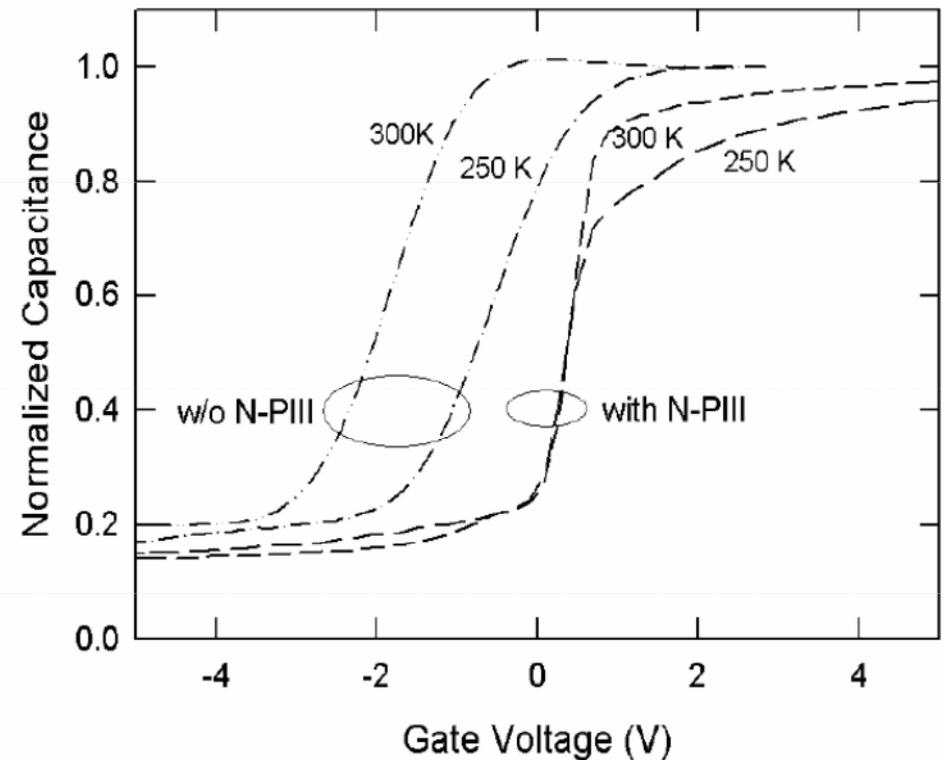
Evidence of V_O in PL Spectra



PL of as-deposited (dotted) and annealed (line) HfO_2.

- Short-wave absorption edge in the excitation PL spectrum of HfO_2 film can be attributed to transition from valence band to the O vacancy levels.
- The "vacancy zone" is formed below of E_C.
- The position of the absorption edge agrees with the position of the O vacancy levels with respect to The HfO_{2-x} valence band.

V_O Reduction with N



- Incorporation of N atoms into a metal oxide film can suppress the vacancies effectively.
- Pronounced reduction in the flatband shift of the temperature-dependent *C-V* characteristics was found.
- Leakage current can be reduced remarkably due to the suppression of the V_O centers.

2. *Intrinsic oxygen vacancies*

- N fills up the V_O center, replaces the nearest neighbor O site to V_O and make the V_O centers inactive.

