Radical Oxidation of Ge for Interface Gate Dielectric GeO_2 Formation in MOS gate stacck

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Introduction: Ge MOS technology

- Ge as a performance booster
  - High electron/hole mobility
  - High process compatibility
  - Low temperature process
  - Possible V_{dd} scaling

	Si	Ge
Electron μ (cm^2/Vs)	1600	**3900**
Hole μ (cm^2/Vs)	430	**1900**
Band gap (eV, 300K)	1.12	**0.66**
Dielectric constant	11.9	**16**
Melting point (^oC)	1415	**937**

- Key issues: Interface property of Ge MOS gate stack
  - GeO_2 is regarded as a promising interface gate dielectrics*
  - Since GeO_2 decomposition/GeO evaporation temperature is very low (430^{o}C), low temperature oxidation is needed with high density of oxidant source

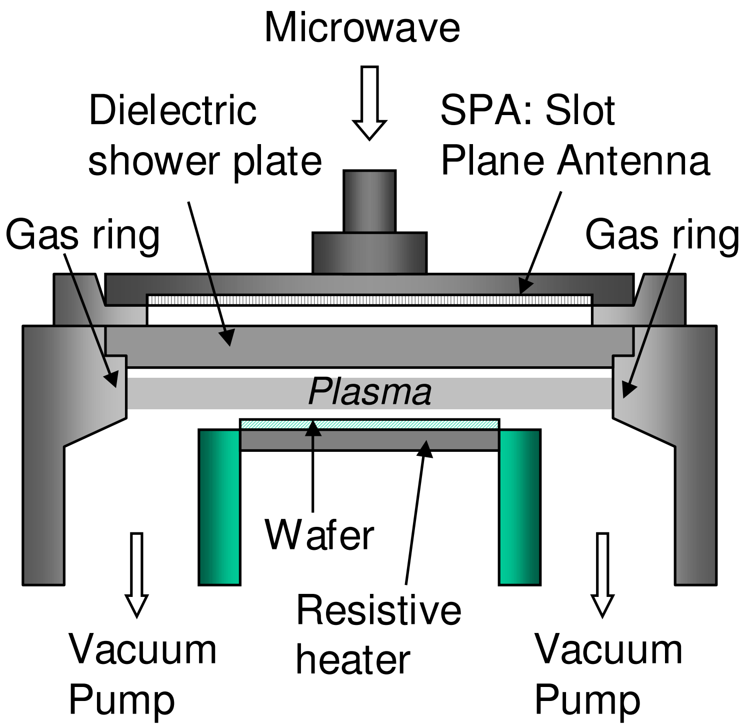
*D. Kuzum, IEDM2007,T. Takahashi, IEDM2007, Y. Nakakita, IEDM2008

