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Ab initio modeling of electronic and optical properties of hafnium silicates

Li-Ping Feng *, Zheng-Tang Liu, Bing Xu

State Key Lab of Solidification Processing, College of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an, Shaanxi 710072, China

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ABSTRACT

Ab initio calculations are used to investigate the electronic structure and optical properties of crystalline monoclinic hafnium silicates ($Hf_{1-x}Si_xO_2$) as a function of silicon content x ($x = 0$, 0.25, 0.50, and 0.75). Densities of states (DOS), electronic band gaps, refractive indices and extinction coefficients of $Hf_{1-x}Si_xO_2$ are calculated through a screened exchange (sX) method within the local density approximation (LDA). Calculational results of the DOS of $Hf_{1-x}Si_xO_2$ indicate that these oxides are insulators. Electronic band gaps of $Hf_{1-x}Si_xO_2$ are found to increase with increasing the silicon content. The results of optical constants of $Hf_{1-x}Si_xO_2$ show that increasing silicon content produces a lower refractive index and a smaller extinction coefficient. The present predicted results exhibited a good agreement with the recently reported experimental observations.

1. Introduction

In order to continue scaling electronic devices, an alternative gate material with high-k oxides has been proposed for capacitors, memories, and optoelectronic devices in future CMOS generations. In particular, $Hf_{1-x}Si_xO_2$ are of great interest because they remain amorphous up to higher temperatures and preserve a lower leakage current than pure HfO_2 [1,2]. Moreover, hafnium silicates can minimize the occurrence of grain boundaries [3]. In addition to their potential use as gate dielectric, $Hf_{1-x}Si_xO_2$ may also be used as optical coatings because of their low refractive index and low extinction coefficient [4].

Properties of amorphous $Hf_{1-x}Si_xO_2$ have been extensively studied, and some theoretical analyses have been applied to explain experimental observations. However, crystalline state $Hf_{1-x}Si_xO_2$ has received little attention. Recently, Tomida [5] has observed that the dielectric constant ε of crystalline tetragonal $Hf_{1-x}Si_xO_2$ can reach 27, substantially larger than that of amorphous state $Hf_{1-x}Si_xO_2$ ($\varepsilon \leqslant 20$). Furthermore, it was experimentally demonstrated that stabilization of the high permittivity crystalline state hafnium silicates can be achieved by Si incorporation [6]. Hence, it acquires prime importance to determine the performance of crystalline state $Hf_{1-x}Si_xO_2$, which may be the high-k candidates as gate dielectric replacement. Electronic properties of $Hf_{1-x}Si_xO_2$ used as gate dielectrics should be understood well before actual use. Additionally, accurate knowledge of the refractive indices and absorption coefficients is indispensable for understanding the electronic structure of $Hf_{1-x}Si_xO_2$ as well as for the design and analysis of various optoelectronic devices. These considerations call for a systematic theoretical study of electronic and optical properties of $Hf_{1-x}Si_xO_2$ as a function of silicon content x.

In this paper, discussions will focus on the influence of Si doping on the electronic structure and optical properties of crystalline monoclinic $Hf_{1-x}Si_xO_2$. DOS, electronic band gaps, refractive indices and extinction coefficients for $Hf_{1-x}Si_xO_2$ in monoclinic phase will be calculated. Results will be compared with previous calculations and experimental data when available.

2. Method

It is well known that first-principles calculation of the electronic structure of semiconductors and insulators using the LDA can give good ground state properties such as total energies and structures, but it usually leads to a severe underestimate of the band gap by typically 30–50% [7]. To solve the band gap problem, the sX method or weighted density approximation (WDA) can be applied. It was widely accepted that the sX method can give good band gaps for a number of semiconductors and oxides [8,9]. Moreover, the sX method can be used as a better functional during the

* Corresponding author. Tel.: +86 29 88492178; fax: +86 29 88492642.
E-mail address: phdlpfeng@yahoo.com (L.-P. Feng).

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energy minimization than the WDA [10]. Accordingly, in this paper ab initio modeling were performed with the sX method of Bylander and Kleinman [11], which takes a screened version of the Hartree–Fock exchange function plus the correlation function from LDA,

$$V_{sX}(r,r') = -\sum_i \frac{\psi_i(r)e^{-k|r-r'|}\psi_j^*(r)}{|r-r'|} \quad (1)$$

here V_{sX} is the non-local screened exchange potential, Ψ are the Kohn–Sham orbitals and k is the Thomas–Fermi screening wavevector.

Supercells for $Hf_{1-x}Si_xO_2$ containing 96 atoms with silicon content $x = 0$, 0.25, 0.50, and 0.75 were generated by substituting Hf atoms with Si atoms in monoclinic phase. The valence electron wave functions are expanded in plane-wave basis sets. The core-valence interactions are described by norm-conserving pseudopotentials ([12] for Hf, [13] for Si and O). The semicore states of Hf are treated explicitly. The Brillouin zone of the supercells is sampled with Monkhorst–Pack k-point grid [14]. For the supercells a $[8 \times 8 \times 8]$ k-point mesh is used. The plane-wave cutoff energy in our calculations is 900 eV. This set of parameters assures a total energy convergence of 1×10^{-6} eV per atom. All calculations are carried out using the implementation provided in the CASTEP software package [15].

In the study of optical properties, refractive indices and extinction coefficients of $Hf_{1-x}Si_xO_2$ are calculated. In the Sellmeier dispersion model, the real part ε_1 and imaginary part ε_2 of the complex dielectric function can be expressed, related to refractive index n and extinction coefficient k, as [16,17]

$$\varepsilon_1 = n^2 - k^2 \quad (2)$$

$$\varepsilon_2 = 2nk \quad (3)$$

According to the Kramers–Kronig relationship, the real and imaginary parts of the complex dielectric function can be derived. Then, the refractive index n and extinction coefficient k can be solved from Eqs. (2) and (3).

