Phase stability of hafnium oxide and zirconium oxide on silicon substrate

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Abstract
Phase stabilities of Hf-Si-O and Zr-Si-O have been studied with first-principles and thermodynamic modeling. From the obtained thermodynamic descriptions, phase diagrams pertinent to thin film processing were calculated. We found that the relative stability of the metal silicates with respect to their binary oxides plays a critical role in silicide formation. It was observed that both the HfO$_2$/Si and ZrO$_2$/Si interfaces are stable in a wide temperature range and silicide may form at low temperatures, partially at the HfO$_2$/Si interface.

The thickness of SiO$_2$ as a gate oxide material in advanced complementary metal oxide semiconductor (CMOS) integrated circuits has continuously decreased and reached the current processing limits[1]. Alternative materials with higher dielectric constants, such as HfO$_2$ and ZrO$_2$, are considered as candidates to replace SiO$_2$ for further improvement of their performance[2]. However, during the thin film deposition or the subsequent rapid thermal annealing, oxides, silicates, and silicides may form at the interface since most high-k materials are metal oxides[3, 4]. Among these interfacial phases, silicides are detrimental to capacitor performance due to their metallic behavior[5]. In this regard, thermodynamic stability calculations and experimental results have shown that the interface between HfO$_2$ and Si is found to be stable with respect to the formation of silicides[4]. On the other hand, the ZrO$_2$/Si interface was found to be unstable around 1000K, which is in contradiction to the calculation by Hubbard and Schlom [2]. It was also observed that the Hf-silicide forms upon decomposition of HfO$_2$ in low oxygen partial pressures [5, 6, 7, 8] and HfSiO$_4$ suppresses Hf-silicide formation[9].

Although the phase stabilities in the Hf-Si-O and Zr-Si-O systems are important, comprehensive thermodynamic explanations are not yet available. In this paper, based on the recently developed thermodynamic descriptions of the Hf-Si-O[10] and Zr-Si-O systems with first-principles calculations and thermodynamic CALculation of PHase Diagrams (CALPHAD) modeling[11], various phase diagrams pertinent to thin film processing are investigated.

In the CALPHAD approach, the Gibbs energies of individual phases in a system are evaluated from the existing experimental data with the so-called sublattice model based on the crystal structures. The Gibbs energies of a higher-order system can be readily extrapolated from the lower-order systems, and any new phases of the higher-order system can be introduced. However, it is not always possible to have enough experimental data for thermodynamic modeling of a system[2] so that theoretical calculations, such as first-principles calculation results, can be used as supplementary experimental data. The Hf-Si-O system was recently modeled with first-principles calculations and the CALPHAD approach[10]. The formation enthalpy for HfSiO$_4$ is calculated from first-principles calculations since no experimental measurement is reported. The reference states of the formation enthalpy for HfSiO$_4$ are derived from the two binary metal oxides as shown in Eqn. 1, where $E$ represents the total energy of each phase. The formation entropy of HfSiO$_4$ was evaluated from the temperature of peritectic reaction, HfO$_2$ + Liquid $\rightarrow$ HfSiO$_4$, in the HfO$_2$-SiO$_2$ pseudo-binary system. The thermodynamic description of the Zr-Si-O system was obtained by combining the previous modelings[12, 13, 14] and first-principles calculation of ZrSiO$_4$ in the present work.

$$\Delta H_f^{HfSiO_4} = E(HfSiO_4) - \frac{1}{2}E(HfO_2) - \frac{1}{2}E(SiO_2) \quad (1)$$

The highly efficient Vienna Ab initio Simulation Package (VASP)[15] was used to perform the density functional theory (DFT) electronic structure calculations. The projector
augmented wave (PAW) method\cite{16} was chosen, and the
generalized gradient approximation (GGA)\cite{17} was used to
take into account exchange and correlation contributions.
An energy cutoff was constantly set as 500 eV for all the
structures, and the Monkhorst-Pack scheme was used for
the Brillouin-zone integrations. For the k-point sampling,
authors aimed all the structures to have the k-point meshes as
close as ( # of atoms in a structure) × k_x × k_y × k_z ≥
5000 k-points. Thus, HfSiO_4 and ZrSiO_4, for example, have
8 × 8 × 8 k-point meshes. The calculated results of metal
oxides and silicates are listed in Table 1.

