XPS Study of Ultrathin GeO_2/Ge System

Akio Ohta, Hiroaki Furukawa, Hiroshi Nakagawa, Hideki Murakami,
Seiichirou Higashi and Seiichi Miyazaki
Graduate School of Adavanced Sciences of Matter, Hiroshima University.
Kagamiyama 1-3-1, Higashi-Hiroshima 739-8530, Japan
TEL: +81-82-424-7648 ,FAX: +81-82-422-7038 E-mail: semicon@hiroshima-u.ac.jp

1. Introduction

Recently, there is much interest in High-k/Ge FET for the high performance application because of higher intrinsic mobility of Ge than that of Si [1]. The control of interfacial oxidation between high-k and Ge substrate is the one of key issues. It has been reported that the interfacial oxide layer was formed by post deposition anneal (PDA) in a similar fashion as a high-k/Si(100) systems [2]. However, the potential barrier height between ultrathin GeO_2 and Ge substrate especially conduction band (CB) offset is still a matter of research.

In this work, we extended our research to the GeO_2 formed by UV-O_3 oxidation on Ge substrate. Energy band profile and defects state density for the ultrathin GeO_2/Ge(100) structures were characterized by photoemission measurements and compared with SiO_2/Si(100) case.

2. Experimental

After wet-chemically cleaning p-type Ge(100) and Si(100) substrate, oxide layer was formed by UV-O_3 treatment at room temperature in ~9.0 torr. The electronic states of GeO_2/Ge(100) and SiO_2/Si(100) structures were characterized by in-situ X-ray photoelectron spectroscopy (XPS) and total photoelectron yield spectroscopy (PYS).

3. Results and Discussion

From the XPS analysis, we have found that Ge(100) surface is oxidized in a layer by layer manner using by UV-O_3 as well as Si(100) as shown in Fig. 1. And, UV-O_3 oxidation rates between GeO_2 and SiO_2 are almost constant in the oxide film thickness region below ~1nm.

The chemical composition of the ultrathin GeO_x films formed by UV-O_3 is almost constant in the thickness range from 0.4 to 1.9nm (Fig. 2.). Because of the fact that Ge $L_3M_{23}M_{23}$ auger signals overlap with the energy loss spectrum of

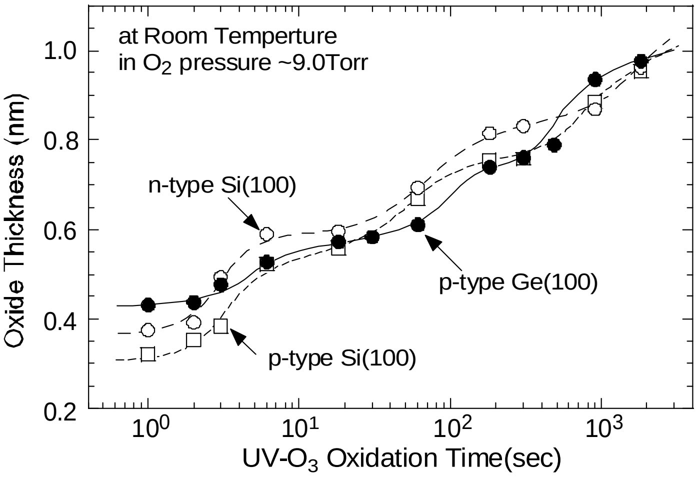

Fig.1 UV-O_3 oxidation rate for the p-type Ge(100), p-type and n-yep Si(100) at the room temperture in 9.0 Torr

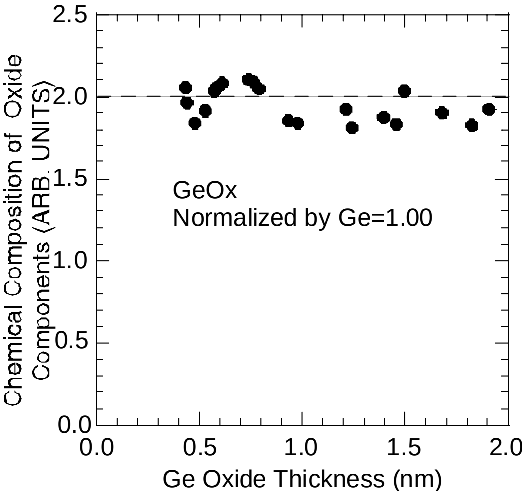

Fig.2 Chemical Composition of Oxide components for the Ultrathin GeO_2 formed by UV-O_3