3. Electronic properties

Fig. 1 shows the partial and total DOS of HfO_2 ($x = 0$). It is found that the lower valence band from −18 eV to −15 eV is composed of O-2s states. The upper valence band in the energy ranges from −5 eV to 0 eV is essentially dominated by O-2p states, with a minor presence of Hf-d states from the hybridization with the O-2p states. Moreover, the s state of O atom and s, p states of Hf atom are also contributing to the upper valence band, but the values of densities of these states are quite small compared to O-2p and Hf-d states. The presence of these orbitals in the bonding states regions indicates a covalent bonding in the material. The unoccupied conduction band from 5.6 eV to 10 eV consists essentially of Hf-d states. Our calculated results of the DOS of HfO_2 agree with previous theoretical work [18].

Fig. 2 displays the total DOS of $Hf_{1-x}Si_xO_2$ at $x = 0.25$, 0.50, and 0.75. After Si incorporation, the valence and conduction bands of $Hf_{1-x}Si_xO_2$ ($x > 0$) are wider than that of pure HfO_2. And the band widths increase with increasing silicon content x, which indicates the covalent bond getting stronger in $Hf_{1-x}Si_xO_2$. Furthermore, it can be also seen from Fig. 2 that the conduction bands of $Hf_{1-x}Si_xO_2$ are far from the Fermi level with increasing x. On the other hand, the observed flatness of the valence bands shows that these Hf–silicates are insulators, which is consistent with experimental findings [19,20].

For HfO_2, the electronic band gap was calculated with the sX method and was found to be 5.5 eV, which is in good agreement with experimental data [21]. For $Hf_{1-x}Si_xO_2$ ($x \geqslant 0$), the calculated

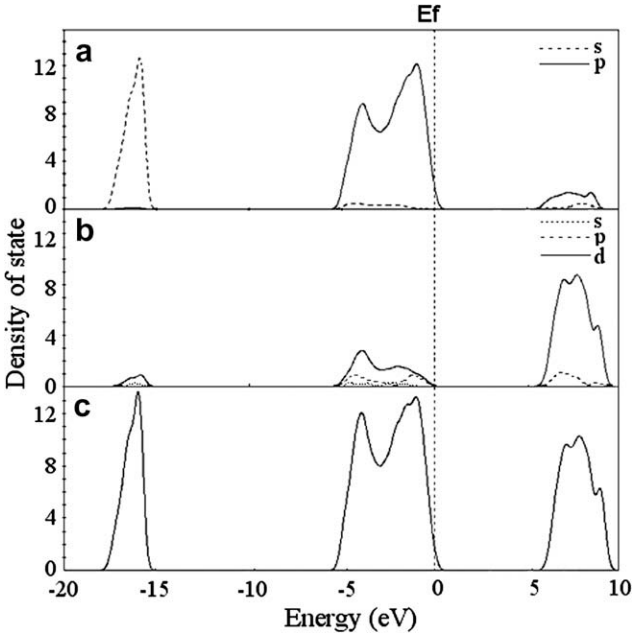

Fig. 1. The atomic projected PDOS of O (a), Hf (b) and total DOS of HfO_2 (c).

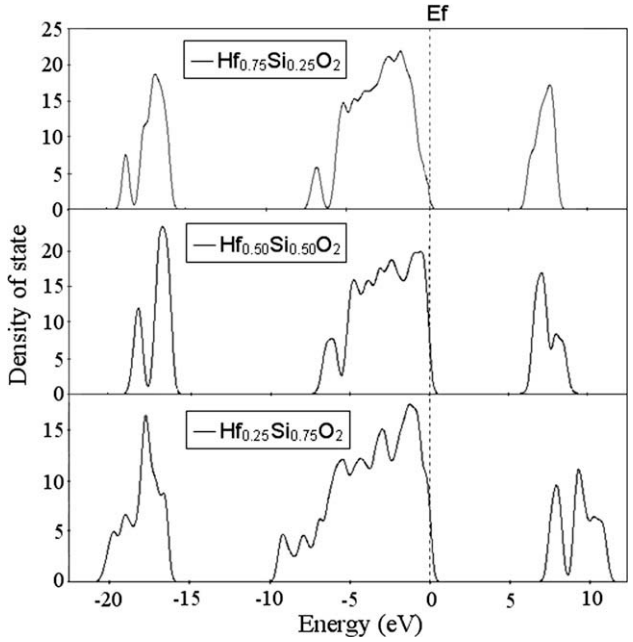

Fig. 2. The calculated total DOS of $Hf_{1-x}Si_xO_2$ at $x = 0.25$, 0.50, and 0.75.

electronic band gaps as a function of x are given in Fig. 3, where they are compared with experimental values [21–23]. In Fig. 3, it is clearly that different literature reported different experimental data for the band gaps of $Hf_{1-x}Si_xO_2$. According to our calculations, the results are in agreement with the most recent experimental observations of Jin [21], whereas earlier experimental data give higher band gaps for hafnium silicates [22,23]. Compared with previous theoretical works, calculational results are a little less than those of Broqvist [24] because of the different model structure. For all studies, the band gaps of $Hf_{1-x}Si_xO_2$ are found to increase with increasing silicon content. This can be noticed by the presence of an insulating feature as shown in the DOS's of these materials. The conduction bands of $Hf_{1-x}Si_xO_2$ have the tendency to move