Semiconducting phase of hafnium dioxide under high pressure: a theoretical study by quasi-particle GW calculations

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Abstract
The phase stability of the hafnium dioxide compounds HfO2, a novel material with a wide range of application due to its versatility and biocompatibility, is predicted to be achievable by using evolutionary technique, based on first-principles calculations. Herein, the candidate structure of HfO2 is revealed to adopt a tetragonal structure under high-pressure phase with P4/nmm space group. This evidently confirms the stability of the HfO2 structures, since the decomposition into the component elements under pressure does not occur until the pressure is at least 200 GPa. Moreover, phonon calculations can confirm that the P4/nmm structure is dynamically stable. The P4/nmm structure is mainly attributed to the semiconducting property within using the Perdew–Burke–Ernzerhof, the modified Becke–Johnson exchange potential in combination with the generalized gradient approximations, and the quasi-particle GW approximation, respectively. Our calculation manifests that the P4/nmm structure is likely to be metal above 200 GPa, arising particularly from GW approximation. The remarkable results of this work provide more understanding of the high-pressure structure for designing metal-oxide-based semiconducting materials.

1. Introduction
Hafnium oxide HfO2 is a remarkable material with various applications. Currently, the Hafnium oxide-based material is mainly used as the ideal memory material, [1–5] i.e. ferroelectric Si-doped HfO2 [6–9] due to its ferroelectric property. Moreover, as a part of solid oxide-deficient technology, HfO2 is also an attractive material for resistive-switching memories [10–14]. Under a broad range of pressure, HfO2 becomes a superhard material [15–17]. Its physical properties such as structural, electrical, optical, and elastic properties have recently been investigated by computational study [17]. Also, HfO2 is considered an indirect band gap semiconductor with the band gap of 4.62eV. Therefore, it is expected that HfO2 could possibly be utilized as metal-oxide-semiconductor devices in the upcoming generations.

Moreover, HfO2 has been fundamentally studied under high pressure. The phase transition has been demonstrated experimentally by the Raman spectra and x-ray-diffraction technique [18]. As a result, it displayed a monoclinic structure with the space group P21\(\text{c}\), then transformed into an orthorhombic I with the space group Pnma at 10.2GPa, and finally at 37 GPa, it transformed into an orthorhombic II with the space group Pnma. The structural behavior of the Pnma structure of HfO2 was investigated at each pressure [19]. It was discovered that the Pnma structure exhibits dynamical stability, but the structure is thermodynamically stable.
unstable. The meta stability can be observed up to at least 120 GPa. Additionally, it should be noted that the \textit{Pnma} structure exhibits semiconductivity with the band gap of 3.36 eV. Interestingly, there is no previous report on the crystal structure of HfO\textsubscript{2} above 120 GPa. Therefore, the existence of a stable structure with novel property of HfO\textsubscript{2} above 120 GPa could be anticipated.

In this work, HfO\textsubscript{2} will be explored by the evolutionary techniques, based on density functional theory, to predict the novel structure as a function of pressure. Following this, the main attention is turned to the prediction of candidate structures under up to 200 GPa of pressure. As a result of the structural prediction, the stability of the candidate structures will be examined by considering the formation enthalpy. From the results, the existence of the structure confirms the composition of binary hafnium oxides, which is HfO\textsubscript{2}, with respect to pure Hf and O. In other words, the material does not decompose into pure elements under at least 200 GPa of pressure. The remarkable result of the evolutionary techniques displayed a candidate high-pressure phase: a tetragonal structure with a space group of P4/nmm. By considering the physical properties, the P4/nmm exhibits semiconductivity. These findings provide crucial details for fundamental understanding of the structural behaviour and the electronic properties of the HfO\textsubscript{2} at each pressure. Note also that our work provides only HfO\textsubscript{2}. It is because other Hf-O compounds clearly explore further investigation by Zhang \textit{et al} [19].