the primary O1s core line signals [3], we determined the energy bandgap (Eg) of the GeO_2 ultrathin films from energy loss signals of Ge2p 3/2 photoelectrons (Fig. 3). Thus, the Eg of GeO_2 was determined to be 5.70eV±0.05eV in the thickness range from 0.9~1.9nm. This Eg is almost the same as the value of glassy GeO_2 measured by optical reflectance (5.63eV) [4]. To evaluate the valence band (VB) offset between GeO_2 and Ge(100), the VB spectra for GeO_2/Ge(100) were measured and deconvoluted into two components originated from GeO_2 and Ge(100) as shown Fig. 4. In the spectral deconvolution, the VB spectrum separately measured for wet-cleaned Ge(100) was used. From the energy separation of the tops of the deconvoluted VB spectra, the VB offset between GeO_2 and Ge(100) is determined to be 4.00eV±0.05eV. Considering the Eg of crystal Ge (0.66eV) and these result, the CB offset between GeO_2 and Ge(100) is obtained to be 1.04eV (Fig. 5). From the PYS measurements, we found that filled interface states at the GeO_2/Ge(100) is about one order of magnitude lager than that at SiO_2/Si(100) case in the same oxide thickness.

4. Conclusion

For the GeO_2/Ge(100) structure formed by UV-O_3, Ge(100) surface is oxidized layer by layer manner and UV-O_3 oxidation rates between GeO_2 and SiO_2 are almost constant in the oxide film thickness region below ~1nm. The energy band offsets between GeO_2 and Ge(100) are ~4.0eV in the valence band edge and ~1.04eV in the conduction band edge, respectively.

Acknowledgements

This work was partky supported by NEDO/MIRAI project.

Reference

[1] C. O. Chui et al., IEEE IEDM 2003 Technical Digest, pp437-440, 2003.

[2] Krishna. C. Sarawat et al., Ext. Abst. SSDM 2004 pp.718-719

[3] S. Miyazaki zet al., Microelec Eng. **48** (1993) 63.

[4] N. M. Ravindra et al., Phys. Rev. **B36** (1987) 6132.

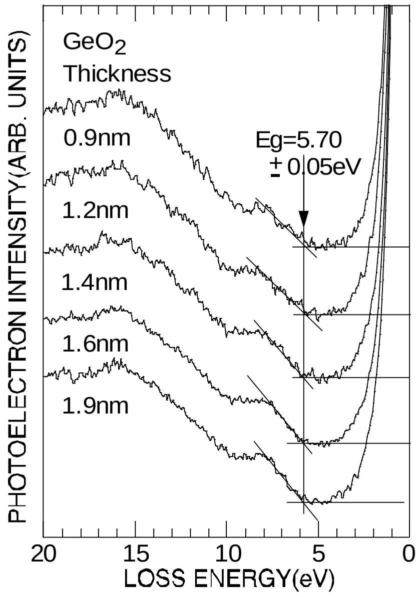

Fig.3 Ge2p 3/2 energy loss spectrum for the UV-O_3 oxidized GeO_2 in the thickness range from 0.9 to 1.9nm.

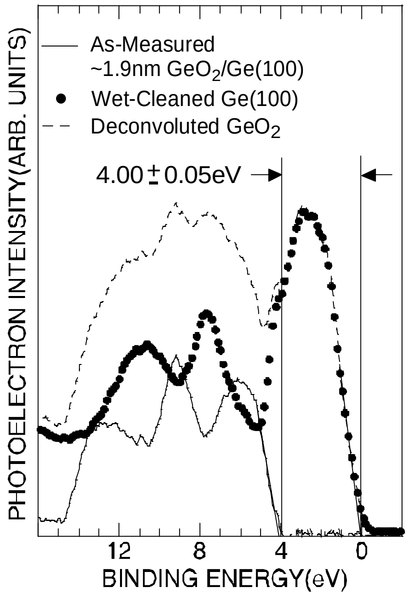

Fig.4 Valence band spectra for ~4.0nm thick GeO_2/Ge(100) structures

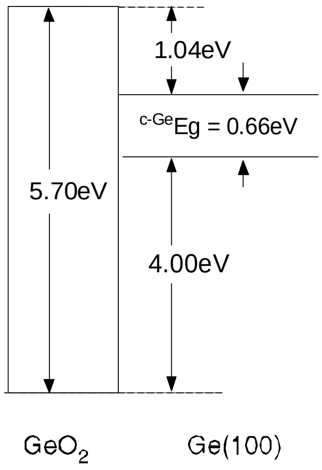

Fig.5 Energy band diagram for GeO_2/Ge(100) structure

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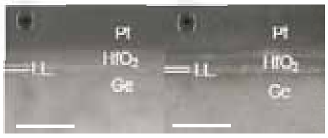
Motivation