From the constructed thermodynamic databases of the
Hf-Si-O and Zr-Si-O systems, the isopleths of HfO_2-Si and
ZrO_2-Si are calculated in order to investigate the stability
range of silicides at the metal oxides/silicon interface and
are given in Figure 1. Calculated results show that HfSi_2
is stable up to 544K based on the formation enthalpy of
HfSiO_4 from first-principles calculations. It is generally ac-
cepted that the uncertainty of the formation enthalpy of in-
termetallic compounds, which originates from the density
functional theory itself, is about ±1 kJ/mol-atom\cite{18,19}.
Thus the associated decomposition temperature of HfSi_2
at the HfO_2/Si interface ranges from 382 to 670K when the
formation enthalpy of HfSiO_4 is adjusted within its uncer-
tainty range from −0.769 to −2.769 kJ/mol-atom. The for-
mation entropy of HfSiO_4 with respect to the binary oxides
was evaluated correspondingly to reproduce its peritectic
reaction at 2023K. Thus the phase stability range of HfSi_2 in
the HfO_2-Si isopleth is not directly correlated with the first-principles calculation of HfSiO_4,
but predicted from the Gibbs energies of other phases, in-
cluding the HfSiO_4 phase, in the Hf-Si-O system. Even with
the uncertainty of formation enthalpy for HfSiO_4, the tem-
perture range for the HfO_2 and Si coexistent phase region
in the isopleth is fairly wide from 670 to 1700K.

For ZrSiO_4, besides the uncertainty of formation en-
thalpy from first-principles in the present work, the per-
tectic reaction (ZrO_2 + Liquid → ZrSiO_4) temperature in
the ZrO_2-Si pseudo-binary is also uncertain from 1910
and 1949K. Thus, the formation entropy of ZrSiO_4 varies
accordingly. The Gibbs energy of ZrSiO_4 at 1000K evaluated
from the formation enthalpy derived from first-principles
and formation entropy evaluated from the peritectic tem-
perture of 1949K (listed in Table 1) is almost identical to
the value used by Hubbard and Schlom \cite{2}. With these
formation enthalpy and entropy values of ZrSiO_4, ZrSi_2 is
completely suppressed by ZrSiO_4 and does not show up in
the ZrO_2-Si isopleth. To make ZrSi_2 appear in the ZrO_2-Si
isopleth, the formation enthalpy of ZrSiO_4 should be more
negative than the first-principles calculation result within
the uncertainty of formation enthalpy and peritectic tem-
perture for ZrSiO_4. When formation enthalpy of ZrSiO_4
with respect to the binary metal oxides is set to its lowest
limit from the uncertainty of first-principles calculations,
ΔH_f^{ZrSiO_4} = −3.358 kJ/mol-atom, and entropy of for-
mation is evaluated as ΔS_f^{ZrSiO_4} = 0.788 J/mol-atom-K, ZrSi_2
is stable up to 879K in the ZrO_2-Si isopleth. Then formation
enthalpy of ZrSiO_4 is ΔH_f^{ZrSiO_4} = −338.568 kJ/mol-
atom with respect to SER (Standard Element Reference)
and this agrees well with the experimental measurement,
−339.033 kJ/mol-atom from Ellison and Navrotsky \cite{20}.
Consequently, the safe temperature range for ZrO_2 to be
stable with Si is between 879 and 1630K, narrower than that
of HfO_2 and Si. However, even with these uncertainties,
both metal oxides are stable with Si approximately above
900K as summarized by Hubbard and Schlom \cite{2}(1000K).

![Figure 1](image_url)

Fig. 1. Calculated isopleths of HfO_2-Si and ZrO_2-Si at 1 atm. Polymorphs of metal oxides for HfO_2 and ZrO_2, i.e. monoclinic, tetrag-
onal, and cubic, are given in parentheses.

These isopleth calculation results are in agreements with
Gutowski et al. [4] for the Hf-Si-O system but not with the Zr-Si-O system. In their calculations, they assumed that thermal effects are of secondary importance for Gibbs energy change so that the contribution from entropy was ignored in the calculations for silicide formation reactions. However, our calculations from the individual thermodynamic databases showed that such an entropy effect cannot be neglected. According to our calculation results, both HfO2 and ZrO2 are stable with Si and this in agreement with the calculation from Hubbard and Schlom [2]. However, ZrSi2 was found at the metal oxide/Si interface in their experiment [4] while HfO2 was stable on Si without any silicides formation when they deposited at 823K and then annealed at 1073K. It can be explained that since their fabrication process was rapid thermal chemical-vapor deposition (RTDVC), it might not have reached the thermodynamic equilibrium state. Furthermore, the oxygen partial pressure of their experiment was not reported. The effect of oxygen partial pressure will be discussed later in this paper.

The calculated isopleths indicate that metal silicates play an important role in the silicide formation as suggested by Takahashi et al. [9] From first-principles calculations, the formation enthalpy of ZrSiO4 is $-2.358 \pm 1 \text{ kJ/mol-atom}$ whereas that of HfSiO4 is only $-1.769 \pm 1 \text{ kJ/mol-atom}$ when the reference states are set to the binary oxides. It is intriguing to see that such a small (0.6 kJ/mol-atom) difference in the formation of metal silicates greatly affects the phase stability at the metal oxides/silicon interface. This can be explained by comparing the relationship between metal oxides, silicates, and silicides in the isothermal section.

