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Thermodynamic stability of binary oxides in contact with silicon

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Using tabulated thermodynamic data, a comprehensive investigation of the thermodynamic stability of binary oxides in contact with silicon at 1000 K was conducted. Reactions between silicon and each binary oxide at 1000 K, including those involving ternary phases, were considered. Sufficient data exist to conclude that all binary oxides except the following are thermodynamically unstable in contact with silicon at 1000 K: Li_2O , most of the alkaline earth oxides (BeO , MgO , CaO , and SrO), the column IIIB oxides (Sc_2O_3 , Y_2O_3 , and Re_2O_3 , where Re is a rare earth), ThO_2 , UO_2 , ZrO_2 , HfO_2 , and Al_2O_3 . Of these remaining oxides, sufficient data exist to conclude that BeO , MgO , and ZrO_2 are thermodynamically stable in contact with silicon at 1000 K. Our results are consistent with reported investigations of silicon/binary oxide interfaces and identify candidate materials for future investigations.

I. INTRODUCTION

The fabrication of oxide thin-film microstructures on silicon substrates offers tremendous opportunities for the future of microelectronic devices. Such microstructures would allow oxide layers to be fully integrated with silicon circuitry and the broad variety of optical, electronic, and magnetic properties of oxides to be utilized on-chip. If high dielectric constant (ϵ_r) oxides, ferroelectric oxides, high transition temperature (T_c) superconducting oxides, or magnetic oxides could be combined with existing semiconductor technology, the materials properties available for use in microelectronics would be drastically enhanced, allowing improved functionality and performance to be realized. Unfortunately, direct growth of these oxides on silicon is frequently accompanied by extensive interdiffusion or chemical reactions that degrade the properties of the oxide, the underlying silicon, or both.¹⁻⁸ Consequently, the focus of a great deal of materials research has been devoted to overcoming these obstacles through the identification of compatible buffer layers for use between silicon and the desired oxide layers.⁷⁻⁹

Several factors must be considered in selecting materials for use as buffer layers between silicon and a particular oxide: chemical reactions, interdiffusion, thermal expansion match, crystal structure, and lattice match are some of the most important.⁸⁻¹⁰ Extensive chemical reaction between the buffer layer material and silicon or between the buffer layer material and the overlying oxide can result in the formation of interfacial phases that often result in a loss of epitaxy. Interdiffusion

among silicon, the buffer layer, and the overlying oxide can severely degrade the desired properties of these materials. For example, impurities diffusing into an oxide superconductor film can lower the T_c , reduce the temperature coefficient of resistivity, and increase the normal-state resistivity.¹¹ Impurities diffusing into the silicon substrate, especially those that produce deep levels such as the yttrium, barium, and copper constituents of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ high T_c superconductor, dramatically alter carrier concentration profiles and lower carrier lifetimes in the silicon.^{7,12} Thermal expansion mismatch must be minimized to prevent cracking due to thermally induced strains upon cooling after growth, especially if these strains lead to a state of tension in the overgrown oxide films, which is typically the case due to the low thermal expansion coefficient of silicon. In addition, the crystal structure and lattice match between each of the layers must be considered when epitaxy is desired. Ideally, a buffer layer for the growth of an oxide on silicon should provide a nonreactive diffusion barrier and a stable nucleation template for the subsequent epitaxial growth of the overlying desired oxide.

This paper addresses the issue of chemical reaction between silicon and binary oxide buffer layers. Specifically the thermodynamic stability of binary oxides in contact with silicon for potential use as epitaxial buffer layers between silicon and oxide thin films was examined at 1000 K, since this is a typical deposition temperature for the epitaxial growth of oxides. Thermodynamic instability is a necessary, but insufficient criterion to conclude that an interface *will* react. It indicates the presence of a driving force for reaction, but it is possible for a kinetic barrier to limit the extent of reaction or even prevent a thermodynamically unstable interface from reacting at all. Of course, at the relatively high

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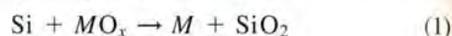
temperature considered, 1000 K, such kinetic barriers must be significant to prevent interaction. Reactions involving gaseous species were not considered as it was desired to test the stability of the interface between two solids (silicon and the binary oxide) and there is thus no free volume in which a gas can exist. Most of the binary oxides considered in this comprehensive study were determined to be thermodynamically unstable in contact with silicon and consequently were eliminated. For many of the remaining materials the calculations were unable to be completed due to the lack of thermodynamic data for silicides, ternary phases, or both. These materials could neither be eliminated nor determined to be stable. Existing experimental results indicate that many of these remaining materials are stable in contact with silicon; those that have not been reported warrant experimental investigation. Finally, sufficient data exist to conclude that BeO, MgO, and ZrO₂ are thermodynamically compatible with silicon.