★ There is much interest in High-k/Ge FET for the high performance application because of higher intrinsic mobility of Ge than that of Si

Control of Interface Oxide Layer Between high-k and Ge(100)

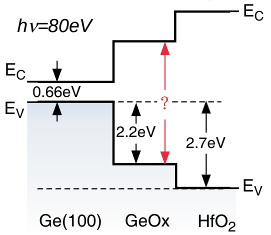
- Good Thermal Stability
- Lower Defect Density

As-Deposited   500°C N_2-Anneal



Krishna. C. Saraswat et al., Ext. Abst. SSDM 2004. pp.718-719

- **Energy Band Diagram for HfO_2/GeOx/Ge(100)**



Krishna. C. Saraswat et al., Ext. Abst. 10th Workshop on Gate Stacks. pp1-6

This Work Characterization of Chemical and Electronic Structures for GeO_2/Ge(100) System

SAMPLE PREPARATION

Ge(100) substrate
p-type ($\rho = 0.9\sim13.5\Omega/cm^2$)
Precleaning 20% HCl (5min)
10% H_2O_2 (5min)
2.5% HF (1min)
Pure Water Rinse

Si(100) substrate
p-type ($\rho = 0.01\sim0.02\Omega/cm^2$)
n-type ($\rho = 0.08\sim0.12\Omega/cm^2$)
Precleaning
$NH_4OH:H_2O_2:H_2O=0.15:3:7$(80°C, 10 min)
4.5% HF (1min)
Pure Water Rinse

UV-O_3 Oxidation : GeO_2(~2.0nm)
VUV 172nm : 7.2eV
at Room Temperture in O_2 : ~9.0Torr
Based Pressure: ~8.0x10^{-8}Torr
in-situ XPS・PYS

Thermal Oxidation : GeO_2(2.8~15.5nm)
500~600°C
in dry O_2 ~0.2L/min
760Torr
XPS

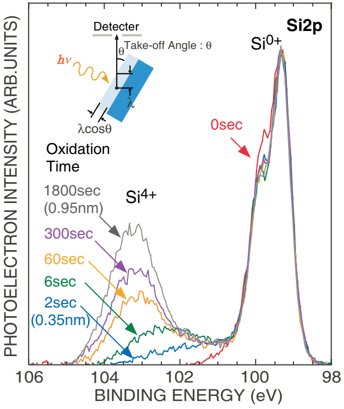
MEASUREMENTS

- X-ray Photoelectron Spectroscopy (XPS) Monocrolized Alkα : 1486.71eV
  - Core-line Spectra (Si2p,Ge2p,Ge3d and O1s) ⇨ Chemical Bonding Feature
  - O1s and Ge2p 3/2 Phoroelectron Energy Loss Spectra
  - Valence Band Spectra ⇨ Energy Band Profiles for GeO_2/Ge(100) System
- Total Photoelectron Yield Spectroscopy (PYS)
  ⇨ Energy Distribution of Electronic Defect Density

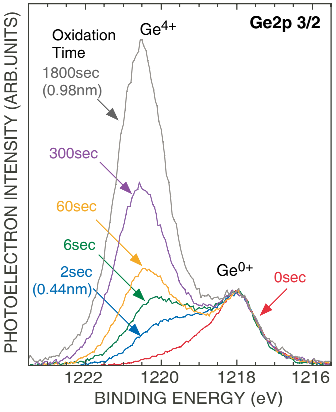
Si2p and Ge2p 3/2 Spectra for UV-O_3 Oxidized Si(100) and Ge(100) Substrate