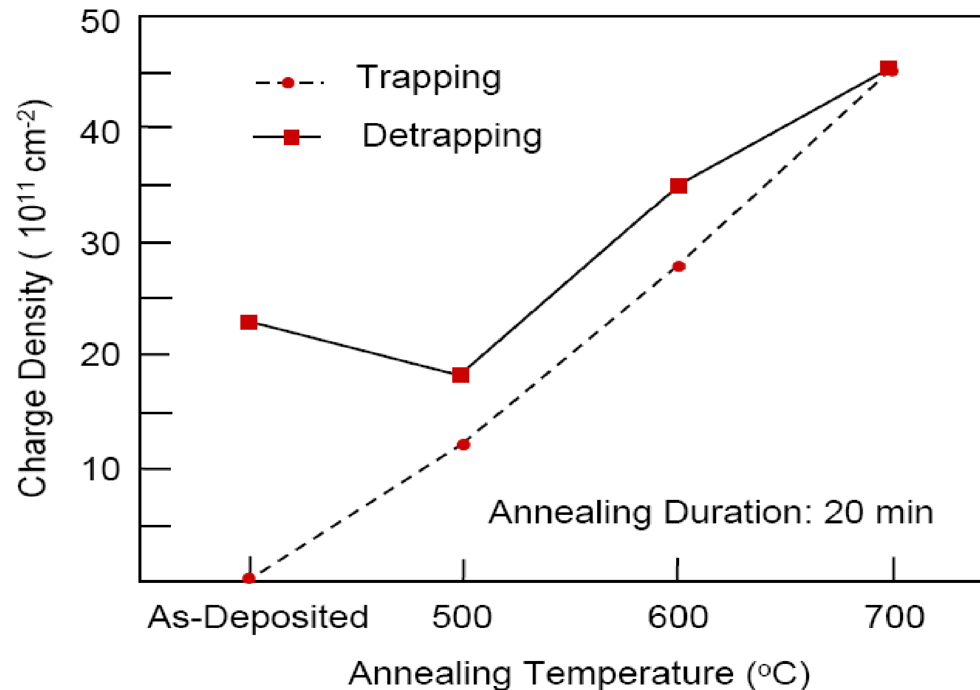
  - The two electrons trapped at the V_O level are transferred to N 2*p* orbital at the top of the valence band and the V_O related gap state disappears. The neutral V_O^0 is converted into positively charged V_O^{2+}.

3. Oxygen interstitials

- According to the theoretical calculation by Foster et al., both atomic and molecular incorporation of O into monoclinic HfO_2 are possible but atomic O incorporation is more energetically favorable.
- For atomic O incorporation, the O_I can be in the form of either a fourfold-coordinated tetragonally or threefold-coordinated trigonally.
- The interstitial O atoms and molecules can trap electrons from injected from Si. The charged defect species are more stable than neutral species.

4. Grain boundary states

Evidence of GB States



- For as-deposited samples, most of the trapped charges cannot be discharged in the detrapping experiment indicating the presence of a large amount of O vacancies in the film.
- At 700 °C, almost all trapped charges were de-charged indicating that most of deep V_O states have been suppressed.
- But 700 °C annealed sample was found to have a lot of shallow states which are attributed to the present of large amount of grain boundary shallow traps.

5. Extrinsic defects: Water-related defects

The Sources

- TM/RE oxides are easier to be contaminated by foreign atoms.

- The precursors used for the CVD or ALD processes generally contain: *carbon*, *hydrogen* and *oxygen*, thus, water and other byproducts often contaminate the films.

- Water-related groups are found in HfO_2 films. Even with prolonged high-temperature annealing, it was found that the H_2O and OH groups are still detectable.

- Forming gas annealing for reducing the defect density is actually involved the passivation of dangling defects with H.

5. Extrinsic defects: Water-related defects

The Effects:

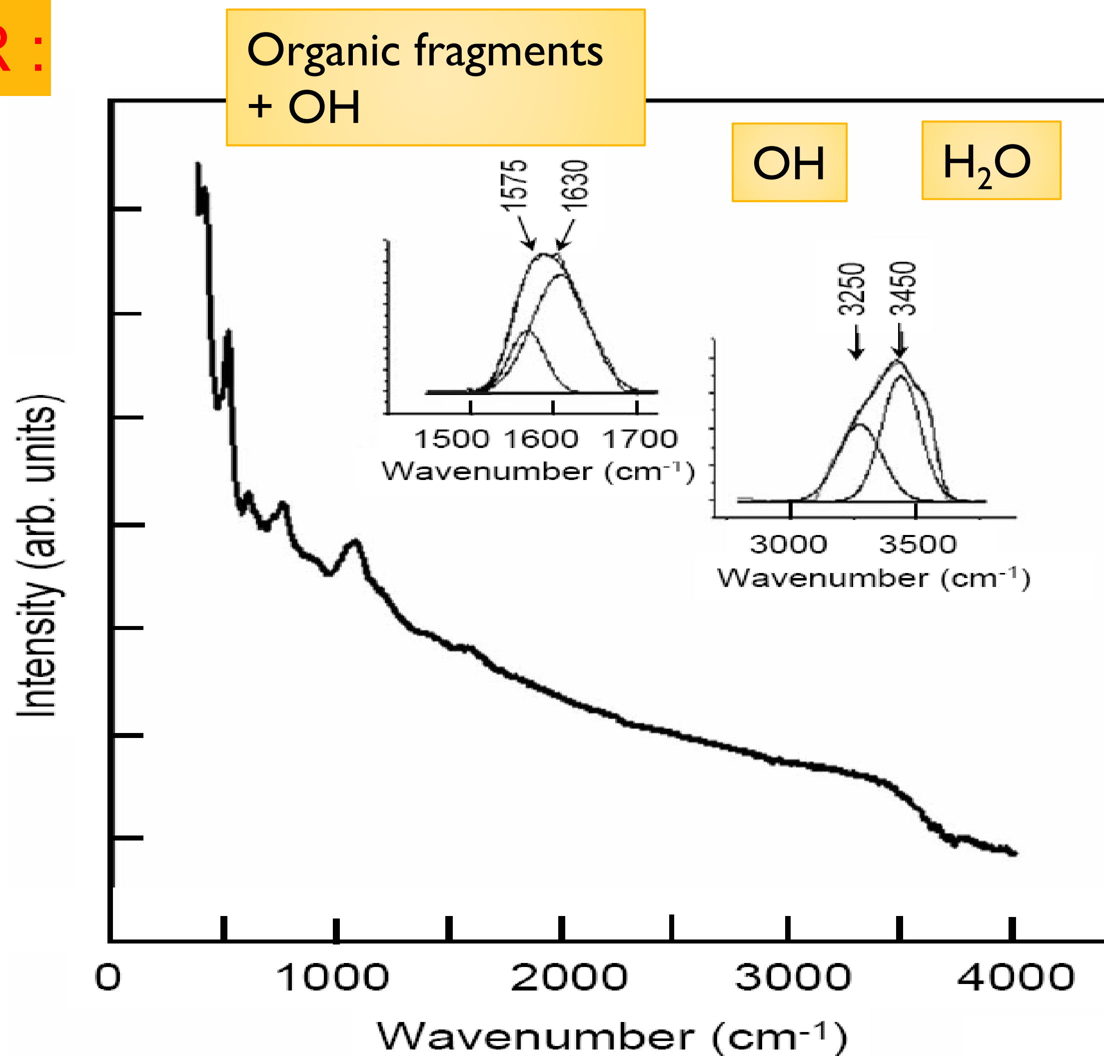
- In high-k TM/RE oxide, the passivation of V_O results in the formation of more stable V_O-H complex which is a positive fixed charge in the film. This is one of the reasons for high positive fixed charge in The HfO_2.

- Hydrogen atoms may also be incorporated into the dielectric films as interstitials and bonded to threefold-coordinated O atoms. When hydrogen is bonded to a fourfold-coordinated O of the oxide network, one of the four metal-O bonds is nearly broken.

- H atoms can be released under high-field or hot carrier stressing and has been proposed as a mechanism for defect generation.