II. METHOD

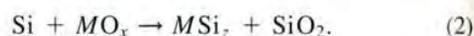
In order to narrow down the list of binary oxides that could be stable in contact with silicon at 1000 K, possible reactions between each binary oxide and silicon, for which thermodynamic data existed, were considered. Any reaction leading to a lowering of the Gibbs free energy of the system ($\Delta G < 0$) allowed the binary oxide to be eliminated from further consideration. This is not to say that the reaction found was the most favorable of all possible reactions, but the identification of any reaction products more stable than silicon in contact with the binary oxide implies that the latter interface is thermodynamically unstable. Identification of the most stable reaction products was not our goal, and in many cases cannot be accomplished due to insufficient thermodynamic data. The method employed is the same as that used by Beyers¹³⁻¹⁶ to determine the *M-Si-O* phase diagrams for *M* = Ti, Zr, Ta, Mo, and W. Here it is applied to all elements of the periodic table in order to identify prudent choices of silicon-compatible binary oxides for subsequent experimental studies.¹⁷

Although there are many possible reactions, several key reactions can be identified by considering the phase diagram of a *M-Si-O* system. This phase diagram contains silicon, the binary oxide under consideration, *MO_x*, and all the possible products of a reaction between silicon and the binary oxide. In general this phase diagram will contain ternary *M-Si-O* phases, but due to the lack of thermodynamic data for ternary phases, we first consider the phase diagram of a *M-Si-O* system free of ternary phases and containing only one binary oxide (*MO_x*) of the element *M*, as shown in Fig. 1.^{15,16} Ti-Si-O is an example of a system free of ternary phases. For the binary oxide to be stable in contact with silicon, a tie-line must exist between *MO_x* and silicon. The existence of such a stable

tie-line constrains the rest of the phase diagram, since the crossing of tie-lines is forbidden (a consequence of the Gibbs phase rule as described in the Appendix). There are only three possible types of *M-Si-O* phase diagrams. These are shown in Fig. 1 and referred to as "metal oxide dominant," "SiO₂ dominant," and "no phase dominant,"¹⁸ following the work of Beyers.^{15,16} In this study we are interested only in the metal oxide dominant-type, since it is the only type having a tie-line between *MO_x* and silicon. Thermodynamic data may be used to determine which of these three types of phase diagrams a particular *M-Si-O* system belongs to. A reaction flowchart allowing this determination is given in Fig. 2. For the purposes of the present study, any system that fails ($\Delta G < 0$) a reaction along the path to the metal oxide dominant-type system can be eliminated from further consideration. The (unbalanced) reactions along this path are

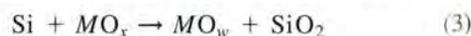


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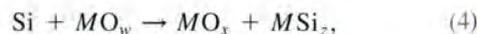


if an element has multiple silicides, the most silicon-rich silicide (*MSi_z*) should be used in Eq. (2).¹⁹ Any system that fails Eq. (1) can be eliminated from further consideration. Any system that passes ($\Delta G > 0$) Eq. (1) but fails Eq. (2) can also be eliminated. This conclusion is true even if the *M-Si-O* system contains ternary phases or multiple binary oxides *MO_x*, because failing Eq. (1) or (2) implies that silicon is thermodynamically unstable in contact with the binary oxide.

If the *M-Si-O* system contains more than one *MO_x* binary oxide, then after passing ($\Delta G > 0$) Eqs. (1) and (2), reactions involving *MO_x* binary oxides on both sides of the equation must also be tested. The *M-Si-O* systems that passed Eqs. (1) and (2) had at most two *MO_x* binary oxides. For systems containing two binary oxides the additional (unbalanced) reactions to be tested are



and



where *MO_x* and *MO_w* are the two binary oxides (*MO_x* being the more oxygen-rich), at least one of which has passed Eqs. (1) and (2). Equation (3) needs to be tested only when *MO_x* has passed Eqs. (1) and (2). Similarly, Eq. (4) needs to be tested only when *MO_w* has passed Eqs. (1) and (2). If an element has multiple silicides, the most silicon-rich silicide (*MSi_z*) should be used in Eq. (4).²⁰ If the *M-Si-O* system fails ($\Delta G < 0$) Eq. (3), then a stable tie-line does not exist between silicon and *MO_x* and it may be eliminated from further consideration. Similarly, if it fails Eq. (4), then a stable tie-line does not