Photoelectron Take-off Angle = 15°

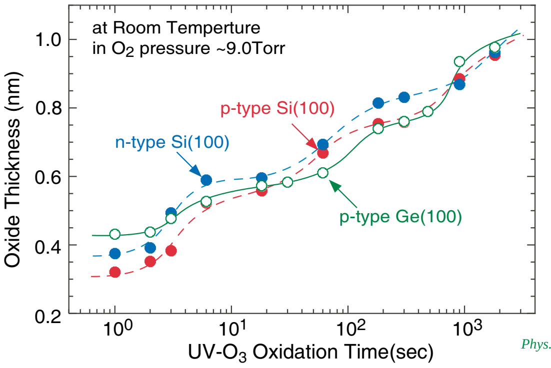
p-type Si(100) $Si2p^{0+}$ 3/2 : 99.3eV



p-type Ge(100) $Ge2p^{0+}$ 3/2 : 1218.0eV



UV-O_3 Oxidation Rate for p-type Ge(100), p-type and n-type Si(100)



Bond Length

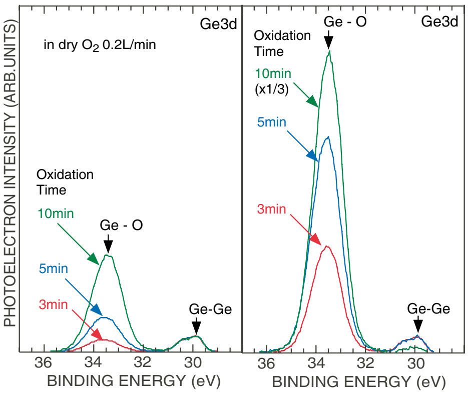
Si-O	0.161nm
Ge-O	0.169nm

*N. M. Ravindra et. al., Phys. Rev. B **69**, 195204 (2004)*

Ge3d Spectra for Thermally-grown GeO_2/Ge(100) Structure

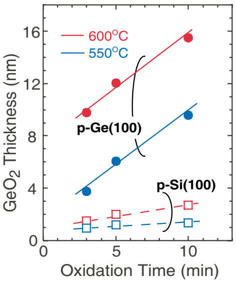
Photoelectron Take-off Angle = 90° $Ge3d^{0+}$ 7/2 : 29.9eV

