Structural and optical properties of carbon contaminated HfO_2: First principle study

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Abstract

The role of substitution carbon defect on the structural properties and dielectric constant of monoclinic hafnium dioxide was investigated by adopting density functional theory calculations. Local vibration modes for various doping mechanisms of carbon have also included in the calculations. Results show that carbon substitution for oxygen is more energetically favorable than substitution for hafnium. Additionally, carbon has an anisotropic and divergent impact upon the dielectric constant based upon hosted site. For oxygen site, the dielectric constant achieves 4.709, whereas it decreases to 4.128 for the case of both hafnium sites. Calculated vibrational frequencies (836.09, 862.39 and 1507.64 and 1508.55) provide valuable information toward verifying the existence of carbon in m-HfO_2.

الخلاصة

تمت دراسة الخواص التركيبية وثابت العزل الكهربائي لثنائي اوكسيد الهفنيوم ذات التركيب احادي الميل والمشوب بالكاربون. كما شملت الدراسة ايضا انماط الاهتزاز الموضعية لمواقع التشويب المختلفة. بينت النتائج ان الكاربون يمكن ان يحل محل الاوكسجين بصوره اكثر استقرارا من احلاله بدلا من الهفنيوم. اضافة الى ذلك فأن الكاربون له تأثير غير متناظر ومختلف على ثابت العزل وذلك اعتمادا على الموقع الذي يشغله الكاربون في التركيب. ففي حالة التشويب في موقع الاوكسجين فان ثابت العزل الكهربائي يصل الى 4.709 في حين يكون مقداره 4.128 في حالة الهفنيوم. أما ترددات انماط الاهتزاز فقد تم حسابها وقد وجد بأنها تساوي (836.09, 862.39, 1507.64, 1508.55) والتي توفر معلومات كافية لغرض التحقق من وجود الكاربون في هذه المادة عملياً.

1. Introduction:

The semiconductor industries are derived by two main characteristics, which are performance and portability. These desirable properties have been achievable by scaling down the integrated circuits in electronic devices according to Moor's law [1]. This law has been adopted as benchmark by the devices' industries. The ongoing shrinking of electronic devices components has faced a technical limitation leading to device failure [2]. This is belonging to the demand for new effective dielectrics to alternate traditional oxide [3]. Hafnium dioxide (HfO_2), known as hafinia, has been proposed as an effective oxide for this purpose [4]. The high permittivity of around 25-30 [5] and the wide band gap around 5.8 eV [6] of HfO_2 make this material as on of the convenient replacement for SiO_2. Hafnium dioxide is an inorganic compound and generally exists in both crystalline and amorphous states. It crystallizes in three different phases, which are cubic, tetragonal and monoclinic. These three phases of hafnium dioxide are shown in Figure.1.

Hafnium dioxide thin film can be deposited using low temperature deposition method, but the crystallization temperature of HfO_2 is low [7]. Hence, in a high temperature fabrication processing, the HfO_2 tends to crystallize. The monoclinic phase is the most stable phase in the ambient temperature [8]. Therefore, the monoclinic phase is adopted as reference material in this study. Chemical vapor deposition method is commonly used for growing gate oxide for a long time, but it is not suitable for depositing HfO_2. The main issue in this method is the organometallic derived source materials such as $Hf(O\text{-}t\text{-}C_4H_9)_4$ and $Hf(NO_3)_4$ [9]. The abundance of oxygen in these sources leads to HfO_2 with an oxygen rich environment. Thus, it is difficult to avoid the unwanted interfacial layer of SiO_2. The developed atomic layer deposition method is more preferable method to fabricate HfO_2 film. Metal precursor used for metal source does not have oxygen in its structure. The $Hf[N(C_2H_5)_2]_4$ is generally preferred precursor for depositing HfO_2 film in the nano-scale [10]. However, recent experimental studies suggest that the HfO_2 film produced by atomic layer deposition method using metal organic Hf

precursor such as $Hf[N(C_2H_5)_2]_4$ contains carbon impurity[11,12,13]. The accidental doping of carbon is expected to have noticeable impact upon the properties of HfO_2 film. The microscopic investigation of such impact hasn't been documented yet. Thus, the impact of carbon on the structure and optical properties of HfO_2 film is the main motivation of the current study.