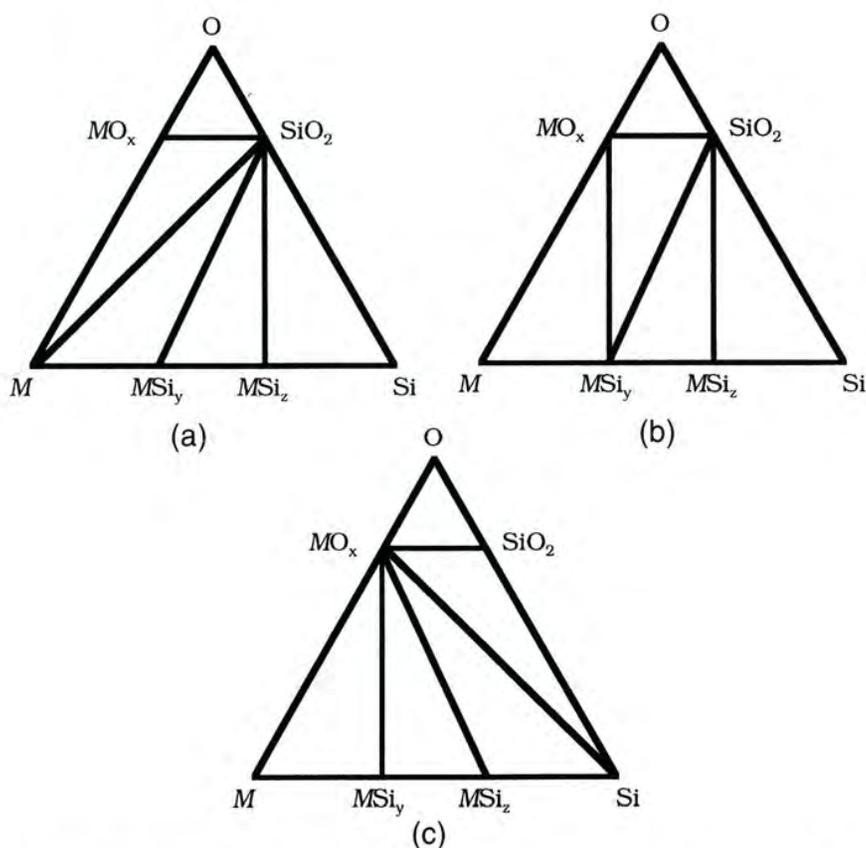


FIG. 1. The three types of M - Si - O phase diagrams at fixed temperature and pressure: (a) SiO_2 dominant, (b) no phase dominant, and (c) metal oxide dominant (after Ref. 13).

exist between silicon and MO_w and it may be eliminated. A flowchart showing these reactions and the resulting phase diagrams is given in Fig. 3.²¹

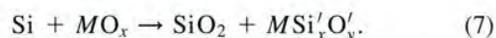
If the M - Si - O system contains ternary phases, then after passing ($\Delta G > 0$) Eqs. (1) and (2) [and Eqs. (3) or (4) if the system contains more than one MO_x binary oxide], further reactions involving ternary products must be tested. In general, the relevant reaction to test is that at the crossing of two potential tie-lines. For the case at hand, the relevant crossing is between the Si - MO_x tie-line with one dictated by the location of the ternary phase(s). If a ternary phase (MSi_xO_y) which exists at 1000 K lies on the tie-line between silicon and the binary oxide (MO_x), silicon will not be thermodynamically stable in contact with MO_x and the system can be eliminated from further consideration. No such examples were found. If all of the ternary phases existing at 1000 K are on only one side or the other of the Si - MO_x tie-line, the relevant reactions depend on which side they occur, as shown in Fig. 4. If all of the ternary phases lie above the Si - MO_x tie-line [as shown in Fig. 4(a)], the relevant (unbalanced) reactions are



and



whereas if all of the ternary phases lie below the Si - MO_x tie-line [as shown in Fig. 4(b)], the relevant (unbalanced) reaction is



Equations (5) and (6) need to be evaluated only for those ternary oxides (MSi_xO_y) that are positioned such that the triangle MSi_xO_y - MO_x - Si does not contain any other ternary oxides.²² Those ternary oxides satisfying this condition are shown as solid dots in Fig. 4(a). Equation (5) needs to be evaluated only for the most silicon-rich silicide (MSi_z).²³ Only if Eqs. (5) and (6) are passed ($\Delta G > 0$) by all such ternary oxides, can the Si - MO_x tie-line be concluded to be thermodynamically stable. Similarly, Eq. (7) needs to be evaluated only for those ternary oxides ($MSi'_xO'_y$) that are positioned such that the triangle $MSi'_xO'_y$ - MO_x - Si does not contain any other ternary oxides.²² The ternary oxides satisfying this condition are shown as solid dots in Fig. 4(b). Only if Eq. (7) is passed by all such ternary oxides, can the Si - MO_x tie-line be concluded to be thermodynamically

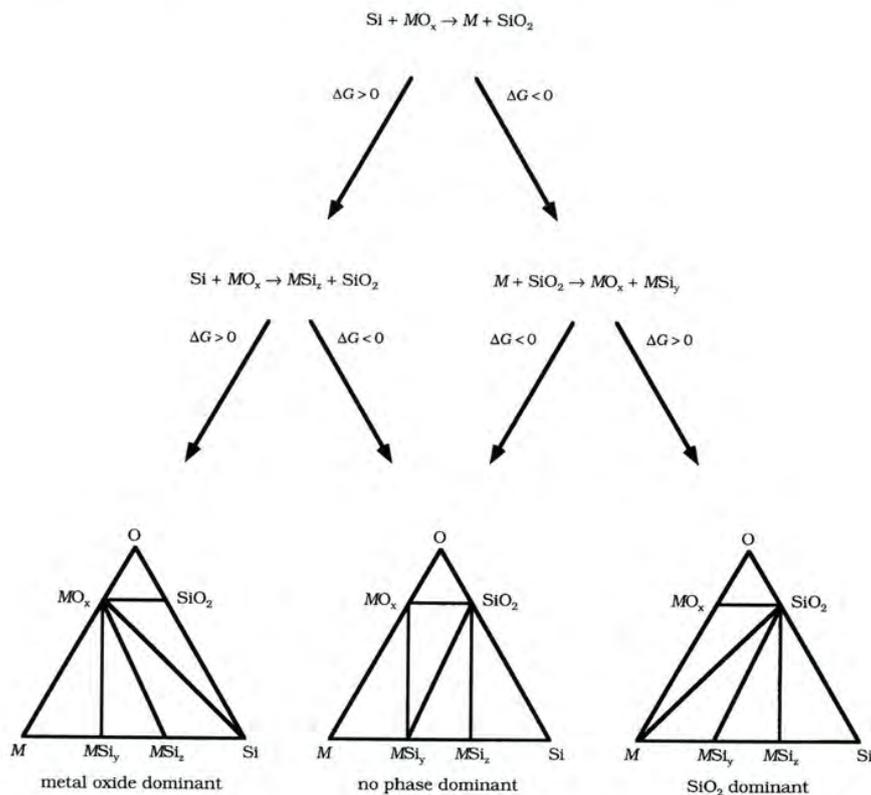
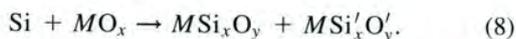