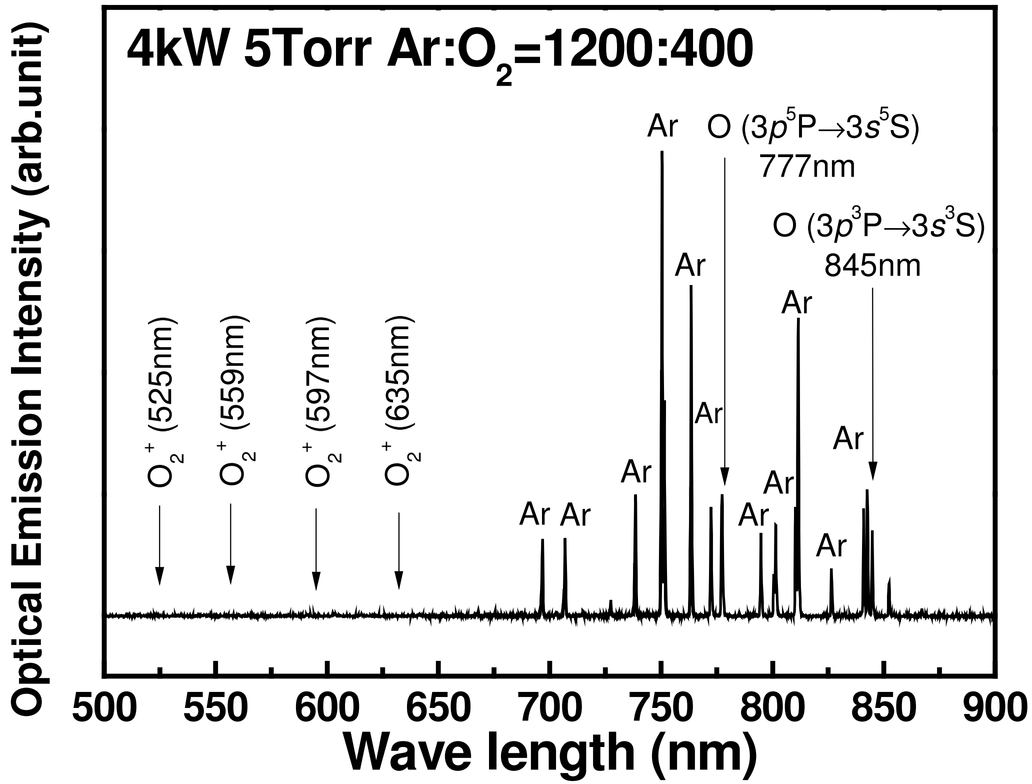
Slot-Plane-Antenna (SPA) system*

- High density/highly reactive atomic oxygen radicals (O*) generation
- Enables low temperature oxidation
  - **Below 400^{o}C** for Si and Ge

*T. Ohmi et al., Proc of IEEE 2001

T. Sugawara et al., JJAP 2005





Objectives

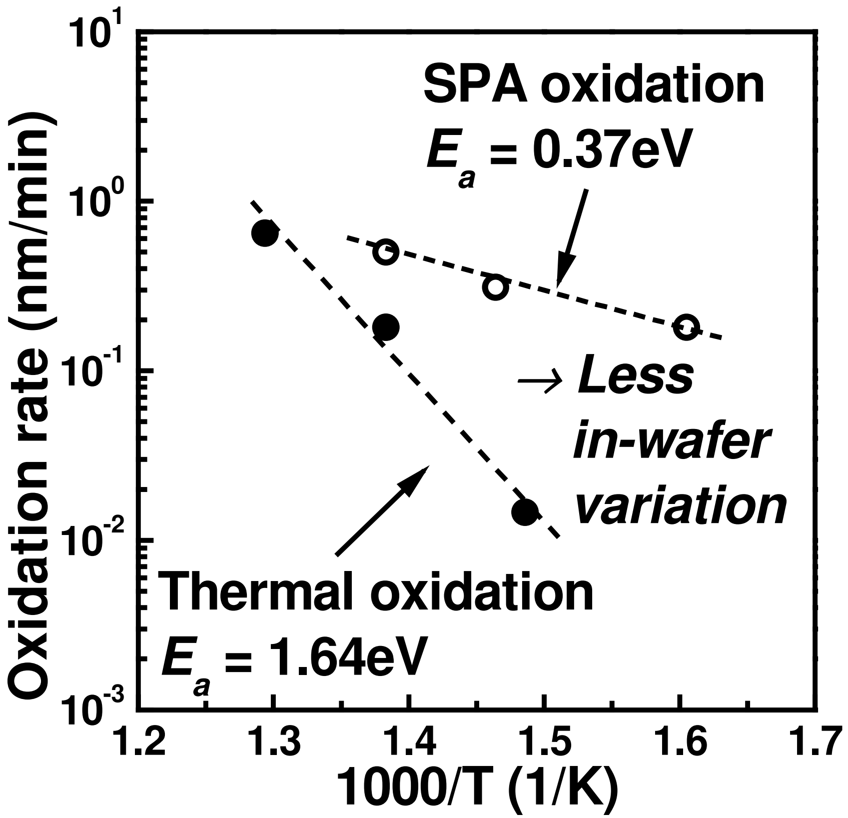
- Study oxidation kinetics of radical oxidation
  - Comparing to thermal oxidation
- Examine the electrical property of interface gate dielectric GeO_2
  - CV characteristics of MOS capacitor
  - Thermal stability
  - Band alignment

Experiments

- Sample preparation
  – (100) and (111) Ge surface was cleaned by PRS100 organic remover and by HCl/HF
  – Surface was oxidized by Slot-Plane-Antennal (SPA) radical oxidation system
    - Thermal oxidation was also done as a reference
- Kinetics study
  – Thickness was measured by ellipsometry and XPS
- Electrical property
  – 5nm ALD Al_2O_3 was deposited on GeO_2/Ge
  – Sputtered Al metal pad
  – 400^oC FGA anneal
  – XPS was used to identify surface chemical property
  – Synchrotron radiation photoemission spectroscopy (SRPES) was used for band offset measurement