2. Methods

The computation implemented the universal Structure Predictor: Evolutionary Xtallography (USPEX) [20] and the Vienna \textit{ab initio} simulation package (VASP) [21] which utilizes the density functional theory. In all subsequent generations, the random symmetric algorithm employed 40% heredity, 20% random symmetric, 20% soft mutation, and 20% transmutation operators. We then studied the system under the pressure range of 150 to 200 GPa with up to four formula units. There are 1702 configurations which possess the lowest enthalpy in 56 consecutive generations. A convergence test on plane-wave basis set was performed. As a result, the cutoff energy of 700 eV was achieved. This value is used for the formation enthalpy carried on the generalized gradient approximation of the Perdew–Burke–Ernzerhof (GGA–PBE) functional [22]. The projector augmented wave (PAW) method [23] and the conjugate gradient scheme, both implemented in the VASP code, [21] were used for the calculation of the ground state energy. The pseudocore radii of Hf and O are 2.4 Bohr and 1.1 Bohr, respectively, which are small enough to ensure that no overlap of spheres will occur under compressed conditions. The tetragonal structure was calculated with an initial Brillouin-zone (BZ) sampling grid of spacing \(2\pi \times 0.02 \, \text{Å}^{-1}\) in order to guarantee the convergence of the derived ground-state energy. To confirm the dynamical stability, the structure was calculated by using the \textit{ab initio} lattice dynamics with the supercell approach, as implemented in the VASP code together with the PHONOPY package [24]. As for the density of states, the modified Becke-Johnson (mBJ) exchange potential [25] with the GGA functional was used to fully take into account the energy gap. To further investigate the energy gap, the tetragonal structure was performed a self-energy \(\Sigma\) of a many-body system of electrons, also known as GW approximation [26–29]. One of the well-known GW approximation, the technical details of how the GW approximation is implemented have been described extensively in [28, 29]. The present work has been calculated within a single-shot calculation (\(G_{S}W_{0}\)) by neglecting all off-diagonal matrix elements of the self-energy \(\Sigma\) as well as performing a Taylor expansion of the self-energy \(\Sigma\) around the quasiparticle eigenvalues.

3. Results and discussion

The formation enthalpy of HfO\textsubscript{2} is presented in the convex hulls, as shown in figure 1, the possibility of HfO\textsubscript{2} existence under compression can be verified. We first investigated the thermodynamic stability from 150 to 300 GPa by using first-principles calculations. It should be noted that our calculations were performed at a temperature of 0 K, indicating that the enthalpy can confirm a phase stability under high pressure [30–38]. This is due to the fact that there is no entropy contribution. As a result, the relationship between pure elements Hf and O displayed the formation of HfO\textsubscript{2}. We considered the compositions of HfO\textsubscript{2}, bcc–Hf and C2/m–O [40]. The stability of HfO\textsubscript{2} is presented within the connected lower convex wrapper, indicating that there is new high-pressure phase found above 150 GPa: the tetragonal structure with the space group of P4/nmm. Considering the pressure of 150 GPa, the aforementioned theoretical findings manifested that the \textit{Pnma} structure is a metastable structure, and it is in good agreement with those previously reported by Zhang \textit{et al} [19]. Moreover, we further explored the P4/nmm and \textit{Pnma} structures by considering entropy \(S\) contribution, which is obtained as

\[
S = -k_B \sum_{\nu \in \Omega} \ln[1 - \exp(-\hbar \omega_{\nu \Omega}/k_B T)],
\]  

(1)
where \( \nu \) and \( q \) are band index and the wave vector, respectively. \( \omega \) is the phonon frequency at \( \nu \) and \( q \). \( T \) is temperature. \( k_B \) and \( \hbar \) are the Boltzmann constant and the reduced Planck constant, respectively. The relative Gibbs free energy showed that the P4\(_{\overline{2}}\)/nmm structure is thermodynamically stable favored over the Pnma structure by approximately 0.01 eV at a temperature 300 K and a pressure of 150 GPa. As the temperature is increased, it can see that the Pnma structure is thermodynamically stable at a temperature of 500 K and 1000 K.

