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Microscopic Effect of Nitrogen Doping on Dielectric Constant of Hf-silicate

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1. Introduction

Hafnium-silicates (HfSiOs) are, recently, one of most promising high-*k* gate dielectric materials for next generation CMOS transistor. It is experimentally known that nitrogen doped HfSiOs (HfSiON) have several favorable properties as gate dielectric: *e.g.* the high thermal stability of the amorphous state, more enhanced dielectric constant, drastically reduced leakage current through the dielectric layer, suppressed boron diffusion coefficients [1,2].

Recently, theoretical studies have been made by first-principles, for N doped Hf-oxides, investigating the effect of N doping on their electronic bands and leakage current characteristics [3,4]. However, the microscopic origin of the dielectric constant enhancement due to the N doping has still remained unclear. Dielectric constant of high-*k* gate dielectrics in the CMOS operation frequency range originates from the electronic and lattice polarization of the dielectrics, so that a first-principles study is necessary to clarify the origin.

In this study, effects of N doping into HfSiOs on their dielectric response have been investigated by first-principles. Effects of N doping on the electronic and lattice polarization contribution to dielectric constant are clarified, analyzing the electronic band structure and lattice vibration of HfSiOs in detail.

2. Methods and Models

First-principles calculations were based on the density functional theory (DFT) within the local density approximation (LDA). Kohn-Sham equations were solved by plane wave pseudo-potential (PWPP) method self-consistently, and dielectric constants were evaluated by considering both the electronic and lattice polarization contributions [5,6,7].

Calculations well reproduced experimental dielectric constants for α-quartz (α-SiO_2), hafnon ($HfSiO_4$) and monoclinic hafnia (m-HfO_2) as listed in Table I. Note the total dielectric constant of these materials; the value increases as the Hf content is increased, and the trend is similar to that observed in amorphous HfSiOs [1,2]. The trend is due to the significant increase of the lattice polarization contribution to total dielectric constant.

As model HfSiON structures, we used the super-cell of $(HfSiO_4)_8$ with the some O atoms of which being replaced by N atoms and O vacancies. Two insulating HfSiON model structures having a closed shell electronic structure were investigated (Fig.1). The first model has four N atoms and two vacancy sites (V^o), having a realistic N concentration of about 9 % ($Hf_8Si_8O_{26}N_4(V^o{}_2)$ model). The configuration of N atoms and V^o sites in the model is energy-optimized by calculating energies of models having several N and V^o configurations. We found that N atoms at the nearest neighboring site of V^o are energetically favored, as in the case of HfO_2 [4]. To clarify N effects on dielectric constant, $Hf_8Si_8O_{30}(V^o{}_2)$ model having no N atom but V^o also was studied.

3. Results and Discussion

Calculated dielectric constants of $Hf_8Si_8O_{32}$, $Hf_8Si_8O_{30}(V^o{}_2)$ and $Hf_8Si_8O_{26}N_4(V^o{}_2)$ models are listed in Table II, along with the electronic and lattice polarization contribution to dielectric constant. $Hf_8Si_8O_{26}N_4(V^o{}_2)$ model has a higher dielectric constant than those of other models having no N atom, being in accord with experiments, which show the dielectric constant of HfSiOs can be increased by N doping [1,2]. The higher dielectric constant of $Hf_8Si_8O_{26}N_4(V^o{}_2)$ model originates from the significant increase of the lattice polarization contribution. The electronic polarization contribution to total dielectric constant also is increased in $Hf_8Si_8O_{26}N_4(V^o{}_2)$, compared with that of $Hf_8Si_8O_{32}$ model. To understand the results, we analyzed the contributions to total dielectric constant in relation to the electronic band structure and lattice vibration.

Fig.2 shows calculated electronic density of states (DOS) of these models. Significant differences are seen between the models in DOS around band gap. $Hf_8Si_8O_{26}N_4(V^o{}_2)$ model has valence bands with N-*p* character over those with O-*p* character, in energy, and therefore has a reduced band gap. The electronic transition from the N-*p* bands to the conduction bands accounts for the increase of electronic dielectric constant, compared with that of $Hf_8Si_8O_{32}$ model. Besides, $Hf_8Si_8O_{26}N_4(V^o{}_2)$ model has mid-gap V^o levels. The electronic transitions from valence bands to the V^o levels also contributes to the higher electronic dielectric constant.

In addition, from comparison between Fig.2(b) and (c), the mid-gap V^o levels in HfSiOs are found to be elevated by about 2 eV due to N doping, similar to the V^o levels in HfO_2 [4]. This implies that N doping drastically reduces the electron leakage current through HfSiOs gate dielectrics, as proposed for HfO_2 [4].