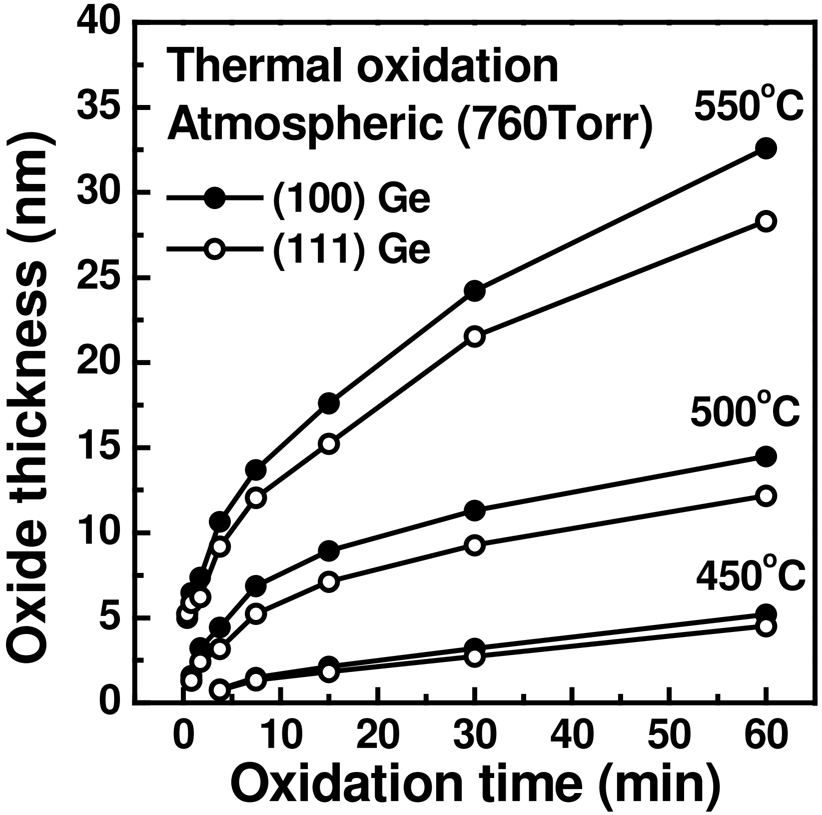
Activation energy of Ge oxidation

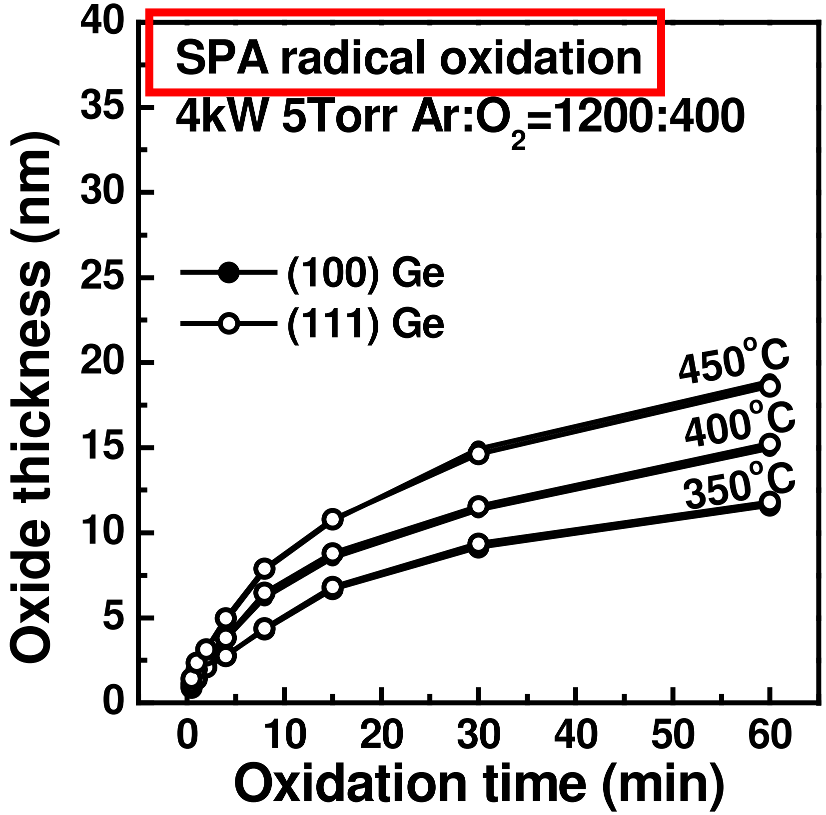
- Temperature dependence
  - Radical oxidation has lower activation energy (0.37eV) than thermal oxidation (1.64eV)
  - Due to high reactivity of radicals with small radius



Oxidation rate (1)