2. Computational Methodology:

All the calculations have been carried out using density-functional theory within the local density approximation [14] as implemented in AIMPRO code [15]. The super-cell approach was adopted to represent pure and defective system of HfO_2**.** Super-cell with more than 48 atoms is usually needed to calculate accurate energies and properties of the system under consideration. However, simulating and optimizing a super-cell of 12 atoms have been employed to optimize the wave function basis set for carbon defect. In other word, the 12 atoms super-cell has been used to find the suitable basis set of carbon. The procedure can be described as follow: One Hf atom has been replaced by one C atom in the 12-atoms super-cell and the model is optimized. This procedure has been repeated seven times and each time different wave function basis set of carbon atom is considered. For instance, the CO_2 basis set of C implies that the C atom has been described as C in CO_2 molecule and similarly for other basis set (CO, diamond, graphite, SiC and CH_4) of C. Table.1 shows the different basis set, the corresponding number of basis functions for describing C atom and the total energy of the related C doped HfO_2 structure.

It is obvious from the table that the wave function basis set of carbon monoxide (CO) with 40 functions has the lowest energy. It implies that CO basis set is the best basis set for describing C in m-HfO_2. The behavior is belonging to the formation of carbon oxide when carbon has been incorporated in m-HfO_2. The divergence in number of functions between CO and CO_2 basis sets explains the difference between total energies of these sets. In other word, the more function used to describe C atom the more gain in the total energy of the doped system. Similarly, CO

basis set with 40-functions has lowest energy than CO with 28-functions. However, the number of functions for a given basis set is limited by the computational cost of the calculation. Therefore, the CO basis set of C with 40 functions per atom has been considered as a reference for the further calculation in this study.

The complex dielectric function *ε(ω)* is utilized to investigate the optical properties of materials including the dielectric constant. The formula of *ε(ω)* can be written as[16]:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \quad \text{.....(1)}$$

Where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ refer to the real and imaginary part of the dielectric functions, respectively. The $\varepsilon_2(\omega)$ can take the formula [17,18]:

$$\varepsilon_2(\omega) = \left[\frac{4e^2\pi^2}{\omega^2 m^2}\right] \sum_{i,j} \int \langle i|M|j\rangle^2 f_i(1-f_i) * \delta(E_f - E_i - \omega) d^3k \quad \text{.....(2)}$$

Where M represent the dipole matrix, j and i refer to final and initial states, respectively, Fermi distribution function of ith state is denoted by f_i and the energy of electron in i^{th} state is denoted by E_i . Using the Kramers-Kroning relation [18,19] the real part of dielectric function can then be derived from the imaginary part as:

$$\varepsilon_1(\omega) = 1 + \frac{2P}{\pi} \int_0^{\infty} \frac{\omega' \varepsilon^2(\omega') d\omega'}{(\omega'^2 - \omega^2)} \quad \text{.....(3)}$$

where P is the principle value of integration. Obtaining the real and imaginary parts of dielectric function provides valuable information towered calculation of other optical properties.

Calculation of vibrational frequencies is an essential part in defect modeling as they are directly connected to experimental observables such as infrared absorption (IR) [20] and Raman scattering [21,22]. These techniques have been widely employed to detect the point defect in solids. So, prior calculations of vibrational frequencies provide significant

information regarding the presence of defect. In the current paper, the vibrational modes of C doped m-HfO_2 have been calculated according to following procedure. The force constants have to be calculated in advance, as they are important to calculate vibrational frequency. They can be calculated from the second derivative of total energy as function of atomic displacement. A system of a given atomic positions (*x*,*y* and *z*) is self consistently optimized to its minimum energy. The optimized system is then perturbed throughout displacement of atom *a*, with atomic mass m_a, from the first optimum position along *r* direction by an amount *d*. The perturbed system is then optimized and in this step, the atom *b* in the perturbed system will be affected by force along *n* direction $f_{bn}^{+}(a,r)$. The first atom (*a*) is then displaced by the same displacement but in opposite direction (-*d*) and in this case the atom *b* will be under the effect of $f_{bn}^{-}(a,r)$ force. The second derivative is then extracted as [23]:

$$Q_{ar,bn} = \frac{f_{bn}^{+}(a,r) - f_{bn}^{-}(a,r)}{2d} \text{.....(4)}$$

The mass-weighted dynamical matrix is then calculated:

$$L_{ar,bn} = \frac{f_{nb}^{+}(a,r) - f_{nb}^{-}(a,r)}{2d\sqrt{m_a \quad m_b}} \text{.....(5)}$$