5. Extrinsic defects: Water-related defects

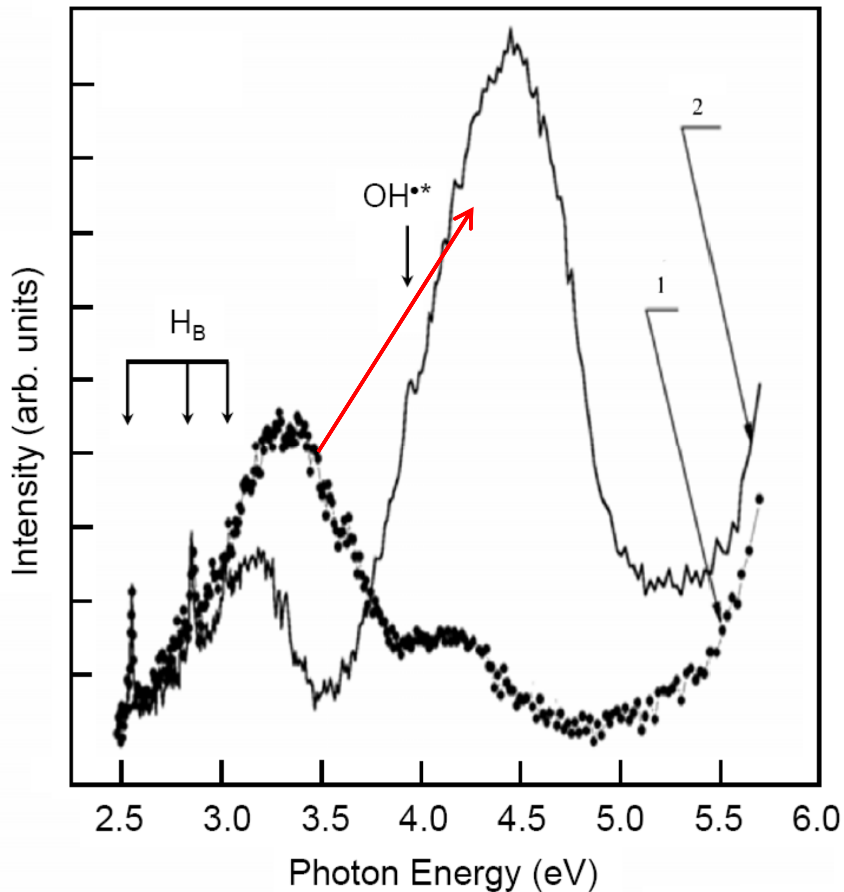
Evidence of IR :



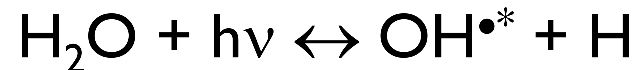
Infrared spectrum of the HfO_2 film prepared by ALD method.

5. Extrinsic defects: Water-related defects

Evidence of PLE:



- The PL intensity of this peak increases remarkably by using 5.1 eV photon excitation which is able to break the H-OH bonds in the water molecules.
- The decomposition of water molecule in The HfO_2 films upon photon absorption can be described by:



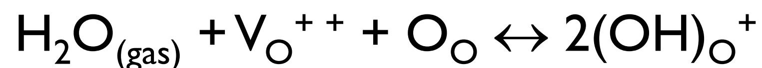
$$H_2O + h\nu \leftrightarrow OH^{\bullet *} + H$$

where $OH^{\bullet *}$ is radical in the electronic-excited state.