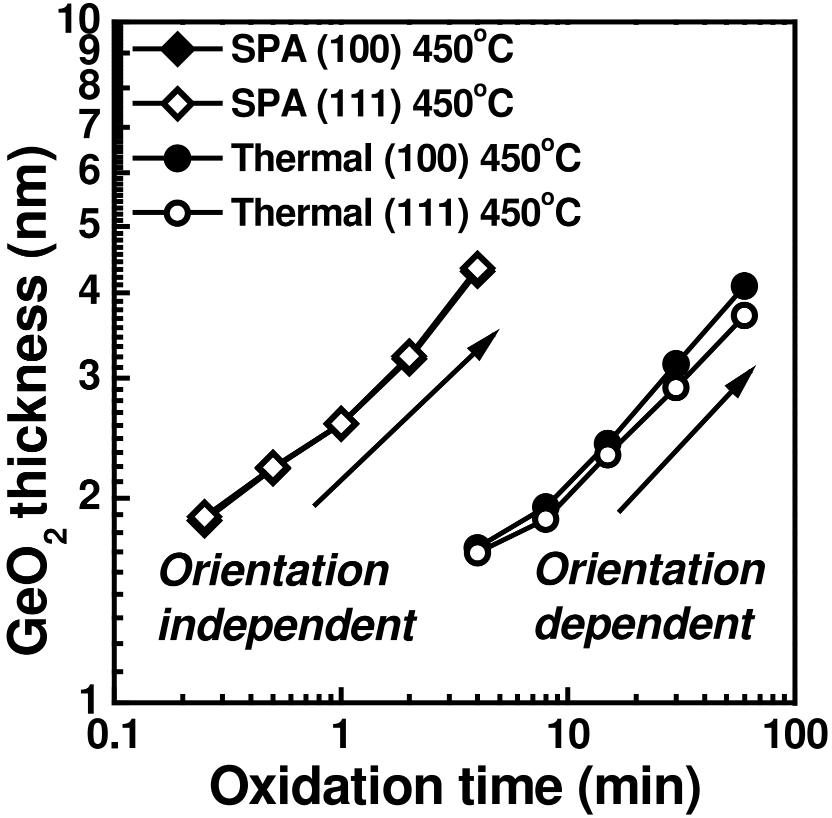
- Radical vs thermal oxidation (ellipsometry)
  - No orientation dependence was observed in radical oxidation between (100) and (111) Ge
  - Faster oxidation on (100) Ge, opposite to Si

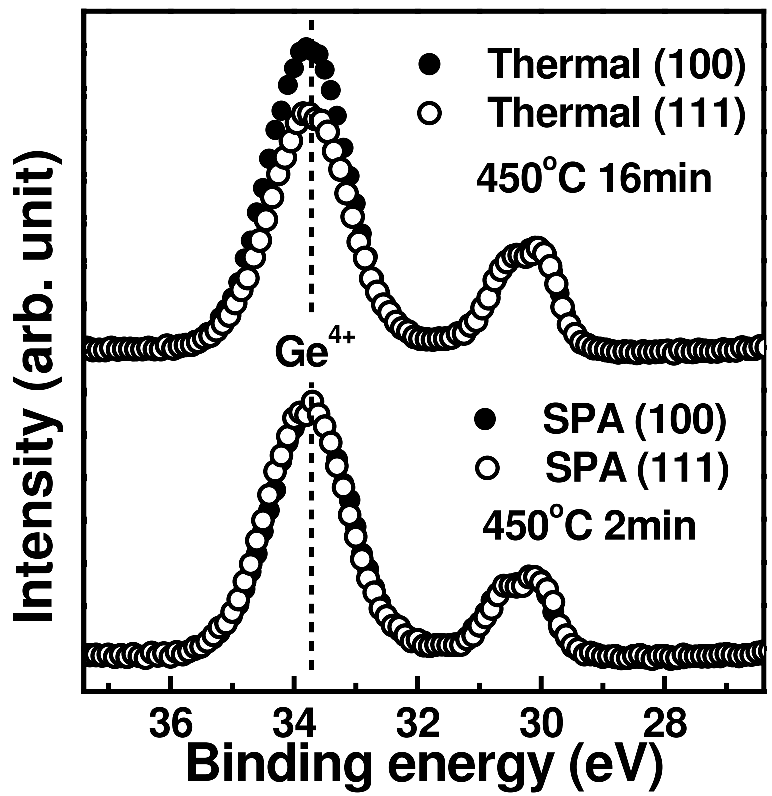




Oxidation rate (2)

- Radical vs thermal oxidation (XPS)
  - No orientation dependence was observed in radical oxidation between (100) and (111) Ge
  - Faster oxidation on (100) Ge, opposite to Si