Isothermal sections of the Zr-Si-O system at two different temperatures, 500K and 1000K, are calculated (see Figure 2) to investigate the phase relationship regarding the decomposition of ZrSi2 at the ZrO2/Si interface. The two different three-phase regions, ZrSiO4+ZrO2+ZrSi2 and ZrSiO4+ZrSi2+Si, in the 500K isothermal section are intersected by the line connecting ZrO2 and Si. Therefore, ZrSi2 can be found in the thin film process. However, the 1000K calculation shows that ZrO2 is stable with the Si substrate without any silicide formation as there is a tie line connecting ZrO2 and Si. Isothermal sections of Hf-Si-O at the same temperatures, 500K and 1000K, showed similar phase stabilities as Zr-Si-O[10].

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**Table 1**

First-principles calculation results of metal oxides and metal silicates.

| Phases                  | Group | a   | b   | c   | α  | β  | γ  | Total energy (eV/atom) | $\Delta H_f^a$ (kJ/mol-atom) | $\Delta S_f^{a,b}$ (J/mol-atom-K) |
|------------------------|-------|-----|-----|-----|----|----|----|------------------------|-------------------------------|----------------------------------|
| HfO2                   | P21/c | 5.135 | 5.194 | 5.314 | 90 | 90 | 90 | -10.210                | -                            | -                               |
| ZrO2                   | P21/c | 5.221 | 5.287 | 5.398 | 90 | 90 | 90 | -9.5376                | -                            | -                               |
| SiO2                   | P321  | 5.007 | 5.007 | 5.496 | 90 | 90 | 90 | -7.9581                | -                            | -                               |
| HfSiO4                | $I4_1$/amd | 6.616 | 6.616 | 6.004 | 90 | 90 | 90 | -9.1024                | -1.769                      | -0.219                           |
| ZrSiO4                | $I4_1$/ amd | 6.698 | 6.698 | 6.038 | 90 | 90 | 90 | -8.7723                | -2.358                      | -0.275                           |

$^a$ Formation enthalpies and entropies of metal silicates are expressed with respect to their binary oxides.

$^b$ Formation entropies are evaluated from temperature of peritectic reactions (MO2 + Liquid → MSiO4).

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**Fig. 2.** Calculated isothermal sections of Zr-Si-O at (a) 500K and (b) 1000K. Tie lines are drawn inside the two phase regions.

According to the calculation results of isopleths and isothermal sections of the Hf-Si-O system, HfO2 and Si...
should be stable at the temperature range between 670K and 1700K. However, it is reported that under oxygen-deficient conditions, Hf-silicide forms at the HfO₂/Si interface even in this temperature range. Wang et al. [6] found that oxygen-deficient HfOₓ<2 consumes the oxygen in the SiO₂ thin layer covered on the silicon substrate to form fully oxidized metal oxide. Even the layer of silicides will be decomposed along with the progress of HfOₓ<2 deposition. The recent work from Miyata et al. [7] also confirmed the formation of nanometer-scale HfSi₂ dots on the newly opened void surface produced by the decomposition of HfO₂/SiO₂ films at the oxide/void boundary in vacuum.

To further understand the effect of the oxygen partial pressure, the phase diagrams of oxygen partial pressure-temperature are calculated and shown in Figure 3 with the ratio between the metals (Hf and Zr) and Si set to 1. It should be mentioned here that the oxygen partial pressure in these calculations are the local oxygen pressure at the interface, which is extremely low. Consequently, both systems initially form only metallic silicides. As oxygen partial pressure increases, part of the silicides transform into metal oxides. Afterwards, HfO₂ and Si are stable in the Hf-Si-O system as confirmed by experiments.[5, 6, 7, 8] Then, HfO₂ is in equilibrium with HfSiO₄. In the Zr-Si-O system, with further oxidation, ZrO₂ is stable with Si. However, the phase region is narrower than that of the Hf-Si-O system. This is in agreement with Copel et al. [3] that ZrO₂ is vulnerable to high temperature vacuum annealing. Therefore, it is possible to have a stable ZrO₂/Si interface, but this is very challenging in the high vacuum condition.

In summary, with the thermodynamic descriptions of the Hf-Si-O and Zr-Si-O systems developed by the CALPHAD technique, isopleths and isothermal sections can be readily calculated. It is found that the HfO₂/Si interface is thermodynamically stable between 670 and 1700K as far as oxygen partial pressure is high enough to keep HfO₂ stable. ZrO₂/Si interface is stable between 879 and 1630K, but in the oxygen-deficient condition, the processing window for a stable ZrO₂/Si interface is very narrow. Both metal oxides are stable with a Si substrate above 900K, even with the uncertainties of the formation enthalpies and entropies for metal silicates.

This work is funded by the National Science Foundation (NSF) through grants DMR-0205232 and 0510180. First-principles calculations were carried out on the LION clusters at the Pennsylvania State University supported in part by the NSF grants (DMR-9983532, DMR-0122638, and DMR-0205232) and in part by the Materials Simulation Center and the Graduate Education and Research Services at the Pennsylvania State University.

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Fig. 3. Partial pressure of oxygen vs. temperature phase diagrams for (a) Hf-Si-O and (b) Zr-Si-O systems when xoHf/xoSi=1. SiO₂(T) and ZrO₂(Q) represent Quartz and Tridymite, respectively.
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