Electronic structure characterization of La incorporated Hf-based high-k gate dielectrics by NEXAFS

Takashi Yamamoto[1, 2], Singo Ogawa[1], Masahiro Kunisu[1], Junichi Tsuji[1], Koji Kita[3], Masayuki Saeki[2], Yudai Oku[2], Hiroaki Arimura[2], Naomu Kitano[2], Takuji Hosoi[2], Takayoshi Shimura[2], and Heiji Watanabe[2]

[1] Toray Research Center Inc., [2] Department of Material and Life Science, Graduate School of Engineering, Osaka University, [3] Department of Material Engineering, The University of Tokyo

E-mail address: Takashi_Yamamoto@trc.toray.co.jp

Abstract

The electronic structures of lanthunum (La) incorporated hafnium (Hf)-based oxides (HfLaO) and their silicate (HfLaSiO) films were investigated by the Near Edge X-ray Absorption Fine Structure (NEXAFS) technique. The oxygen (O) *K*-edge spectra, which reflected the hybridized Hf 5*d* state with the O 2*p* orbital, were found to reveal features of the unoccupied state of the metal oxides, as well as the conduction-band edge. We also found that, while La incorporation into the Hf-based oxides simply changed the features of the conduction-band structure, subsequent thermal annealing of the La-incorporated films led to a conduction-band edge shift due to an interface silicate reaction and/or local bond rearrangement depending on the La concentration and annealing temperature. The impact of La incorporation into the Hf-based high-*k* materials on the electronic structure is discussed by taking into account the intrinsic nature of these metal oxides.

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[1] *Toray Research Center Inc., 3-7 Sonoyama 3-chome, Otsu, Shiga 520-8567, Japan*

[2] *Department of Material and Life Science, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan*

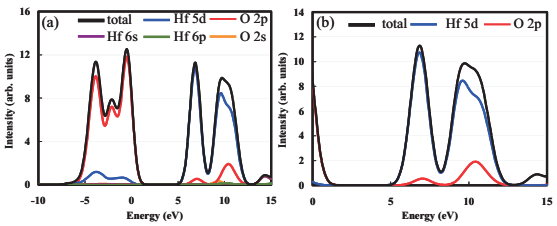
[3] *Department of Material Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*

Introduction

- Dual high-k technology has been proposed, in which different high-k materials are used for p-channel and n-channel FETs.
- However, the electronic structure, especially for the characteristics of the conduction-band minimum which affecting nFET performance with La-incorporated Hf-based oxides, has not been fully understood yet.
- Near Edge X-ray Absorption Fine Structure (NEXAFS) is a powerful technique for investigating electronic structure.
- In this study, we investigated electronic structure of HfLaO and HfLaSiO gate dielectrics by means of NEXAFS method.

DOS of cubic-HfO_2 by DV-Xα calculation

Calculation: DV-Xα, Structure model: cubic HfO_2



The density of state around the conduction-band minimum is formed by hybridization between Hf 5*d*-state and O 2*p* orbital.

Study of HfLaO electronic structure

Type 1

Structure: HfLaO (20nm) / SiO_2 (600 nm) / Si Substrate

Composition: Hf:La=10:0, 7:3, 5:5, 3:7

Deposition Method: Co-Sputter

Type 2

Structure: HfLaO (1 nm) / SiO_2 (1 nm) / Si Substrate

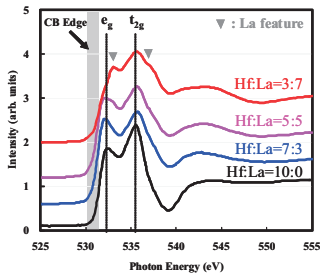
Composition: Hf:La=7:3, 3:7

Deposition Method: Co-Sputter

Annealing Condition: 600°C in N_2

O *K*-edge spectrum of thick HfLaO

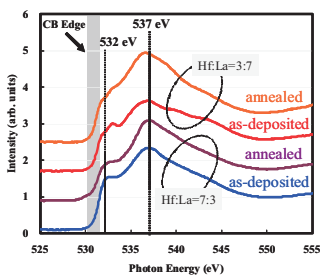
Samples: HfLaO (20 nm) /SiO_2 (600 nm) /Si Sub. (Hf:La= 10:0, 7:3, 5:5, 3:7)



These distinct changes indicate that La incorporation into HfO_2 results in changes in conduction-band structure.

O *K*-edge spectrum of thin HfLaO

Samples: HfLaO (1 nm) /SiO_2 (1 nm) /Si Sub. (Hf:La= 7:3, 3:7)



The structural change of Hf-based oxides by interfacial silicate reaction also causes changes in conduction-band structure.

Study of HfLaSiO electronic structure

Type 1

Structure: HfLaSiO / Si Substrate

Composition: Hf:La=1:0, 3:1, 1:1

Deposition Method: co-sputter SPIR method

Annealing Condition: 850°C

Type 2

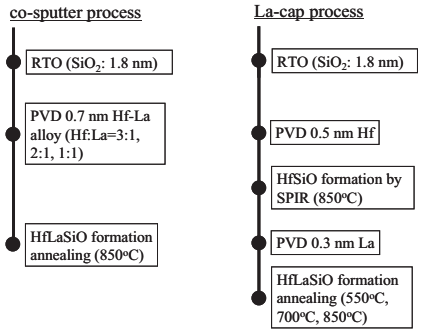
Structure: HfLaSiO / Si Substrate

Composition: Hf:La=5:3

Deposition Method: La-cap SPIR method

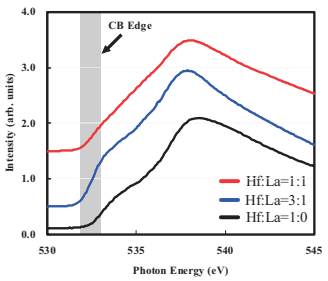
Annealing Condition: 550°C, 700°C, 850°C

HfLaSiO fabrication process



O *K*-edge spectrum of "co-sputter" HfLaSiO

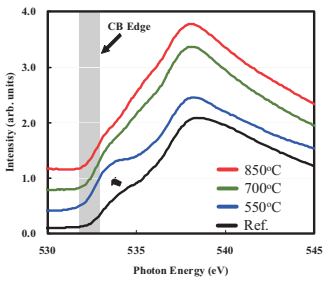
Samples: Co-sputter HfLaSiO /Si Sub. (Hf:La= 1:0, 3:1, 1:1)



The conduction-band edge of the HfLaSiO phase has shifted lower photon energy.

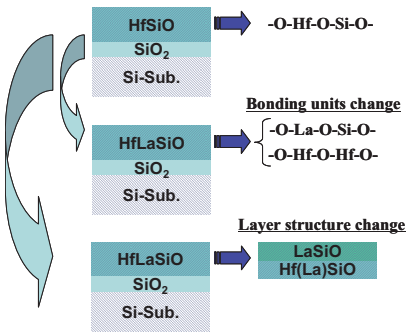
O *K*-edge spectrum of "La-cap" HfLaSiO

Samples: La-cap HfLaSiO /Si Sub. (Annealed temp. = 550°C, 700°C, 850°C)



The La incorporation by SPIR annealing at 550°C again resulted in increased absorption intensity around 532 eV.

Mechanism of the changes in spectrum



Conclusion

- It was found that the conduction-band edge structure formed by hybridized Hf 5*d* state with O 2*p* orbital is modulated by La incorporation.
- We also found that, whereas the electronic structure of thick HfLaO films is simply determined by the La concentration, the electronic feature of thin HfLaO and HfLaSiO films is modified by interface silicate reaction and/or change in the local bonding configuration driven by thermal annealing.
- As a results, the conduction-band edge of these metal oxides after annealing is mainly determined by HfO_2-like bonding. These findings provide a guideline for designing electric properties of La-incorporated Hf-based high-k gate dielectrics.