To understand the structural behavior, it should be noted that the entropy \( S \) increased with increasing temperature. We therefore suggested that the Pnma structure stable structure depended on the term of \(-TS\). Here, we suggested that the Pnma structure is a high-temperature phase. The Pnma structure, however, beyond the scope of this work, and the issue clearly deserves further investigation—for example, the issue of the dynamical stability at high temperature and electronic properties investigation. Subsequently, the convex hulls showed that the Pnma structure is holding the meta-stable structure with respect to the P4\(_{\overline{2}}\)/nmm structure. Therefore, it can be implied that the P4\(_{\overline{2}}\)/nmm structure is thermodynamically stable and is favored over the Pnma by neglecting entropy based on the density functional theory, the formation enthalpy alone is sufficient to confirm phase stability at the temperature of 0 K. Focusing on the P4\(_{\overline{2}}\)/nmm structure, the structure is stable up to at least 200 GPa. Interestingly, the new high-pressure structures do not decompose into pure elements up to at least 200 GPa, resulting in the evidence of phase stability in HfO\(_2\).

The possibility of finding an electron in the neighboring space of HfO\(_2\) can be measured by the electron localization function (ELF) [41], as reported in figure 2, where the structure of HfO\(_2\) is presented as shown in figure 2 (a). The tendency of ELF in HfO\(_2\) is described by the uniform distribution of electron gas with the same density [31, 32, 38, 42–46]. For the P4\(_{\overline{2}}\)/nmm structure, the calculated ELF reveals a set of chemical bonding at the pressure of 150 GPa. The distances between the first (Hf–O) and second (O–O) nearest neighbors (NN) read 1.9374 Å, and 2.3477 Å, respectively. As a result of the P4\(_{\overline{2}}\)/nmm structure, it can be observed that the electron would accumulate around the Hf and O atoms, respectively. It should be noted, however, that the O atoms are not likely to bond.

The dynamical stability of the P4\(_{\overline{2}}\)/nmm structure can be confirmed by considering the phonon calculation. We investigated the structures which was obtained from the relative enthalpy calculations and discovered that the two new high-pressure structures exhibited negative enthalpies of formation relative to Hf and O; however, it...
is not enough to guarantee the thermodynamic stability. As a result, the P4/nmm structure is dynamically stable at a pressure of 150 GPa, as shown in figure 3. It is because the structures lack the imaginary frequencies that the P4/nmm structure is thermodynamically stable.

We will now discuss electronic property of HfO₂ which is shown in figure 4, as implemented in the density of states (DOS). The DOS has been extensively studied the structural behaviour in several materials. Also, the DOS has been reported in the literature that as the compound systems are useful in achieving in electronic structure. For this reason, it should be noted that, in [48–50] Here, it can be observed that the P4/nmm structure is semiconductor. Following this, a structural property indicates that, in the PBE method, band gap semiconductors with energy gap of 0.77 eV (figure 4(a)). By taking into consideration the fact that the performance of mBJ for the semiconducting property is more accurate as the calculated energy gaps precision would be similar to the hybrid functional, the mBJ method is likely to solution in energy gap of 1.52 eV. By investigating the energy gap, we have chosen to use GW approximation within a single-shot calculation (\( G_0W_0 \)). At this stage, the \( G_0W_0 \) method displayed a large energy gap of 3.05 eV as shown in figure 5. Therefore, it is mentioned that in the PBE method, the energy gap is likely to be underestimated. With increasing pressure, the PBE method shown that the band gap semiconductors with energy gap of 0.15 eV. Also, the estimated the band gap semiconductors is still large in the P4/nmm structure with energy gap of 1.01 eV by using the mBJ method at a pressure of 200 GPa, as shown in figure 4(b). Interestingly, the remarkable result of the \( G_0W_0 \) method displayed that the P4/nmm structure is metal because there are electrons occupied at the Fermi level (figure 4(b)). Besides, we provide for comparison the values of energy gap evaluated by a different set of parameters, as shown in table 1. It should note that previous calculations and experimental data are revealed the energy gap of the other phases because our work calculated the P4/nmm structure at high pressure and experimental studies do not yet provide the energy gap above 150 GPa. Therefore, we proposed the theoretical result of the P4/nmm structure which may guild further experimental studies.
Yet, a more significant change in structural behavior is observed when the pressure increased. As mentioned above, the discovery of apparent metallicity prompts us to further study. It is worth mentioning again that the P4/nmm structure is likely to be metal at a pressure of 200 GPa. Herein, we consider the energy gap as a function of pressure from 150 GPa to 200 GPa. Firstly, the PBE method shown that the estimated energy gap increased gradually from 150 GPa to 180 GPa. Next, the energy gap rose dramatically at a pressure of 190 GPa. After that, the energy gap decreased rapidly at a pressure of 200 GPa. For the case of the mBJ method, the energy gap increased suddenly from 150 GPa to 160 GPa. Then, there was a gradual decrease to 190 GPa, and it decreased suddenly at a pressure of 200 GPa. By employing the G0W0 method, our results reveal that, arising particularly from a single-shot calculation, the estimated energy gap decreased gradually from 150 GPa to 170 GPa. Then, we found that it reached a peak of 3.14 eV at a pressure of 180 GPa. After that, the energy gap decreased suddenly from 190 GPa to 200 GPa. These analyses, based on our findings showing the P4/nmm structure accepted to be metallicity above 200 GPa. Consequently, it should be suggested in the sense that it may be possible to obtain a new phase above 200 GPa.