The eigenvalues are then obtained from the diagonalization of the matrix in equation.5. The calculated eigenvalues j_i are representing to $\sqrt{k/m^*}$ which used to calculate the vibrational mode frequencies n_j as:

$$n_j = \frac{1}{2pc}\sqrt{\frac{k}{m^*}} \text{.....(6)}$$

Where *c* is the velocity of light, *k* is the force constant and *m** is the reduced mass.

3. Results and Discussion

3.1 Structural properties

The crystal structure of pure m-HfO_2 (carbon free structure) is shown in Figure.2. It is clear from the figure that the carbon might be incorporated with many possible sites in m-HfO_2. As substitution defect, carbon might either substituting for oxygen or hafnium ion. In either case there are two non-equivalent sites to be coordinated by carbon defect. In other word, carbon has four possible substitution sites in HfO_2. Thus, any of remaining sites in the crystal structure of m-HfO_2 should be equivalent (has the same bonding environment) to one of these four sites.

The fully optimized structures of carbon substituting for oxygen and hafnium are clarified in Figure.3.

It is obvious from the figure that carbon has induced structural perturbation in m-HfO_2. The perturbation can be characterized by the stress and strain induced by incorporation of carbon. Forming and breaking bonds as well as the bond length are very important characters to analyze the impact of carbon doping on the structural properties of m-HfO_2. Investigations of these parameters provide valuable information regarding the impact of defect (carbon in our case) on the crystal structure of the host. The bond length of bonds between carbon and any of surrounding atoms (either oxygen or hafnium) for the four possible sites of carbon in m-HfO_2 are listed in Table.2. Corresponding bond lengths in the pure system have also been listed for comparison.

Figure.3 and Table.2 show that incorporation of carbon induced noticeable crystal distortion around the defect. The distortion can be viewed clearly from the tension in bond length in case of carbon substitution for oxygen in O-1 site. The tension in bond length is up to %9. However, the breaking of C-Hf bond in case of carbon substation for oxygen in O-2 case leads to higher in total energy of the system. In case of carbon at hafnium site and for both sites (Hf-1 and Hf-2), carbon is bonded to only three oxygen ions whereas hafnium in the same site in pure system was connected to six oxygen ions. Furthermore, high values

of compression in bond length for these cases lead to hander the energies in comparison with carbon substitution for oxygen. Figure.4 shows the total energies of defective systems. The ionic character of bonding in the system under consideration is the reason behind the large difference in the total energies between oxygen site and hafnium site.

Figure.4 and table.2 show that more the number of bonds those broken or changed, higher the total energy of the system. The comparison between two oxygen sites reveals that O-2 coordination site which previously had four bonds in pure m-HfO_2 has higher total energy than O-1 coordination site in which only the bond lengths have changed. Similarly, when hafnium sites are compared with oxygen sites, it is clear that carbon at hafnium sites are higher in total energy since that hafnium is bonded to seven oxygen atoms in pure system whereas carbon in the same site is bonded to only three oxygen atoms. So, it is wise to reveal that carbon has the favorability to substitute oxygen in m-HfO_2 system.

3.2 Dielectric constant

Dielectric constant can be defined as the ratio of stored electric energy when voltage is applied relative to the permittivity of vacuum. The dielectric material is polarized once placed in an electric field [24]. The polarization may arise due to electronic polarization, which arise due to displacement of electronic cloud with respect to the center of its nuclei in an external applied field, atomic polarization, dipolar polarization, and/or space charge polarization [25]. The electronic part of static dielectric constant for pure and carbon doped m-HfO_2 is shown in Table.3.