Lattice dielectric constants of the models were analyzed in terms of Born effective charge and lattice vibration mode. It is noted that there is no remarkable difference in Born effective charge of Hf, Si and O atoms between $Hf_8Si_8O_{32}$ and $Hf_8Si_8O_{26}N_4(V^o_2)$ models, even in that of atoms located near to the N and V^o sites. Fig.3 shows weighted phonon DOS (WPDOS) of the models; the WPDOS is non-zero for infra-red active modes, and the integration of WPDOS gives lattice dielectric constant [8]. Overall, there are some high peaks at frequencies of $Hf_8Si_8O_{32}$ infra-red modes. $Hf_8Si_8O_{26}N_4(V^o_2)$ model has additional low WPDOS in the low-frequency region of 50 - 300 cm^{-1}, and these low-frequency modes make the lattice dielectric constant of the model higher. It is found that these low-frequency phonon modes are mainly due to the displacement of Hf and/or Si atoms located near to N and V^o sites.

4. Conclusions

Effects of nitrogen doping on the Hf-silicates dielectric constant have been examined by first-principles. It is shown that the nitrogen doping increases the dielectric constant of the silicates, enhancing both the electronic and lattice polarization contributions. The lattice polarization originating from low-frequency phonon modes is found to play the substantial role in the dielectric constant enhancement in N-doped Hf-silicates. Furthermore, it is found that the nitrogen doping significantly reduces the electron leakage current through Hf-silicates gate dielectrics.

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Table I: Calculated total dielectric constants, and electronic and lattice polarization contributions to the dielectric constants, of gate dielectric materials in the crystal phase.

Material	Total	Lattice	Electron
α-SiO_2	4.9	2.3	2.6
$HfSiO_4$	9.7	5.8	3.9
m-HfO_2	15.2	10.2	5.0

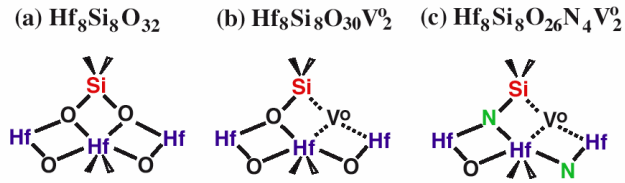

Fig.1: Schematic illustrations of Hf-silicate model structures: (a) $Hf_8Si_8O_{32}$; (b) $Hf_8Si_8O_{30}(V^o_2)$; (c) $Hf_8Si_8O_{26}N_4(V^o_2)$.

Table II: Calculated total dielectric constants and electronic and lattice polarization contributions to the dielectric constants, of Hf-silicate models.

Model	Total	Lattice	Electron
(a) $Hf_8Si_8O_{32}$	9.7	5.8	3.9
(b) $Hf_8Si_8O_{30}(V^o_2)$	10.9	6.4	4.5
(c) $Hf_8Si_8O_{26}N_4(V^o_2)$	11.5	7.1	4.4

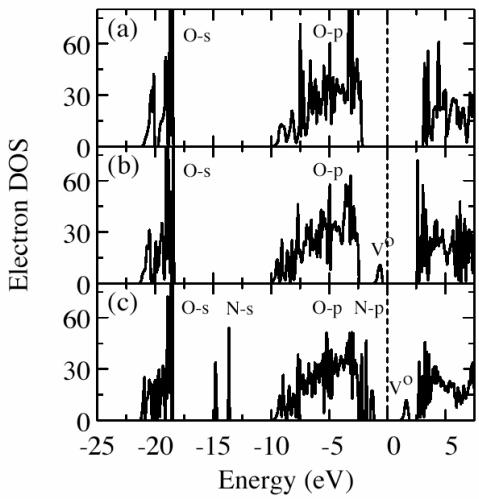

Fig.2: Electronic density of states (in states/eV/cell) for (a) $Hf_8Si_8O_{32}$, (b) $Hf_8Si_8O_{30}(V^o_2)$ and (c) $Hf_8Si_8O_{26}N_4(V^o_2)$ models. Occupied (unoccupied) states are located below (above) energy origin.

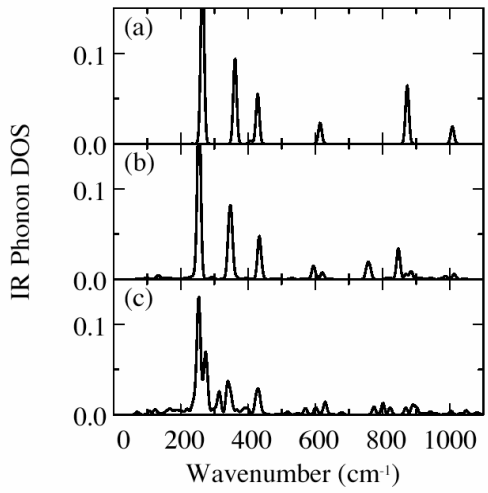

Fig.3: Weighted infra-red active phonon density of states at Γ point (in states/cm^{-1}/cell) for (a) $Hf_8Si_8O_{32}$, (b) $Hf_8Si_8O_{30}(V^o_2)$ and (c) $Hf_8Si_8O_{26}N_4(V^o_2)$ models.