5. Extrinsic defects: Water-related defects

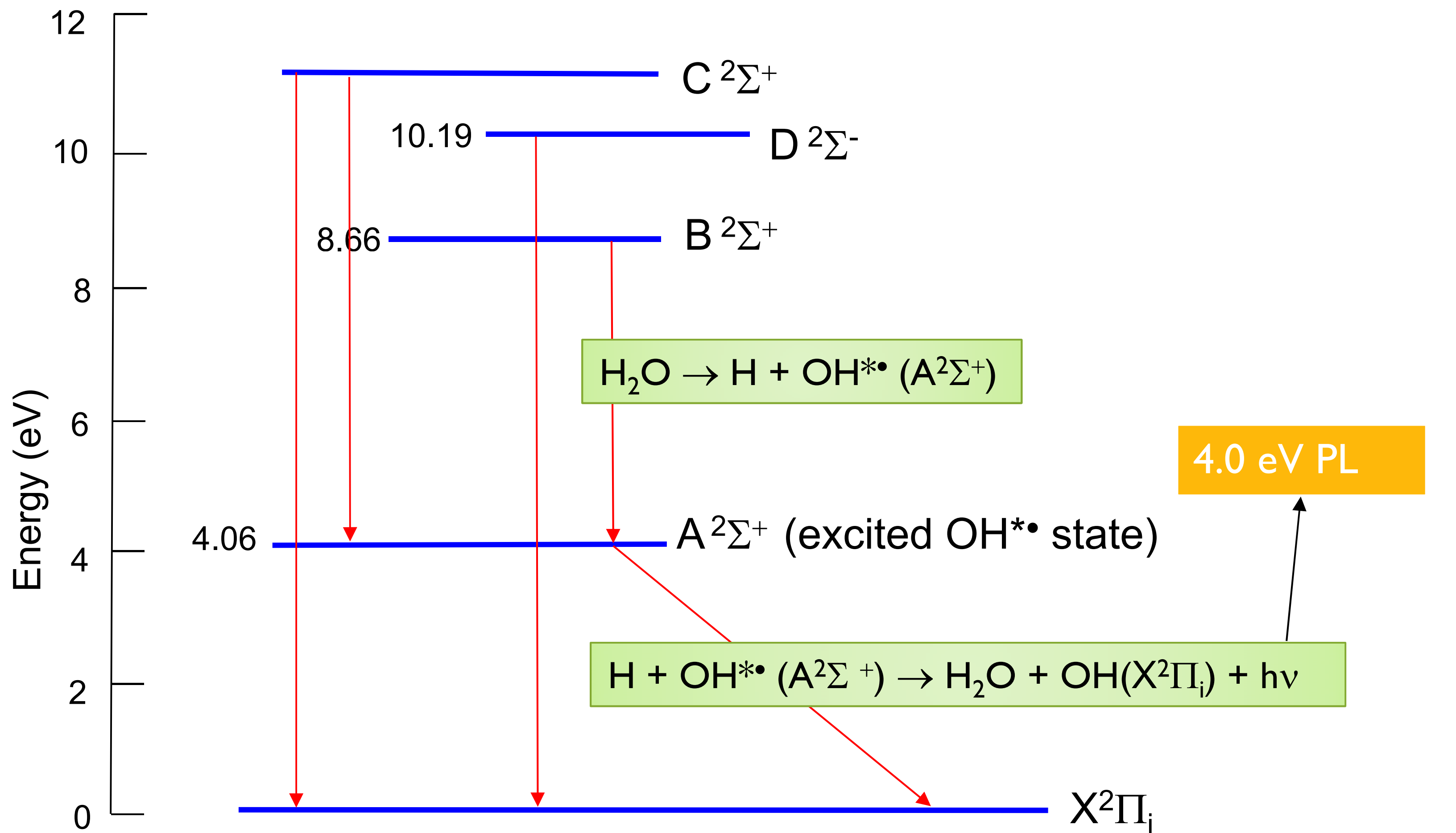
Mechanisms

- In the TM/RE oxides, water can be incorporated into the films during the film deposition via the oxygen vacancies according to:



- The double negatively-charged oxygen anion is converted in to a positively-charged $(OH)^{+}_{O}$ where the oxygen has a single negative charge.

- Since the OH^- anions in the oxygen lattice points are loosely-coupled with H atoms, they can hop over the film via the defects.
- As the absorption energy of H_2O molecules is closed to the band-to-band transition energy, the energy is able to set the water into excited state (H_2O^*) and result in the radiation and dissociation of the water molecules into O*, H*, OH^-, or OH^+ fragments.



A vibronic transition model was proposed for the OH defect state conversion.

6. Interface traps

At high-k/Si interface:

-- the interface stress is much larger;
-- the bond strengths are much weaker;
-- larger thermal expansion coefficients of the high-k materials.

➔ *high interface trap density !*

- Formation of a silicate layer at the interface will help to release the interface strain and thus improve the interface properties.
- Proper thermal annealing may allow the film to relax to a less-strained interface by forming metal-Si bonds, Si-O bonds, and random bonding silicates in the transition layer.
- ***The role of O!***

6. Interface traps: Role of Oxygen

- *Oxygen is always good except EOT !*

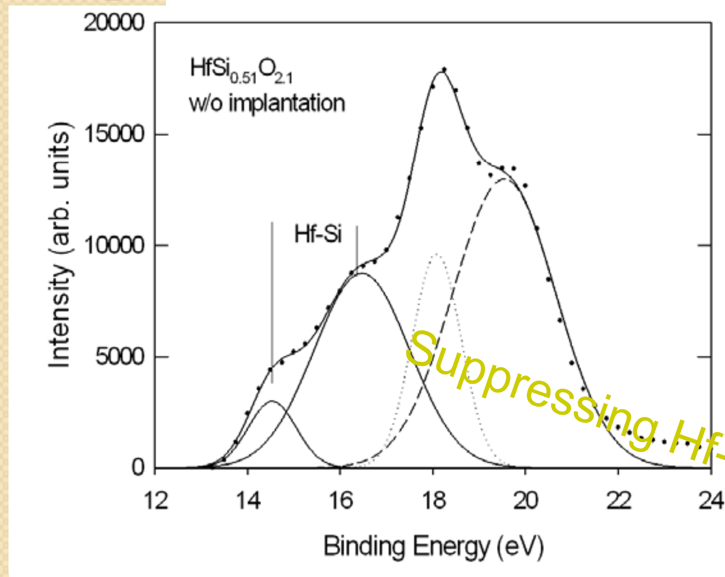
- Oxygen permeability of the thin metal oxide film is quite high and lead to interface oxidation.
- The interface oxidation reactions leads to the formation of SiO_2 or silicates, but it is still difficult to convert the silicide bonds to oxide or silicate bonds.
- The vacancy levels in silicates should be slightly different to the elemental oxides as the vacancy site may have both metal and Si neighbors.