Mechanism of orientation independence

- Thermal oxidation
  - Decomposition/evaporation limited oxidation process because of low decomposition temperature

(1) $Ge + O_2 \rightarrow GeO_2$

(2) $GeO_2 + Ge \rightarrow 2GeO(s)$

(3) $GeO(s) \rightarrow GeO(g)\uparrow$

  - In Si, SiO_2 decomposition/SiO evaporation rate is higher on (111) because of higher stress in SiO_2 on (111)*
  - By the analogy from Si, gross oxidation rate is higher on (100)

*J. R. Engstrom, Surf. Sci 1991

- SPA radical oxidation
  - Oxide formation is dominant because of highly reactive oxygen radicals

(1) $Ge + 2O^* \rightarrow GeO_2$

(2) $GeO_2 + Ge \rightarrow 2GeO(s)$

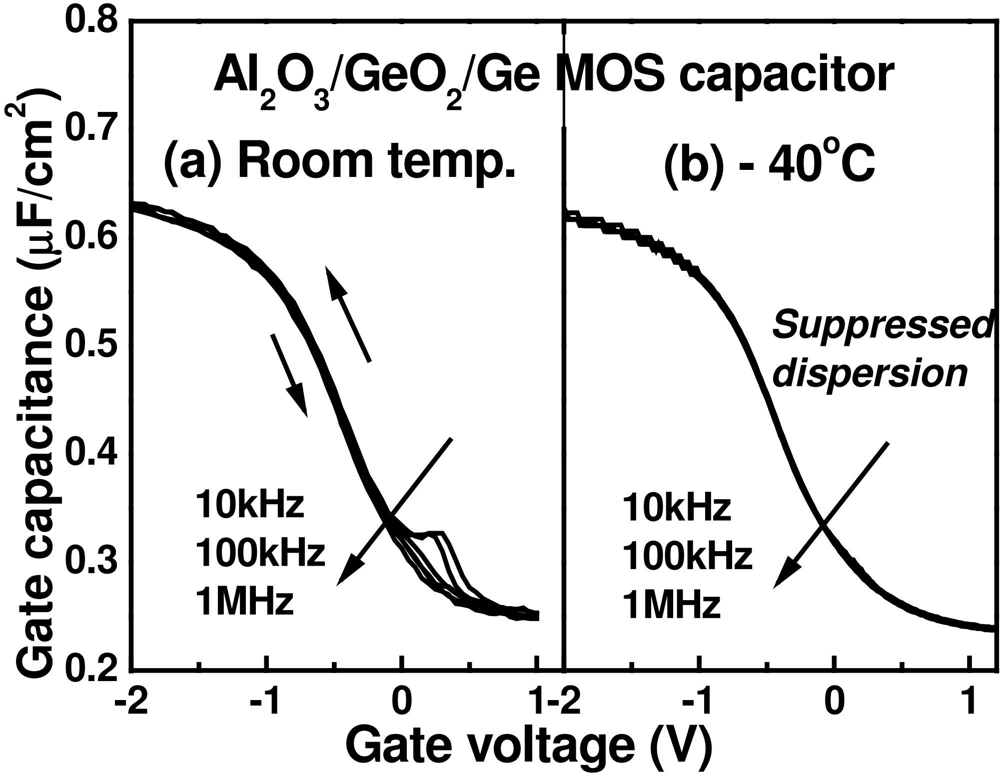
(3) $GeO(s) \rightarrow GeO(g)\uparrow$

  - Lower oxidation process can also suppress decomposition/ evaporation
  - Highly reactive oxygen radicals with small radius can penetrate on any orientated surface nearly at the same rate*