FIG. 2. A reaction flowchart showing what two reactions (unbalanced as-shown) can be used to determine which of the three types of phase diagrams a particular M - Si - O system belongs to if the system contains no ternary phases (MSi_xO_y) and only one M_x phase.

stable. For all but one of the M - Si - O systems that passed Eqs. (1) and (2), all of the ternary phases lay above the Si - MO_x tie-line.

If the M - Si - O system contains ternary phases on both sides of the Si - MO_x tie-line, then in addition to Eqs. (5), (6), and (7), reactions with ternary products lying above (MSi_xO_y) and below ($\text{MSi}'_x\text{O}'_y$) the Si - MO_x tie-line must also be tested:



The only system of this type that passed ($\Delta G > 0$) Eqs. (1) and (2) was the Si - Sc - O system.

The Gibbs free energy change at 1000 K (ΔG_{1000}°) was calculated for each of the above reactions using the available free energies of formation at 1000 K ($G_{f,1000}^\circ$) of each element (M), binary oxide (MO_x , silicide (MSi_z), ternary phases (MSi_xO_y), and of silicon and SiO_2 (quartz). The values of $G_{f,1000}^\circ$ were taken from Refs. 24, 25, and 26. All the data for a single calculation were taken from either Refs. 24 and 25 or from Ref. 26 to maintain consistency. Note that there are slight discrepancies in the tabulated values in these different sources for the same material. No single calculation was made with data from both sources. For the calculations involving Sc_2O_3 , La_2O_3 , Nd_2O_3 , and Gd_2O_3 , Refs. 24 and 25 were used for the values of $G_{f,1000}^\circ$ for silicon, MO_x , MSi_xO_y , and SiO_2 , while

Ref. 27 was used in determining the values of $G_{f,1000}^\circ$ for the corresponding silicides.

For each reaction (appropriately balanced for the particular binary oxide, MO_x , with coefficients ν) $\Delta G_{f,1000}^\circ$ for the complete reaction was determined by subtracting the sum of the free energies of formation of the reactants from the sum of the free energies of formation of the products²⁸:

$$\Delta G_{1000}^\circ = \sum_{\text{Products}} \nu G_{f,1000}^\circ - \sum_{\text{Reactants}} \nu G_{f,1000}^\circ. \quad (9)$$

The magnitude of $\Delta G_{f,1000}^\circ$ indicates the direction of the reaction. A negative value for $\Delta G_{f,1000}^\circ$ indicates that it is thermodynamically favorable for the reaction to proceed to its products. Thus, when it was determined that $\Delta G_{f,1000}^\circ$ for one of the above reactions was negative, indicating that silicon and MO_x are not thermodynamically stable in contact with each other, the respective binary oxide was eliminated from further consideration.

In cases where $\Delta G_{f,1000}^\circ$ is close to zero, it is important to consider the accuracy of the thermodynamic data. When the magnitude of $\Delta G_{f,1000}^\circ$ is less than this accuracy, no conclusion of thermodynamic stability or instability can be made. Unfortunately, the accuracy of thermodynamic data is frequently not given. References 24 and 25 do give an indication of the accuracy of their