550°C   600°C

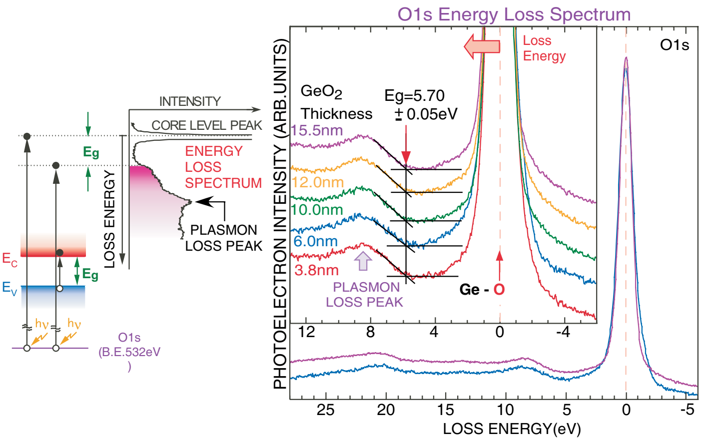


Oxidation Rate for Thermally-grown GeO_2

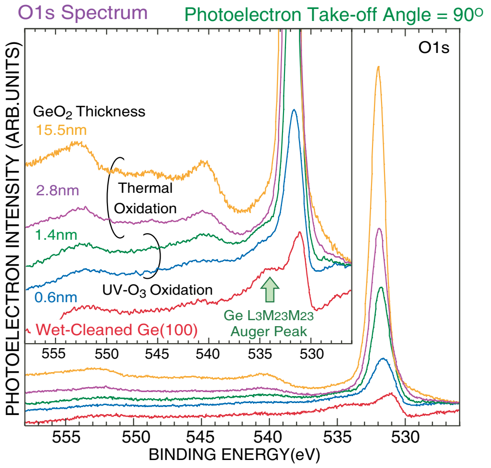
in dry O_2 0.2L/min



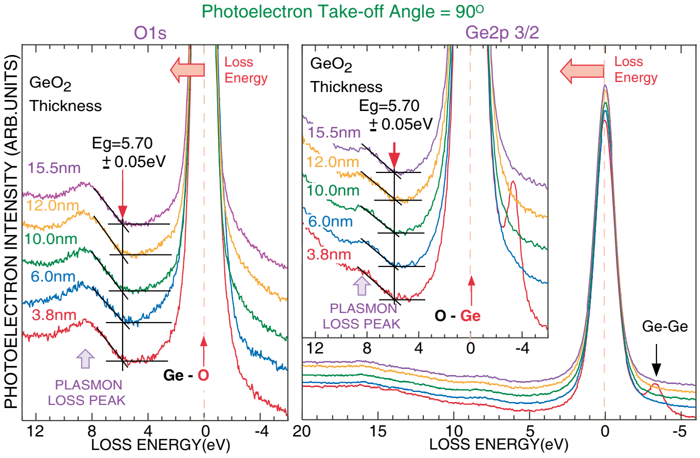
Determination of Energy Bandgap for Thermally-grown GeO_2 Films (3.8~15.5nm) from O1s Photoelectron Energy Loss Spectra



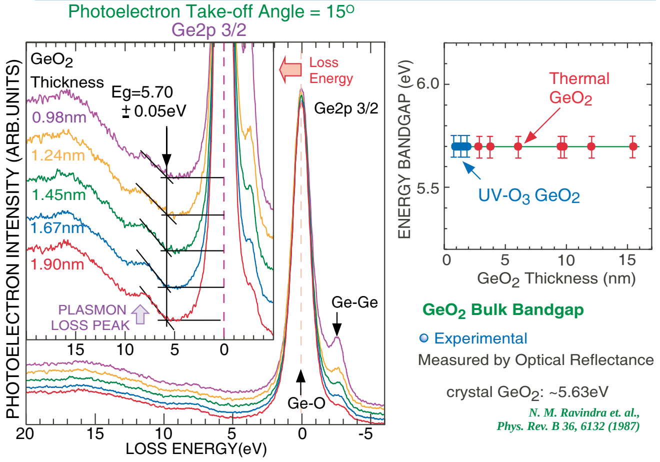
Determination of Energy Bandgap from O1s Photoelectron Energy Loss Spectra



Comparison Between O1s and Ge2p 3/2 Photoelectron Energy Loss Spectra for Thermally-grown GeO_2 films



Determination of Energy Band Gap for UV-O_3 GeO_2 Films (0.98~1.90nm) from Ge2p 3/2 Photoelectron Energy Loss Spectra



GeO_2 Bulk Bandgap

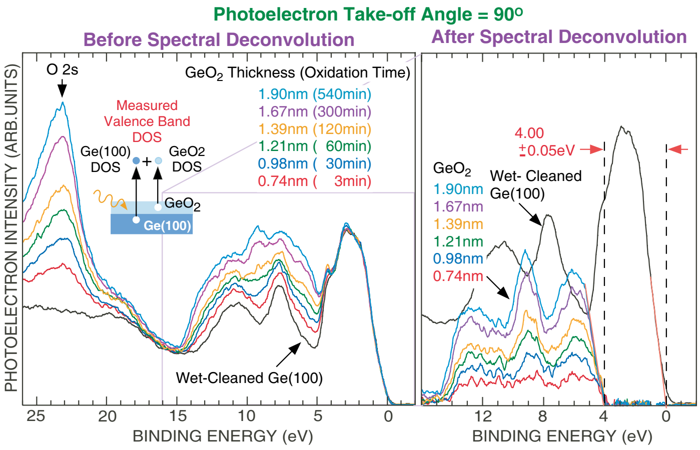
○ Experimental

Measured by Optical Reflectance

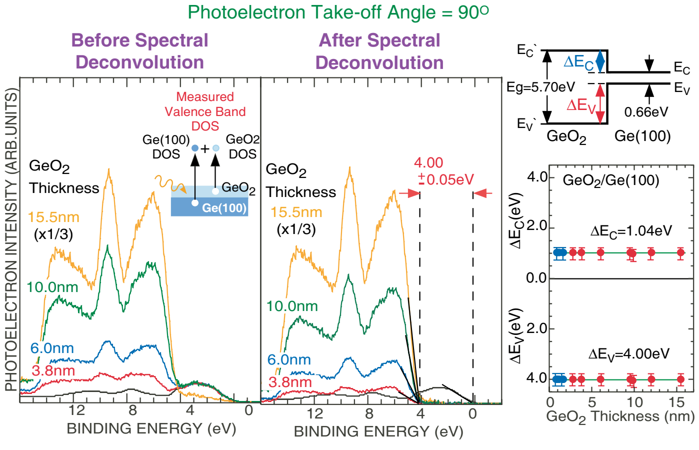
crystal GeO_2: ~5.63eV

N. M. Ravindra et. al., Phys. Rev. B 36, 6132 (1987)

Valence Band Spectra for UV-O_3 Oxidized GeO_2(0.74~1.90nm)/Ge(100) Structure and Deconvoluted Spectra