*T. Ohmi, Proc. IEEE 2001

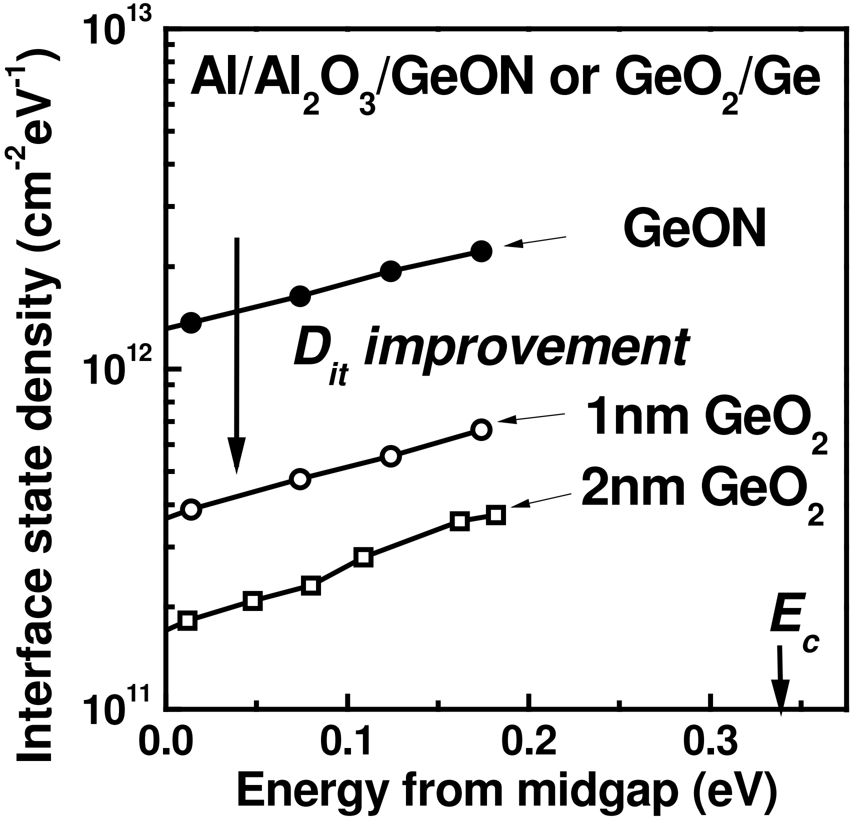
Electrical property of GeO_2/Ge interface (1)

- Al/Al_2O_3/GeO_2/Ge Ge MOS capacitor:
  - 350°C ALD Al_2O_3 deposition + 400°C FGA anneal
  - Very small hysteresis and frequency dispersion
  - Low temperature measurement suppresses frequency dispersion due to minority carrier response



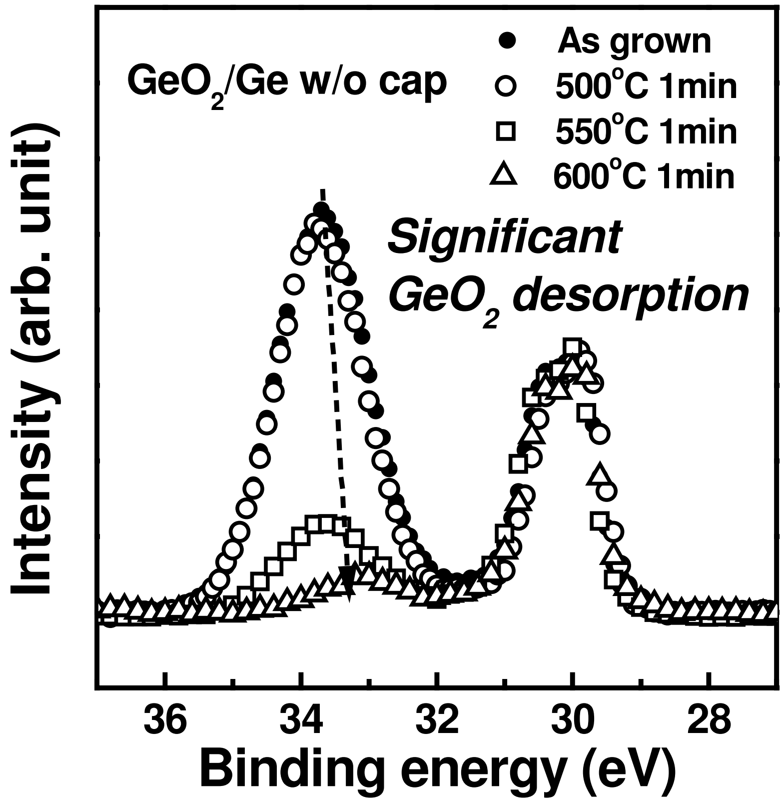
Interface state density (D_{it}) of GeO_2/Ge

- Comparison between GeON and GeO_2
  - D_{it} was measured by conductance method
  - Significant improvement from GeON
  - Achieved $\mathbf{D_{it} = 1.4x10^{11}cm^{-2}eV^{-1}}$ at midgap