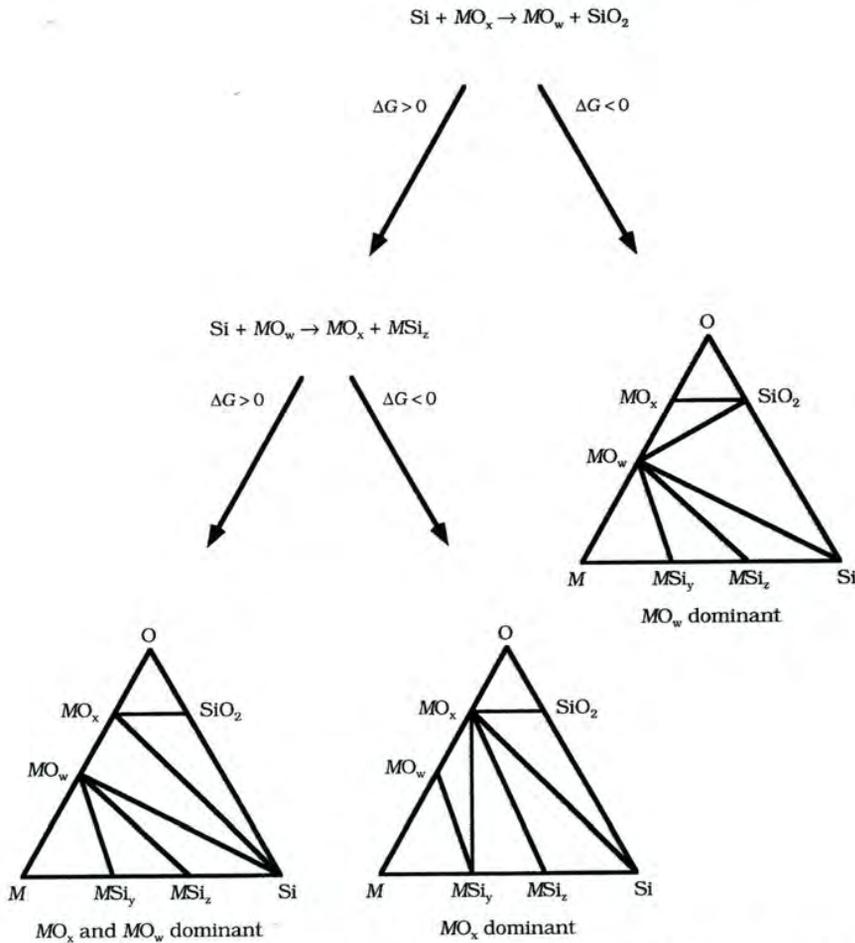


FIG. 3. A reaction flowchart showing what two reactions (unbalanced as-shown) can be used to determine which of the three types of phase diagrams a particular M - Si - O system belongs to if the system is free of ternary phases (MSi_xO_y) and contains two metal oxide phases, MO_w and MO_x , both of which have passed Eqs. (1) and (2).

tabulated thermodynamic data, and for this reason these references were used whenever possible. With the exception of TiSi_2 and ZrSi_2 , all of the thermodynamic data from Refs. 24 and 25 used in the calculations given have a stated accuracy of "C" or better, for those cases where the accuracy was given. This means that the accuracy of the $G_{f,1000}^\circ$ values themselves are better than ± 2.3 kcal/mol at $T = 1000$ K,^{24,25} and implies that the accuracy of the $G_{f,1000}^\circ$ values for the reactions evaluated using these data is better than about ± 5 kcal/mol. The magnitudes of nearly all the reactions calculated are well above this approximate accuracy. For those reactions evaluated using Refs. 24 and 25 where the magnitude of $\Delta G_{f,1000}^\circ$ is less than 5 kcal/mol, the approximate accuracy of the calculated $\Delta G_{f,1000}^\circ$ value is given adjacent to it, based on the stated accuracy of the reference data.

The reactions listed above were used (in the order given) to determine $\Delta G_{f,1000}^\circ$ for each of the binary oxides under consideration in this study (see Table II). Equation (1) was used to determine $\Delta G_{f,1000}^\circ$ for the bi-

nary oxides listed in Table II. Those with a negative value for $\Delta G_{f,1000}^\circ$ were eliminated from further consideration. The remaining materials (see Table III) were tested using Eq. (2). Note that for many of these remaining binary oxides Eq. (2) could not be completed due to the lack of data for the relevant MSi_z phase. Those materials with no known silicides are identified. Equations (3) and (4) were applied to those remaining systems containing multiple binary oxides (see Table IV). Those that failed (a negative value for $\Delta G_{f,1000}^\circ$) were eliminated from further consideration.

Using Ref. 29, all known ternary phases (MSi_xO_y) for the M - Si - O systems of the remaining binary oxides were identified and are listed in Table V. Using Eqs. (5) and (6) $\Delta G_{f,1000}^\circ$ for the remaining binary oxides (for which thermodynamic data for MSi_xO_y phases were available) was calculated and is given in Table VI. A summary of the remaining binary oxides that were not able to be eliminated on thermodynamic grounds is given in Table VII. For three of these sufficient thermodynamic

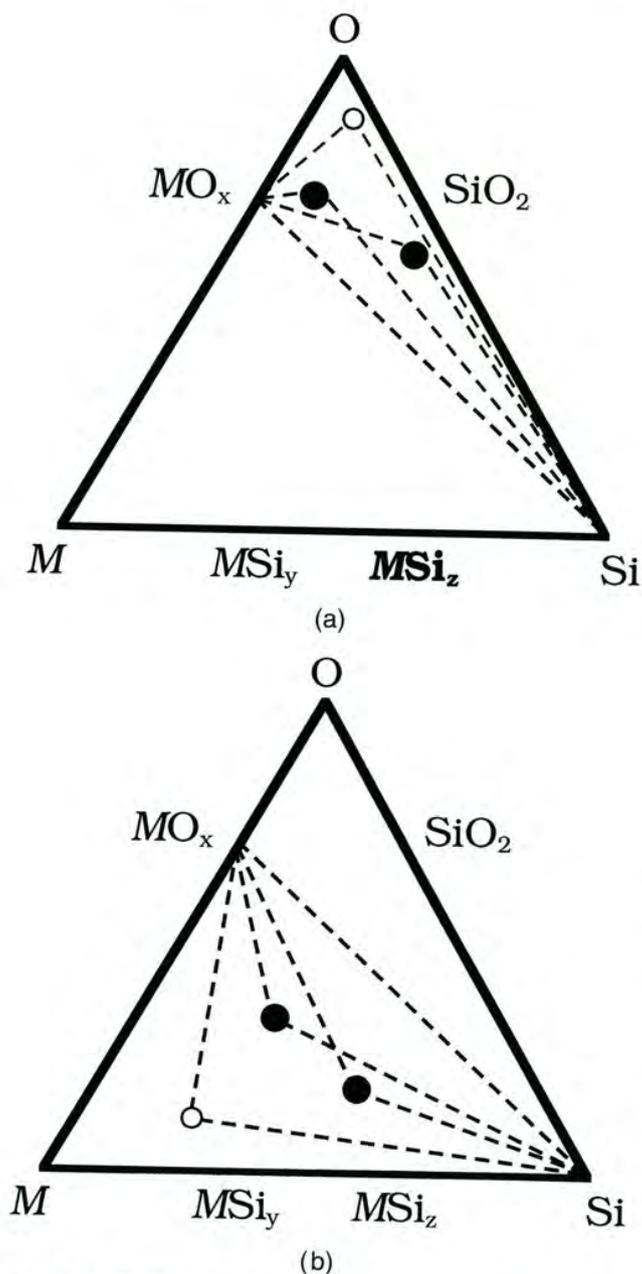


FIG. 4. M - Si - O phase diagrams containing one or more ternary phases (MSi_xO_y , at position of dots) located (a) above the Si - MO_x tie-line and (b) beneath the Si - MO_x tie-line. For case (a) Eqs. (5) and (6) should be used to test the stability of the Si - MO_x tie-line with the ternary phases (MSi_xO_y) indicated by a solid dot. For case (b) Eq. (7) should be used with those ternary phases ($MSi'_xO'_y$) indicated by a solid dot. Ternary phases indicated by hollow dots (those that are positioned such that the triangle MSi_xO_y - MO_x - Si or $MSi'_xO'_y$ - MO_x - Si contains other ternary oxides) do not need to be considered.

data existed to complete the thermodynamic calculations and conclude stability. The remaining 23 materials *might* be stable in contact with silicon at 1000 K. Many of these

materials have already been investigated; the remaining materials warrant study.

III. RESULTS

A. Initial considerations

The goal of this study was to identify potentially compatible binary oxides for use as effective buffer layers or as epitaxial thin films on silicon, by eliminating those that are thermodynamically reactive with silicon. A binary oxide in contact with silicon must be stable not only at the temperature used for its growth, but also at the temperatures used for the growth of additional oxide layers on top of the binary oxide (e.g., oxide superconductors, high ϵ_r insulators, ferroelectrics, ferromagnets, etc.). Typically, substrate temperatures (T_{sub}) between 800 K and 1200 K are used, depending on the particular oxide. Consequently, the free energy calculations of this study were performed at 1000 K.

All naturally occurring elements (M) that form binary oxides (MO_x) listed in Ref. 30 were considered in this comprehensive study. Of these, only nonradioactive oxides that exist as solids at 1000 K were pertinent. Table I lists those binary oxides that were eliminated from further consideration according to these constraints. All the binary oxides remaining after those in Table I were eliminated are contained in Table II, with the exception of SiO_2 , since it is the native oxide of silicon and is the trivial case of an oxide that is stable in contact with silicon. SiO_2 might seem like the obvious choice for integration of silicon with oxide overlayers; however, the amorphous nature of overgrown SiO_2 or SiO_2 formed by the oxidation of silicon (for layers thicker than about 0.5 nm³⁸) makes the growth of epitaxial oxide overlayers on SiO_2 a formidable obstacle.^{39,40}

B. Binary oxides eliminated by considering $Si + MO_x \rightarrow M + SiO_2$ at 1000 K

The binary oxides remaining after those in Table I were eliminated are listed in Table II. Those materials that have a negative $\Delta G_{f,1000}^\circ$ for the reaction $Si + MO_x \rightarrow M + SiO_2$ at 1000 K [Eq. (1)] can be removed from the list of candidates since they are thermodynamically unstable in contact with silicon at 1000 K. From this reaction alone, the binary oxides of 30 elements can be eliminated. No attempt was made to determine the phase diagrams of those binary oxide systems that were dismissed.

C. Binary oxides eliminated by considering $Si + MO_x \rightarrow MSi_z + SiO_2$ at 1000 K

For those materials that passed ($\Delta G > 0$) Eq. (1), $\Delta G_{f,1000}^\circ$ for the reaction $Si + MO_x \rightarrow MSi_z + SiO_2$ at 1000 K [Eq. (2)] was determined in those cases where free

TABLE I. Binary oxides that were deemed unacceptable for integration with silicon at a growth temperature of approximately 1000 K.

Binary oxide (MO_x)	Reason unacceptable ^a	Binary oxide (MO_x)	Reason unacceptable ^a
H ₂ O	MP = 273 K	Pt ₃ O ₄	h
Na ₂ O ₂	DT = 733 K	PtO ₂	MP = 723 K
K ₂ O ₂	MP = 763 K	PtO ₃	c
K ₂ O ₃	MP = 703 K	Ag ₂ O	DT = 403 K
KO ₂	MP = 653 K	Ag ₂ O ₂	DT > 373 K
Rb ₂ O	DT = 673 K	Au ₂ O ₃	DT = 433 K
Rb ₂ O ₂	MP = 843 K	Hg ₂ O	DT = 373 K
Rb ₂ O ₃	MP = 762 K	HgO	DT = 773 K
RbO ₂	MP = 705 K	Ga ₂ O	MP > 933 K
Rb ₂ O ₄	DT = 773 K	In ₂ O	c
Cs ₂ O	MP = 763 K	InO	c
Cs ₂ O ₂	MP = 673 K	Tl ₂ O	MP = 852 K ⁱ
Cs ₂ O ₃	MP = 673 K	Tl ₂ O ₂	MP = 990 K
Oxides of Fr, Ra, Pm, the actinides (Ac to Lr), Tc, Po, At, and Rn	Radioactive	B ₂ O ₃	MP = 723 K
MgO ₂	DT = 361 K ^b	Oxides of C	BP < 280 K
CaO ₂	DT = 548 K	Pb ₂ O	c
SrO ₂	DT = 488 K	Pb ₂ O ₃	DT = 643 K
BaO ₂	MP = 723 K	Oxides of N	BP < 295 K
V ₂ O ₅	MP = 963 K	P ₂ O ₃	MP = 297 K
Nb ₂ O ₃	c	P ₂ O ₄	MP < 373 K
Ta ₂ O ₄	d	P ₂ O ₅	MP = 573 K
CrO	e	Oxides of Po	Radioactive
CrO ₂	MP = 573 K	As ₂ O ₃	MP = 585 K
CrO ₃	MP = 469 K	As ₂ O ₅	DT = 588 K
Mo ₂ O ₃	c	Sb ₂ O ₃	MP = 929 K
Mo ₂ O ₅	e	Sb ₂ O ₅	DT = 653 K
W ₂ O ₅	c	BiO	DT = 453 K
MnO ₂	DT = 808 K	Bi ₂ O ₅	DT = 423 K
Mn ₂ O ₇	MP = 279 K	Oxides of S	BP < 1000 K
ReO ₃	DT = 673 K	SeO ₂	MP = 391 K
Re ₂ O ₇	MP = 570 K	SeO ₃	MP = 590 K
RuO ₄	MP = 299 K	TeO	DT = 643 K
OsO	c	TeO ₃	DT = 668 K
Os ₂ O ₃	c	Oxides of Br	MP < 373 K
OsO ₄	MP = 313 K	IO ₂	DT < 403 K
Co ₂ O ₃	DT = 538 K ^f	I ₄ O ₉	DT = 348 K
RhO ₂	DT = 953 K ^g	I ₂ O ₅	DT = 573–623 K
PtO	DT = 823 K	Oxides of At	Radioactive

^aSee Ref. 30. MP = Melting Point, BP = Boiling Point, DT = Decomposition Temperature.

^bSee Ref. 31.

^cNot listed in Ref. 29.

^dNot stable as a pure phase. See Refs. 32 and 33.

^eNot a stable phase. See Refs. 33, 34, and 35.

^fSee Ref. 36.

^gSee Ref. 37.

^hHigh pressure phase ($P_{O_2} \geq 40$ atm at 1000 K). See Ref. 37.

ⁱSee Ref. 26.

energy data for the silicides were available (see Table III). Beryllium and aluminum do not form silicides,^{29,41} obviating the need to evaluate Eqs. (2) and (5) for BeO and Al₂O₃. The results allowed CeO₂, TiO, Ti₂O₃, and TiO₂ to be eliminated from consideration. The negative value of $\Delta G_{f,1000}^\circ$ for the reactions involving TiO, Ti₂O₃, and TiO₂ indicates that the Ti–Si–O system is a no phase dominant system [see Fig. 1(b)], in agreement with the results of Beyers.¹³ Due to the lack of free energy data for pertinent

silicides, Eq. (2) could not be evaluated for many of the remaining binary oxides.

D. Binary oxides eliminated by considering reactions involving another binary oxide

Reactions involving multiple binary oxides MO_x were considered next. The M–Si–O systems that passed ($\Delta G > 0$) Eqs. (1) and (2) had at most two MO_x binary oxides.

TABLE II. Gibbs free energy change at 1000 K (ΔG_{1000}°) for the reaction $\text{Si} + \text{MO}_x \rightarrow \text{M} + \text{SiO}_2$ (balanced appropriately) for each of the binary oxides remaining after those in Table I were eliminated.

Binary oxide (MO_x)	ΔG_{1000}° per MO_x for $\text{Si} + \text{MO}_x \rightarrow \text{M} + \text{SiO}_2$ (balanced appropriately) (kcal/mol)	Reference(s)	Binary oxide (MO_x)	ΔG_{1000}° per MO_x for $\text{Si} + \text{MO}_x \rightarrow \text{M} + \text{SiO}_2$ (balanced appropriately) (kcal/mol)	Reference(s)
Li ₂ O	+ 24.298	24	Nb ₂ O ₅	- 86.228	24
Na ₂ O	- 20.061	24	Ta ₂ O ₅	- 52.533	24, 25
K ₂ O	- 33.749	24	Cr ₂ O ₃	- 55.275	24, 25
BeO	+ 32.405	24, 25	MoO ₂	- 76.902	24, 25
MgO	+ 30.572	24, 25	MoO ₃	-143.782	24, 25
CaO	+ 39.914	24, 25	WO ₂	- 77.126	24
SrO	+ 30.821	24, 25	WO _{2.72}	-107.195	24
BaO	+ 21.338	24	WO ₃	-121.814	24
Sc ₂ O ₃	+123.105	24, 25	MnO	- 12.752	24, 25
Y ₂ O ₃	+116.823	24	Mn ₃ O ₄	-100.598	24, 25
La ₂ O ₃	+ 98.470	24, 25	Mn ₂ O ₃	- 94.689	24, 25
Ce ₂ O ₃	+104.946	24, 25	TcO ₂ ^a	-112.914	24, 25
CeO ₂	+ 36.290	24, 25	ReO ₂	-126.662	26
Pr ₂ O ₃	+105.768	24, 25	FeO	- 37.774	24, 25
PrO ₂	+ 13.559	24, 25	Fe ₃ O ₄	-160.084	24, 25
Nd ₂ O ₃	+101.692	24, 25	Fe ₂ O ₃	-127.471	24, 25
Sm ₂ O ₃	+103.941	26	RuO ₂	-142.270	26
EuO	+ 33.238	26	OsO ₂	-147.245	24, 25
Eu ₂ O ₃	+ 61.901	26	CoO	- 48.041	24, 25
Gd ₂ O ₃	+101.549	24	Co ₃ O ₄	-227.374	24, 25
Tb ₂ O ₃	+114.762	24, 25	Rh ₂ O ₃	-235.152	24, 25
TbO _{1.72}	+ 38.273	24, 25	IrO ₂	-159.465	24, 25
Dy ₂ O ₃	+112.435	26	NiO	- 51.377	24, 25
Ho ₂ O ₃	+118.450	26	PdO	- 86.066	24
Er ₂ O ₃	+122.030	26	Cu ₂ O	- 64.284	24, 25
Tm ₂ O ₃	+116.654	26	CuO	- 71.375	24, 25
Yb ₂ O ₃	+103.830	26	ZnO	- 28.461	24, 25
Lu ₂ O ₃	+116.965	26	CdO	- 49.433	24, 25
ThO ₂ ^a	+ 75.513	26	Al ₂ O ₃	+ 63.399	24, 25
UO ₂ ^a	+ 43.670	24, 25	Ga ₂ O ₃	- 79.411	24, 25
TiO	+ 17.849	24	In ₂ O ₃	-117.722	26
Ti ₂ O ₃	+ 35.432	24	GeO ₂	- 82.124	26
TiO ₂	+ 7.527	24	SnO	- 43.514	24, 25
ZrO ₂	+ 42.326	24	SnO ₂	- 84.977	24, 25
HfO ₂	+ 47.648	24, 25	PbO	- 59.249	24, 25
VO	- 5.314	24, 25	Pb ₃ O ₄	-269.624	24, 25
V ₂ O ₃	- 30.197	24, 25	PbO ₂	-155.786	24, 25
VO ₂	- 43.280	24, 25	SbO ₂	-110.523	24, 25
NbO	- 10.132	24	Bi ₂ O ₃	-191.853	24, 25
NbO ₂	- 13.872	24	TeO ₂	-140.949	24, 25

^aRadioactive, but still considered since thermodynamic data exist.

Equations (3) and (4) were applied to these systems and the results are given in Table IV. The results allowed PrO₂, Eu₂O₃, and TbO_{1.72} (Tb₇O₁₂) to be eliminated from consideration.

E. Binary oxides eliminated by considering reactions involving ternary phases

The presence of ternary phases at 1000 K in the remaining candidate *M*-Si-O systems is now considered. Table V lists the ternary phases known to exist²⁹ in the systems remaining under consideration and the values of

$G_{f,1000}^\circ$ for those phases for which data exist.^{24,25} Note that all of the remaining *M*-Si-O systems under consideration contain ternary phases. For systems in which data on the relevant thermodynamic phases were not available, Eqs. (5) and (6) were evaluated for all phases for which data were available. Although thermodynamic data for the relevant phases are required to conclude thermodynamic stability, if any of the ternary phases leads to a negative $\Delta G_{f,1000}^\circ$ in Eqs. (5) or (6), the binary oxide can be eliminated.

Table VI contains the results of the relevant thermodynamic calculations [Eqs. (5) and (6)] involving ternary

TABLE III. Gibbs free energy change at 1000 K (ΔG_{1000}°) for the reaction $\text{Si} + \text{MO}_x \rightarrow \text{MSi}_z + \text{SiO}_2$ (balanced appropriately) for each of the binary oxides in Table II that had a positive ΔG_{1000}° for the reaction $\text{Si} + \text{MO}_x \rightarrow \text{M} + \text{SiO}_2$ (balanced appropriately).

Binary oxide (MO_x)	ΔG_{1000}° per MO_x for $\text{Si} + \text{MO}_x \rightarrow \text{MSi}_z + \text{SiO}_2$ (balanced appropriately) (kcal/mol)	Relevant silicide (MSi_z) ^a	Reference(s)
Li ₂ O	b	Li ₂₁ Si ₈	...
BeO	c	c	29
MgO	+23.385	Mg ₂ Si	26
CaO	+17.582	CaSi ₂	24, 25
SrO	b	SrSi ₂	...
BaO	b	BaSi ₂	...
Sc ₂ O ₃	+91.297	ScSi	24, 25, 27
Y ₂ O ₃	b	YSi ₂	...
La ₂ O ₃	+66.372	LaSi _{1.69}	24, 25, 27
Ce ₂ O ₃	+17.896	CeSi ₂	24, 25
CeO ₂	-7.908	CeSi ₂	24, 25
Pr ₂ O ₃	b	PrSi ₂	...
PrO ₂	b	PrSi ₂	...
Nd ₂ O ₃	+76.974	NdSi _{1.8}	24, 25, 27
Sm ₂ O ₃	b	SmSi _{1.4}	...
EuO	b	EuSi ₂	...
Eu ₂ O ₃	b	EuSi ₂	...
Gd ₂ O ