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A Theoretical Study of SiO₂-rich Zr and Hf Silicates as High-k Gate Insulators

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1. Introduction

A practically applicable high-k material should have a dielectric constant greater than that of SiO₂ (3.9) and be chemically inert on a Si substrate. Although considerable effort has been devoted to the development of such materials, only the few materials are currently known. These are Al₂O₃ and the SiO₂-rich Zr and Hf silicates that was developed by Wilk et al.[1] The silicates are mysterious materials because their dielectric constant (c.a. 10) is substantially larger than that of SiO₂ even though the Zr or Hf concentration in them is quite low (3-8 atom %). In this study, we have investigated the dielectric constants of the SiO2-rich Zr or Hf silicates by using electronic-structure based methods. Analysis of the vibrational dielectric constant, Evib, the dielectric constant due to atomic vibration of material, was found to be essential for an accurate estimate of the dielectric constant of high-k materials, including the above SiO2-rich silicates.

2. Method of Analyses

The SiO2-rich Zr and Hf silicates are amorphous materials. To date, the structure of these materials has not been subjected to a thorough experimental investigation yet. We constructed two models of silicates, called models A and B, from the structure of α -Cristobalite (SiO₂). The models were similar to those proposed by Lucovsky and Rayner[2]. Model A had 4-coordinated Zr or Hf atoms, while model B had 6-coordinated Zr or Hf atoms. The unit-cell structures of the models were energy-minimized by using the LDA pseudopotential method with ultrasoft pseudopotentials. CASTEP version 3.8 was used for the psudopotential calculation. The electronic dielectric constants, Eelec, of the models were calculated by using two different methods: the Lorenz-Lorenz (LL) and the random phase approximation (RPA) methods. Metal oxides such as the SiO₂-rich Zr and Hf silicates have metal-oxygen polyhedra as microscopic building units. Polarizabilities α of metal-oxygen polyhedra of models A and B were calculated by using the Becke3LYP molecular orbital (MO) method with the LanL2+POL basis set, and Eelec of the models were estimated from α of the polyhedra by using the LL formula. Gaussian 94 was used for the MO calculation. The RPA calculation of the models were made by using the CASTEP

software.

3. Results and Discussion

Fig.1 shows the energy-minimized unit-cell structure of models A and B for Zr atoms. The experimentally determined unit-cell structures of *α*-Cristobalite and Zircon (ZrSiO₄) are also shown for comparison. Model A had a unit-cell structure similar to that of α -Cristobalite, while mode B had a unit-cell structure considerably different from that of *\alpha*-Cristobalite. Mode B was energetically more stable than model A by 156 kJ mol⁻¹. Fig. 2 is a plot of the average length of Zr-O bonds in model B and Zircon. against the coordination number of the Zr atoms. The ranges of Zr-O bond lengths experimentally observed in several materials are shown for comparison. The average Zr-O bond length in model B was within the range of experimental results. These results indicated that the SiO₂-rich Zr silicates had 6-coordinated Zr atoms rather than 4-coordinated Zr atoms and were structurally similar to Fig. 3 shows the electronic band structures model B. calculated for model B with Zr atoms and that with Hf atoms, along the band structure of *α*-Cristobalite. Model B had a similar electronic structure regardless of whether it had Zr or Thus, the Zr silicates seemed to have a similar Hf atoms. electronic structure to that of the Hf silicates.

Table 1 lists Eelec calculated for a-Cristobalite, Zircon, and models A and B with Zr atoms, along with the corresponding experimentally determined values of Eelec and the electric dielectric constants, ε_{obs} . In the cases of both RPA and LL, the calculation reproduced the experimental \mathcal{E}_{elec} values of the materials but greatly underestimated the \mathcal{E}_{obs} . The degree of underestimation was particularly significant in the cases of Zircon and model B, which had been based on the assumption of similarity to the Zr silicates. The underestimation was essentially due to the neglect of ε_{vib} of the materials. Fig. 4 shows the experimentally determined \mathcal{E}_{elec} and \mathcal{E}_{obs} values for several high-k materials. The materials have very large ε_{vib} . Fig. 4 clearly shows that an estimation of Evib is essential for studying the dielectric constant of a high-k material. A method for estimating Evib of a material was thus developed and applied in calculating the dielectric constant of SiO₂. Results are given in Table The results indicate that the method is suitable for 2.

estimating the dielectric constants of materials and in the design of new high-k materials.

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Fig.1 Unit-cell structures: (a) α -Cristobalite (SiO₂);(b) Zircon (ZrSiO₄); (c) silicate model A; (d) silicate model B.



Fig. 3. Calculated electronic band structures: (a) α -Cristobalite; (b) silicate model B with Zr; (c) silicate model B with Hf.



Fig. 4 Experimentally determined ε_{elec} and ε_{vib} of high-k materials.

References

[1] G. D. Wilk, R. M. Wallace, J. M. Anthony, J. Appl. Phys. 87, 484 (2000).

[2] G. Lucovsky, G. B. Rayner Jr., Appl. Phys. Lett. 77, 2912 (2000).



Fig.2 Plot of Zr-O bond length vs. Zr coordination number

Table 1 Calculated and observed electronic dielectric constants ε_{elec} of materials. Observed ε_{elec} and electric dielectric constants ε_{obs} are also given.

Materials	Calc.		Obs.	
	RPA	LL	ε elec	€ obs
a-Cristobalite	2.7	2.5	2.3	3.9
Zircon	4.7	4.8	3.8	12.6
Model A with Zr	3.0	2.5	—	-
Model B with Zr	3.5	2.8	-	9.5

Table 2 Calculated and observed ε_{elec} and ε_{vib} of SiO₂.

Calc.	Obs.	
2.5	2.4	
1.1	1.5	
3.6	3.9	
	Calc. 2.5 1.1 3.6	