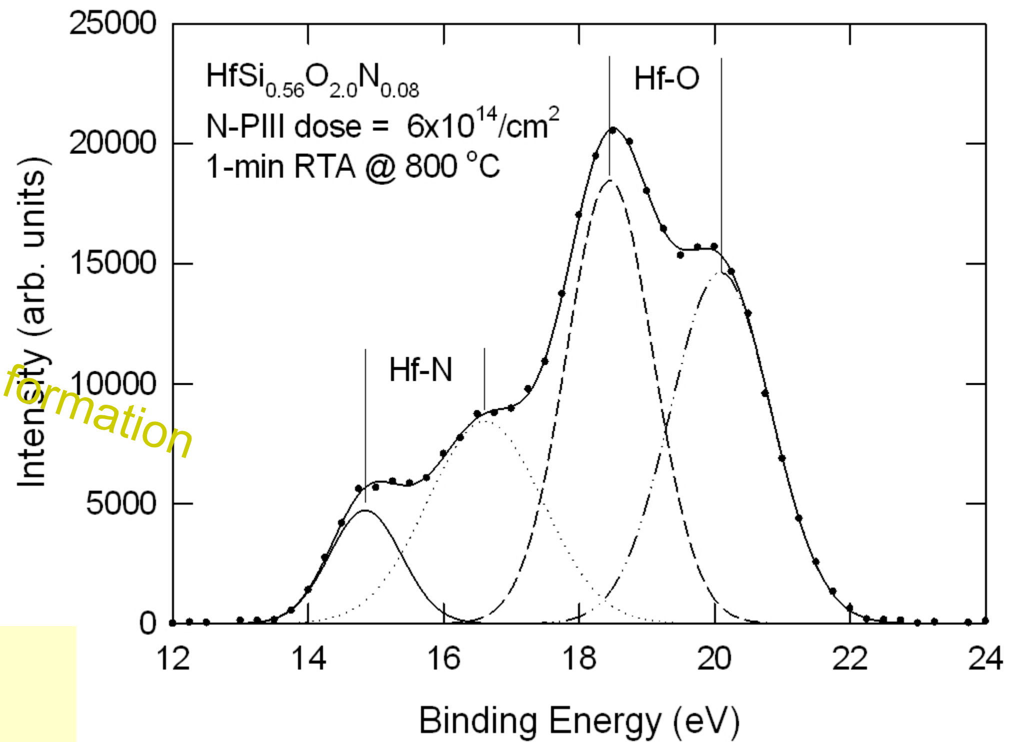
6. Interface traps: Role of Si

- Si can be easily incorporated into the metal oxide networks, particularly at the oxide/Si substrate interface.

➔ made the interface bonding configuration even more complicated.