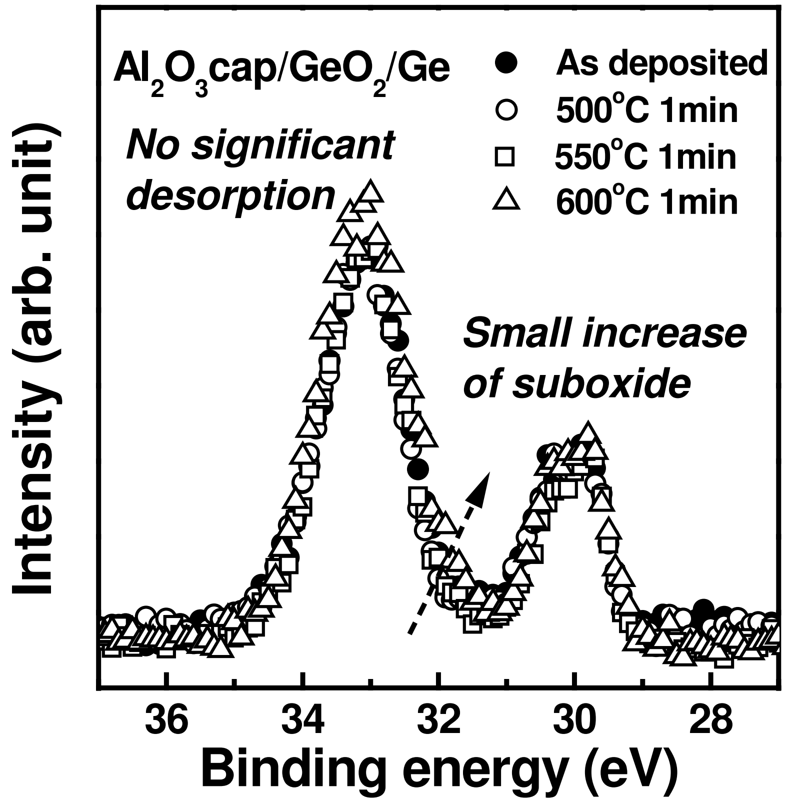


Thermal stability

- GeO_2/Ge
  - Significant GeO_2 decomposition and GeO out-diffusion

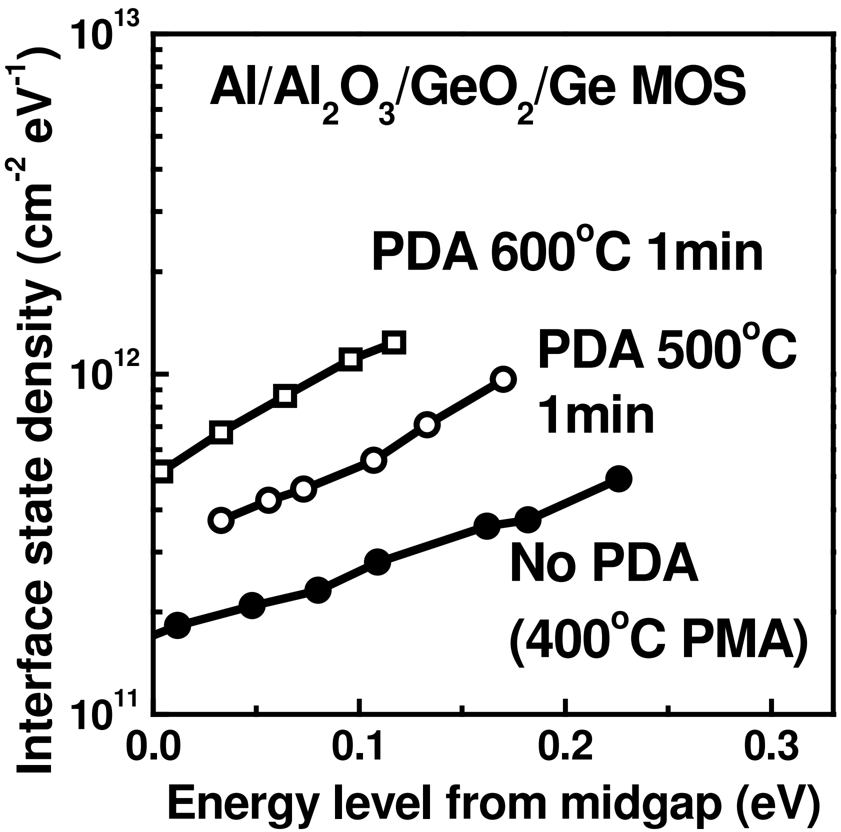


- Al_2O_3/GeO_2/Ge
  - Al_2O_3 works as an out-diffusion barrier and maintained GeO_2
  - Suboxide formation