To this end, all of the present work were carried out the first-principle calculation. It is reported to pay a special attention the predicted high-pressure phase with the P4/nmm structure which is predicted to be a semiconductor. We investigated the energy gap as a function of pressure by using the PBE, the mBJ, and the G0W0 methods. As results, the calculations pointed out that three methods show a similar trend above a pressure of 190 GPa; however, it should note that the P4/nmm structure is still kept a semiconductor up to at least 190 GPa. Furthermore, the HfO2 that was investigated in this study would be superior to the metal-oxide-semiconductor devices of the next generation.
4. Conclusion

In summary, the structural behavior of HfO$_2$ under high pressure demonstrated the stable structures. High pressure phase of hafnium oxides HfO$_2$ is investigated and compared with those of hafnium and oxygen by using the first-principles calculations, based on the density functional theory, to examine the derived-ground state structure. The original hypothesis of the research, which is that HfO$_2$ will remain stable rather than decompose under the pressure of up to at least 200 GPa, was evidently confirmed. Our structural predictions have shown that a candidate high-pressure phase is found above 150 GPa: the tetragonal structure with the space group of P4$_{nmm}$, as its formation enthalpy lies on the Hf-O convex hull envelops. HfO$_2$ displayed physical properties which can be categorized as semiconducting material by using the GGA-PBE method. Following this, the semiconductivity of the P4$_{nmm}$ structure has been investigated theoretically, by considering the modified Becke-Johnson (mBJ) exchange potential formalism of the GGA functional and the GW approximation from 150 to 200 GPa. Moreover, the physical origin of semiconductor, based on the quasi-particle G$_0$W$_0$, manifested that the P4$_{nmm}$ structure is likely to be metal at the pressure of 200 GPa. Our theoretical findings could pave the way for further studies to be conducted in metal oxides and suggests that hafnium oxide could be further investigated experimentally.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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| Phase         | method     | Energy gap (eV) |
|---------------|------------|-----------------|
| P4/nmm-HfO$_2$| GGA-PBE$^a$| 0.77            |
| P4/nmm-HfO$_2$| mBJ$^a$    | 1.52            |
| P4/nmm-HfO$_2$| G$_0$W$_0$$^a$ | 3.05          |
| cubic-HfO$_2$ | GGA-PBE$^a$ | 3.80            |
| cubic-HfO$_2$ | HSE06$^b$  | 5.10            |
| cubic-HfO$_2$ | HSE06$^b$  | 5.38            |
| cubic-HfO$_2$ | PBE0$^b$   | 6.11            |
| monoclinic-HfO$_2$ | Expt.$^c$$^f$ | 5.7        |
| cubic-HfO$_2$ | Expt.$^c$$^f$ | 5.6–6          |
| amorphous-HfO$_2$ | Expt.$^c$$^f$ | 5.5            |