The results of static dielectric constant indicate that carbon induced an anisotropic effect on the dielectric constant. It is clear that carbon substitution for oxygen increased the three components of dielectric constant with *y*-component up to 4.709 for carbon in O-1 site. In contrast and for both sites of carbon substitution for hafnium, the dielectric constant has moderate decreasing up to 4.182 for the *z*-component of both hafnium sites (Hf-1 and Hf-2).

3.3 Vibrational Modes

Calculations of density functional theory become an important partner for experiment since that obtaining microscopic insight of material properties facing experimental limitations. Study of vibrational mode is a powerful tool in characterization material properties. Second derivative of total energies of defective atoms in m-HfO_2 are calculated to obtain local vibration mode frequencies. The calculated vibrational mode frequencies of carbon doped in various sites of m-HfO_2 are tabulated and shown in Table.4. The appearance of peak intensity in experimental techniques like Raman spectroscopy or infrared spectroscopy at any of the obtained frequencies will verify the presence of carbon in m-HfO_2.

4. Conclusion

The role of carbon doped monoclinic HfO_2 have been investigated. Results of structural properties reveal that carbon substitution for oxygen is more favorable than substitution for hafnium. Static dielectric constant is found to be maximizing for carbon in oxygen sites achieving 4.709. In contrast, for all three components, carbon substitution for hafnium decreases the dielectric constant up to 4.182. Local vibrational frequencies (836.09 and 862.39 for oxygen sites and 1507.64 and 1508.55 for hafnium sites) have been reported to guide experimentalists for confirming carbon-doped m-HfO_2.

5. References

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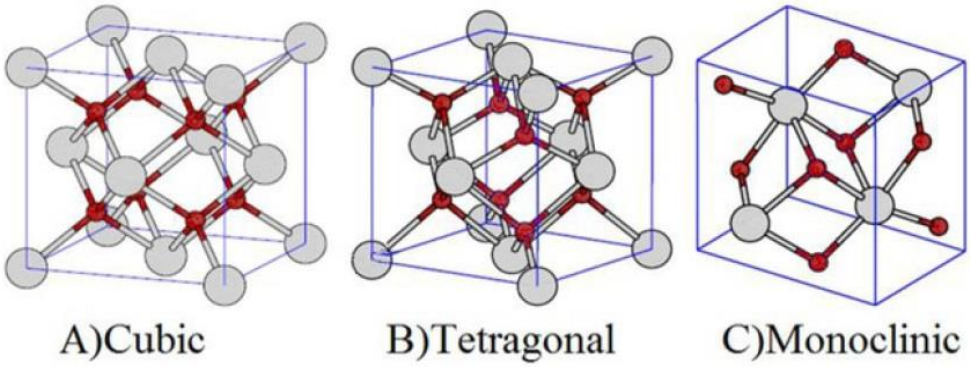

Figure.1: Crystal structure of hafnium dioxide phases, (A) cubic, (B) Tetragonal and (C) monoclinic. Large grey circles represent hafnium atoms and small dark circles represent oxygen atoms.

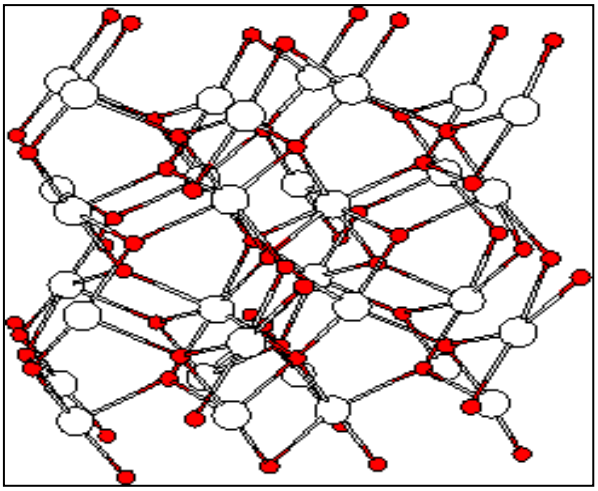

Figure.2 : The structure of super-cell of pure m-HfO2 adopted in modeling carbon substitution for hafnium and oxygen. Large (white) and small (red) atoms represent hafnium and oxygen atoms, respectively.