Thermal stability of electrical property

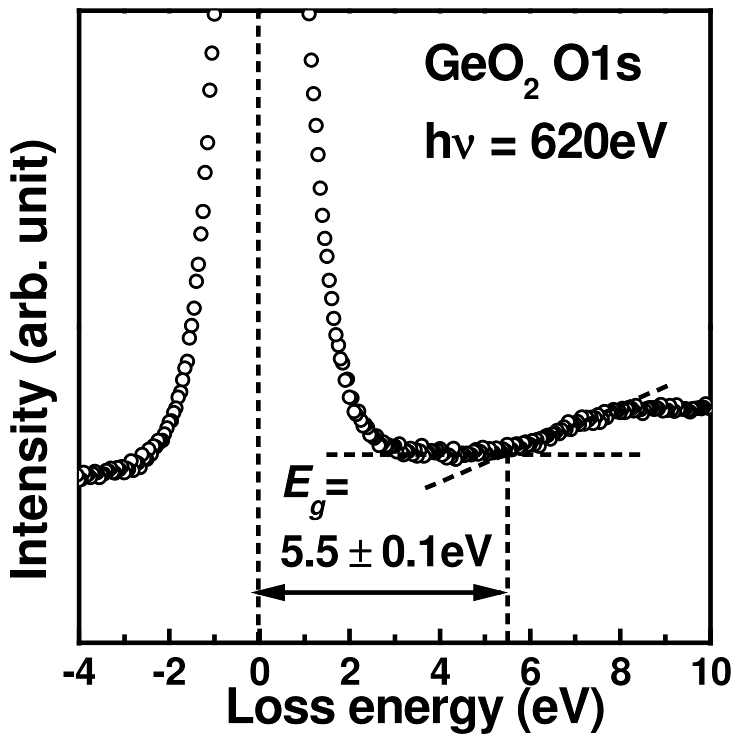
- D_{it} change after PDA
  - D_{it} can still be kept on the order of $10^{11}cm^{-2}eV^{-1}$
  - However, as low thermal budget as possible is required to avoid degradation due to suboixde formation

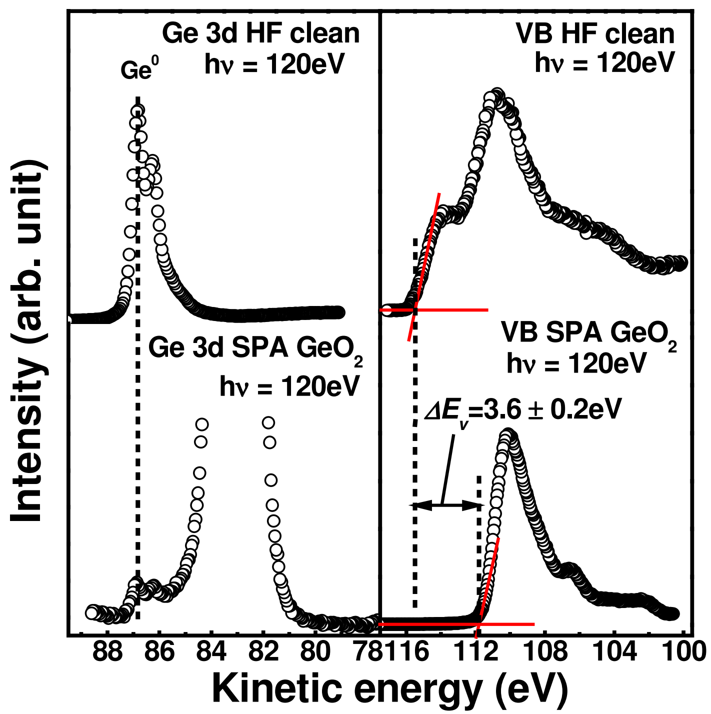


Band diagram by SRPES

- Build band diagram by SRPES
  - $E_{g\mathrm{GeO_2}}$=5.5eV
  - E_c=1.2±0.3eV, E_v=3.6±0.2eV, which satisfies criterion* of band offset > 1eV to suppress leakage

*J. D. Wilk, JAP2001





Summaries

- Orientation-independent oxidation was observed by SPA radical oxidation
  - Highly reactive oxygen radicals with small radius and low activation energy
  - Useful for uniform oxide formation in multi-gate FinFETs or nano-wire FETs
- Obtained excellent CV characteristics and achieved very low D_{it} ($1.4\text{x}10^{11}\text{cm}^{-2}\text{eV}^{-1}$)
- Build band diagram
  - Band offset (E_c=1.2±0.3eV, E_v=3.6±0.2eV) satisfies requirement of leakage suppression

Future works

- Gaurav Thareja will take over this project
- Scalability of GeO_2 interfacial layer
- MOSFET performance with GeO_2 interfacial layer grown by SPA radical system
- Application to multi-gate FET or nano-wire FETs