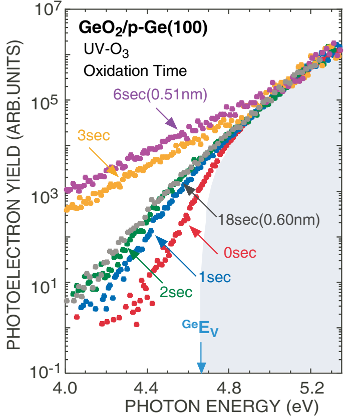


Valence Band Spectra for Thermally-grown GeO_2(3.8~15.5nm)/Ge(100) Structure and Deconvoluted Spectra

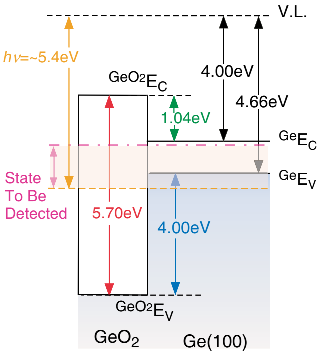


PYS Spectra and Energy Band Diagram for UV-O_3 Oxidized Ge(100)

PYS Spectra

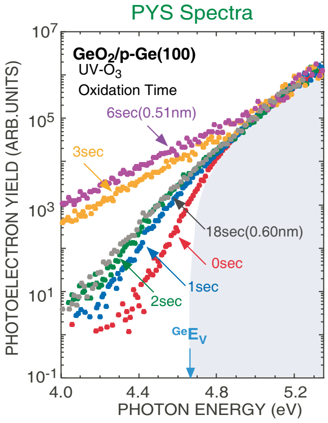


Energy Band Diagram

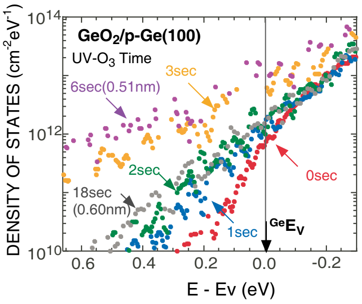


PYS Spectra and Energy Distribution of Electronic Defect States for UV-O_3 Oxidized Ge(100)

PYS Spectra

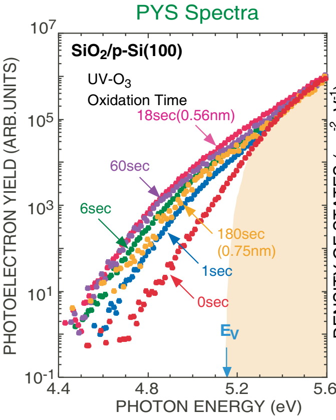


Energy Distribution of Electronic Defect States

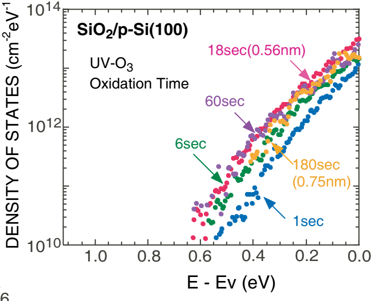


PYS Spectra and Energy Distribution of Electronic Defect States for UV-O_3 Oxidized Si(100)

PYS Spectra



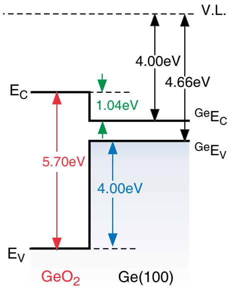
Energy Distribution of Electronic Defect States



Summary

Energy band profile and defects state density for the ultrathin GeO_2/Ge(100) structures were characterized by XPS and PYS

- For the GeO_2/Ge(100) structure formed by UV-O_3, Ge(100) surface is oxidized layer by layer manner and UV-O_3 oxidation rates between GeO_2 and SiO_2 are almost constant in the oxide film thickness region below ~1nm.
- The energy band offsets between GeO_2 and Ge(100) are ~4.0eV in the valence band edge and ~1.04eV in the conduction band edge, respectively.
- From the PYS measurements, filled interface states at the GeO_2/Ge(100) is about one order of magnitude lager than that at SiO_2/Si(100) case in the same oxide thickness.



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