N Doping on HfO_2 : interface improvement

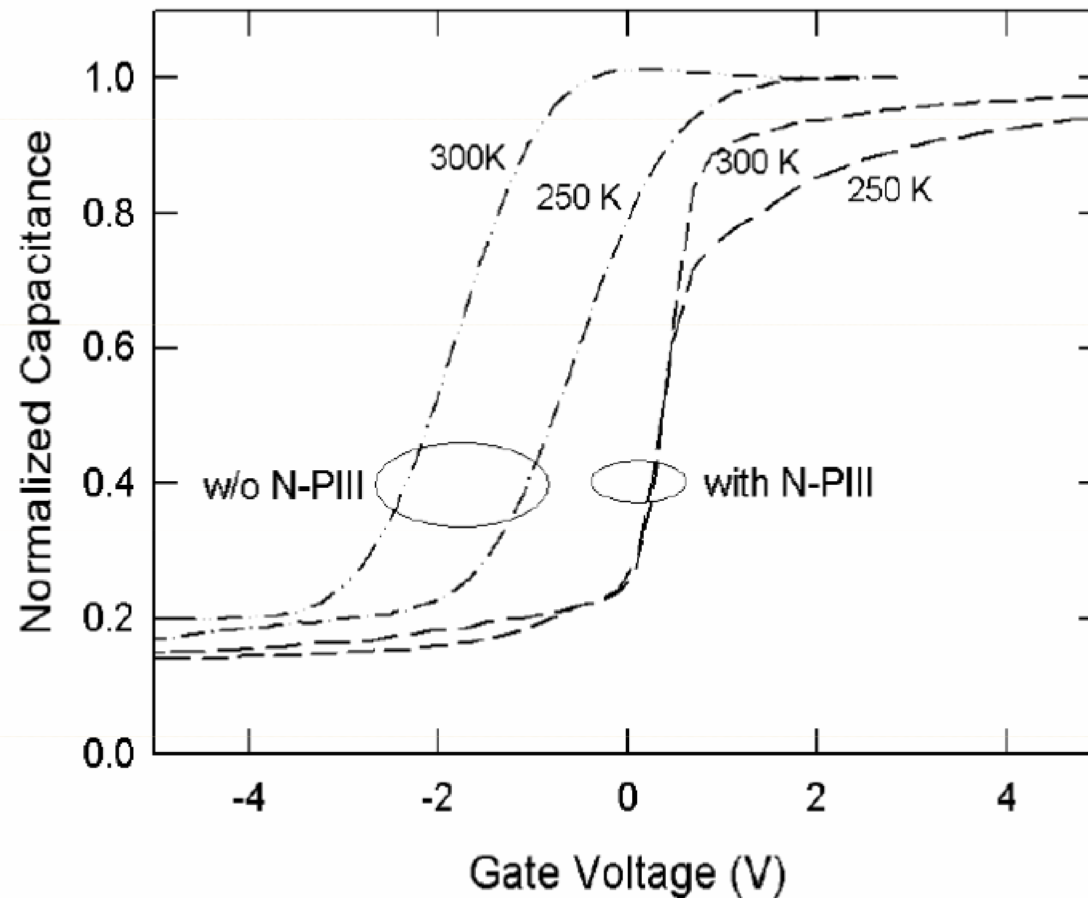




Suppressing Hf-Si formation

- **Hf-N is in a 4-fold coordination ➔ reduce the average atomic coordination number.**

HfO_2 Nitrogen Doping



- Steeper slope → low interface trap density

7. Conclusions

Causes

- The defect and disorder states of hafnium oxide (and other high-k materials) and their impacts are much more complicated than the conventional SiO_2.
- The (Hf, Si, O) ternary interface leading to: Si-O, Hf-O, and Hf-Si bondings.
- Si diffusivity in HfO_2 is high. Bulk silicate is not uncommon.
- The deposition process causes the introduction of significant amount of extrinsic defects and high amount of V_O.
- The deposition/annealing conditions make substrate Si to out diffusion, make bulk O to diffuse into the substrate.

7. Conclusions

Bulk

- Oxygen vacancy is the major source of bulk trap.
- Shallow traps arise from the grain boundary states of the nanocrystllite phases.

Interface

- Metallic bonding has to be avoided. Silicate bonding is more favorable.
- Stress could be the deterministic factor. At high-k/Si interface, the interface stress is much larger and the bond strengths are much weaker; these lead to the high interface trap density.
- Formation of a silicate layer at the interface will help to release the interface strain and thus improve the interface properties.

7. Conclusions

Measures

- Proper thermal annealing may allow the film to relax to a less-strained interface by forming metal-Si bonds, Si-O bonds, and random bonding silicates in the transition layer.
- Some process, such as N and Al doping looks promising for overcoming the effects of defect states in high-k based transistors.
- Metal gate thickness control and CeO_2 capping which control the oxygen supply to the gate dielectric film (see M. Kouda, Ph.D. Thesis) will also help to control the oxygen vacancies and interface structure.

How about La_2O_3 ?

References

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