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
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I. 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!
I. 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.
I. 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 ($< 700 \, ^{\circ}\text{C}$).
- 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.
- $\text{HfO}_2 \, V_O$ 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:

\[
\begin{align*}
\text{HfO}_2 & \leftrightarrow V_{O}^{2+} + \frac{1}{2} O_2 - \Delta G_1 \\
\text{HfO}_2 & \leftrightarrow V_{O}^{2+} + 2e + \frac{1}{2} O_2 - \Delta G_2
\end{align*}
\]

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

Evidence of $V_O$ in PL Spectra

- 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 HfO₂ are possible but atomic O incorporation is more energetically favorable.

- For atomic O incorporation, the O₁ 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$_2$O 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 HfO₂ 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 HfO₂ films upon photon absorption can be described by:

  \[
  \text{H}_2\text{O} + h\nu \leftrightarrow \text{OH}^\bullet + \text{H}
  \]

  where OH• 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:

$$\text{H}_2\text{O}_{(\text{gas})} + \text{V}_\text{O}^{++} + \text{O}_\text{O} \leftrightarrow 2(\text{OH})_\text{O}^+$$

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

- Since the \text{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 \text{H}_2\text{O} molecules is closed to the band-to-band transition energy, the energy is able to set the water into excited state (\text{H}_2\text{O}^*) and result in the radiation and dissociation of the water molecules into \text{O}^*, \text{H}^*, \text{OH}^-, or \text{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. This has made the interface bonding configuration even more complicated.
N Doping on HfO$_2$ : interface improvement

- **Hf-N** is in a 4-fold coordination
  - reduce the average atomic coordination number.
HfO$_2$ Nitrogen Doping

- Steeper slope $\Rightarrow$ 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 nanocrystallite 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 $\text{La}_2\text{O}_3$?
References