$^a$ This work.
$^b$ Reference [31].
$^c$ Reference [52].
$^d$ Reference [53].
$^e$ Reference [54].
$^f$ Reference [35].
$^g$ Reference [56].
$^h$ Reference [57].
References

[1] De S, Qiu B H, Bu W X, Baig M A, Sung P J, Su C J, Lee Y J and Lu D D 2021 ACS Applied Materials 
& Interfaces 13 37029–30
[2] Zhang W, Li G, Long X, Cui L, Tang M, Xiao Y, Yan S, Li Y and Zhao W 2020 Physica Status Solidi (b) 257 1900736
[3] Ledener M et al 2020 Nanomaterials 10 384
[4] Yang X, Bi J, Xu Y, Xi K and Ji L 2021 Applied Physics Express 14 061201
[5] Mikolajick T and Schroeder U 2021 Nat. Mater. 20 718–9
[6] Lee T Y et al 2018 ACS Appl. Mater. Interfaces 11 3142–9
[7] Lee K et al 2019 ACS Appl. Mater. Interfaces 11 30929–36
[8] Li S, Zhou D, Shi Z, Hoffmann M, Mikolajick T and Schroeder U 2021 ACS Applied Materials 
& Interfaces 13 2415–22
[9] Celano U et al 2020 Nanomaterials 10 1576
[10] Lin K L, Hou T H, Shei J, Lin J H, Chou C T and Lee Y J 2011 J. Appl. Phys. 109 084104
[11] Sokolov A S, Jeon Y R, Kim S, Ku B, Lim D, Han H, Chae M G, Lee J, Ha B G and Choi C 2018 Appl. Surf. Sci. 434 822–30
[12] Giovinazzo C, Sandrini J, Shahabadi E, Celik O T, Leblebici Y and Ricciardi C 2019 ACS Applied Materials 
& Interfaces 11 990–9
[13] Aldana S, Garcia-Fernandez P, Romero-Zaliz R, Gonzalez M, Jimenez-Molinos F, Gomez-Campos F, Campabadal F and Roldan J 2020 
J. Phys. D: Appl. Phys. 53 235106
[14] Mahata C, Lee C, Am Y, Kim M H, Bang S, Kim C S, Ryu J H, Kim S, Kim H and Park B G 2020 J. Alloys Compd. 826 154334
[15] Al-Khatatbeh Y, Lee K K M and Kiefer B 2010 Phys. Rev. B 82 144106
[16] Debernardi A 2012 Phys. Rev. B 85 024109
[17] Mazumder J T, Mayengbam R and Tripathy S 2020 Mater. Chem. Phys. 254 123474
[18] Desgreniers S and Lagarec P 1999 Phys. Rev. B 59 8467–72
[19] Zhang J, Oganov A R, Li X, Xue K H, Wang Z and Dong H 2015 Phys. Rev. B 92 184104
[20] Oganov A R and Glass C W 2006 J. Chem. Phys. 124 244704
[21] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169–86
[22] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865–8
[23] Blochl P E 1994 Phys. Rev. B 50 17953–79
[24] Togo A and Tanaka I 2015 Scr. Mater. 108 1–5
[25] Becke A D and Johnson E R 2006 J. Chem. Phys. 122 221101
[26] Hedin L 1965 Phys. Rev. 139 A796–823
[27] Onida G, Reining L and Rubio A 2002 Rev. Mod. Phys. 74 601–59
[28] Arnaud B and Alouani M 2000 Phys. Rev. B 62 6464–76
[29] Lebègue S, Arnaud B, Alouani M and Blochl P E 2003 Phys. Rev. B 67 155208
[30] Tsypaykovskii-aek P, Luo W, Ahuja R and Bovornratanaraks T 2018 Sci. Rep. 8 3026
[31] Tsypaykovskii-aek P, Luo W, Watcharatharapong T, Ahuja R and Bovornratanaraks T 2018 Sci. Rep. 8 53278