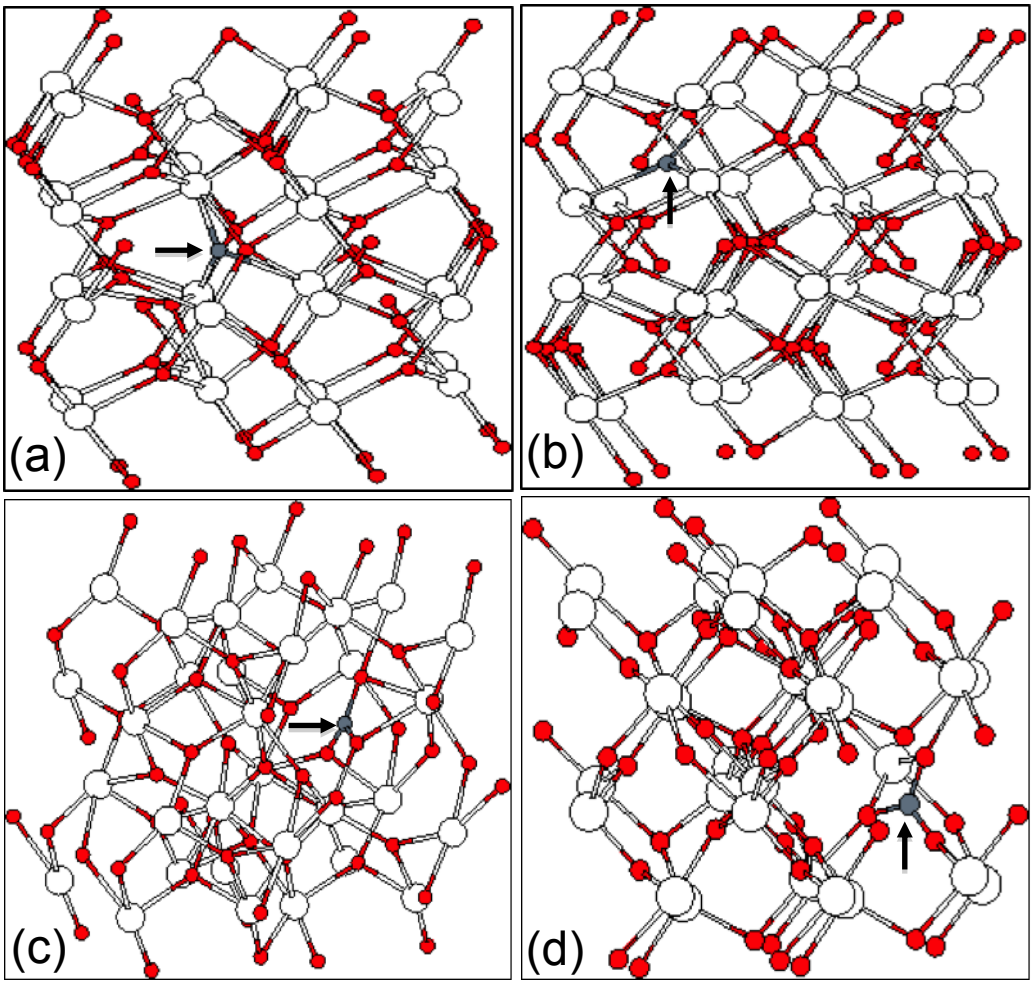

Figure.3: Fully optimized structures of carbon substitution for oxygen and hafnium where (a) O-1 site, (b) O-2 site, (c) Hf-1 site and (d) Hf-2 site. Carbon atom has been highlighted with small arrow in each structure.

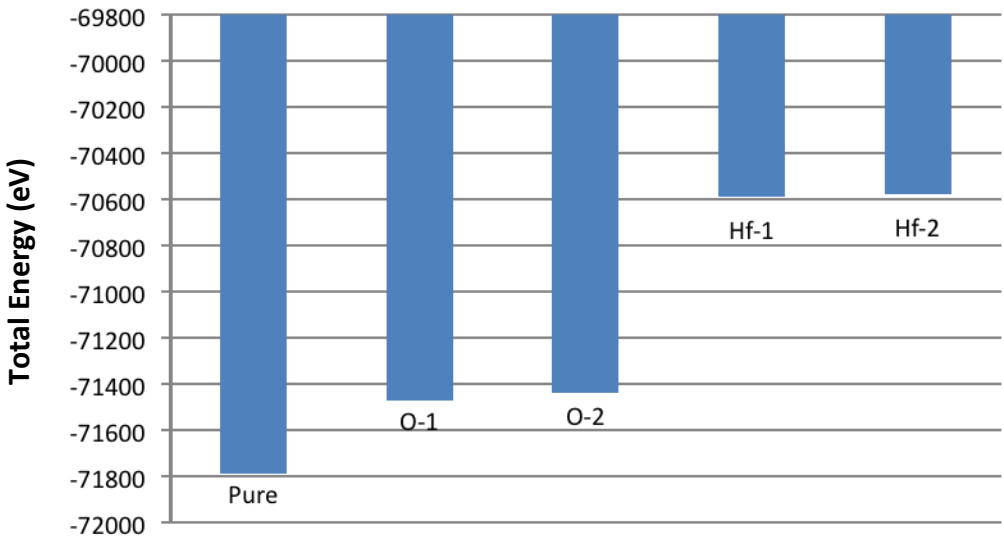

Figure.4: The total energy (in eV) of pure and carbon doped in various sites (shown in Figure.3) in m-HfO_2

Table.1: Wave function basis set of C atom, the number of functions in each basis set and total energies (Hartree) of the corresponding 12-atom defective system of C doped monoclinic HfO_2.

Wave function basis set of C atom	Number of functions to describe one C atom	Total energy of the optimized doped system (Hartree)
CO_2	28	-7754.100004
CO	28	-7753.999140
CO	40	-7754.638079
Diamond	40	-7754.565770
Graphite	32	-7754.498511
SiC	32	-7754.421062
CH_4	28	-7754.426212

Table.2: Bond lengths (Å) and compression and tension of bond lengths (%) between carbon and connected oxygen and hafnium atoms. Corresponding bond lengths in pure (carbon free) m-HfO_2 have been listed for comparison. Highlighted bond lengths show the difference between two hafnium sites.

Selected substitution site of carbon	Bond length (Å)		Compression or tension in bond length (%)
	Pure m-HfO_2	C doped m-HfO_2	
O-1	2.12737	2.32843	9.4
	2.03045	2.14445	5.6
	2.03320	2.13467	4.9
O-2	2.19060	2.10291	-4.0
	2.20593	---	---
	2.15215	2.23959	4.0
	2.11820	2.15625	1.8
Hf-1	3.28095	---	---
	2.03320	1.27517	-37
	2.03045	1.27759	-37
	2.12737	1.30390	-38
	2.11820	---	---
	2.19060	---	---
Hf-2	3.28095	---	---
	2.12737	1.30418	-38
	2.03320	1.27518	-37
	2.03045	1.27832	-37
	2.20593	---	---
	2.19060	---	---

Table.3 Static dielectric constant of pure and carbon doped m-HfO_2

Structure	Dielectric constant		
	X-pol.	Y-pol.	Z-pol.
Pure m-HfO_2	4.448	4.397	4.190
Carbon at oxygen site (O-1)	4.613	4.709	4.361

Carbon at oxygen site (O-2)	4.581	4.560	4.321
Carbon at hafnium site (Hf-1)	4.355	4.374	4.182
Carbon at hafnium site (Hf-2)	4.355	4.374	4.182

Table.4 Local vibrational mode frequencies for carbon in different substitution sites of m-HfO_2

Structure	Vibrational frequency
Carbon at oxygen site O-1	836.09
Carbon at oxygen site O-2	862.39
Carbon at hafnium site Hf-1	1507.64
Carbon at hafnium site Hf-2	1508.55