[32] Tsypaykovskii-aek P, Luo W, Pungtrakoson W, Chuenkingkeaw K, Kaeawmaraya T, Ahuja R and Bovornratanaraks T 2018 J. Appl. Phys. 124 225901
[33] Jimlim P, Tsypaykovskii-aek P, Pakornchoke T, Ektarawong A, Pinsook U and Bovornratanaraks T 2019 RSC Adv. 9 30964–75
[34] Pluengphong P, Bovornratanaraks T, Vannarat S and Pinsook U 2014 Sol. State Commun. 195 26–30
[35] Tsypaykovskii-aek P, Chaimayo W, Pinsook U and Bovornratanaraks T 2015 AIP Adv. 5 097202
[36] Kotmool K, Tsypaykovskii-aek P, Kaeawmaraya T, Pinsook U, Ahuja R and Bovornratanaraks T 2020 The Journal of Physical Chemistry C 124 14804–10
[37] Tsypaykovskii-aek P, Zhang J, Luo W, Ding Y, Ahuja R and Bovornratanaraks T 2021 Physica Status Solidi (b) 258 2000279
[38] Tsypaykovskii-aek P, Phaisangititsakul N, Ahuja R and Bovornratanaraks T 2021 Sci. Rep. 11 1–7
[39] Xia H, Parthasarathy G, Luo H, Vohra Y K and Ruoff A L 1990 Phys. Rev. B 42 6736–8
[40] Ma Y, Oganov A R and Glass C W 2007 Phys. Rev. B 76 064101
[41] Becke A D and Edgecombe K E 1990 J. Chem. Phys. 92 5397–403
[42] Bovornratanaraks T, Tsypaykovskii-aek P, Luo W and Ahuja R 2019 Sci. Rep. 9 2459
[43] Tsypaykovskii-aek P, Chaimayo W, Pinsook U and Bovornratanaraks T 2015 AIP Adv. 5 097202
[44] Tsypaykovskii-aek P, Zhang J, Luo W, Ahuja R and Bovornratanaraks T 2020 Mater. Res. Express 7 086001
[45] Tsypaykovskii-aek P, Yang X, Pluengphong P, Luo W, Ahuja R and Bovornratanaraks T 2020 Sci. Rep. 10 1–8
[46] Tsypaykovskii-aek P, Sukmas W, Ahuja R, Luo W and Bovornratanaraks T 2021 Sci. Rep. 11 1–10
[47] Tsypaykovskii-aek P, Phansuk P, Kaewtubtim P, Ahuja R and Bovornratanaraks T 2021 Comput. Mater. Sci. 190 110282
[48] Momma K and Izumi F 2008 J. Appl. Crystallogr. 41 653–8
[49] Khandy S A, Islam J, Ganai Z S, Gupta D C and Parrey K A 2018 J. Electron. Mater. 47 436–42
[50] Khandy S A and Chai J D 2021 J. Phys. Chem. Solids 154 110098
[51] Khandy S A, Vaid S G, Islam J, Hafiz A K and Chai J D 2021 J. Alloys Compd. 867 158966
[52] Yang Y L, Fan X L, Liu C and Ran X P 2014 Physica B 434 7–13
[53] Hoff R E, Suzuki P R and Pentecost J L 1985 J. Am. Ceram. Soc. 68C–285
[54] Adams D M, Leonard S, Russell D R and Cernik R J 1991 J. Phys. Chem. Solids 52 1181–6
[55] Kukli K, Itanos J, Ritala M and Leskela M 1996 Appl. Phys. Lett. 68 3737–9
[56] Garcia J C, Scalfaro L, Leite J, Lino A, Freire V, Farias G and da Silva E Jr 2004 Appl. Phys. Lett. 85 3022–4
[57] Cherkaoui K et al 2008 J. Appl. Phys. 104 064113
[58] Takeuchi H, Ha D and King T J 2004 Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films 22 1337–41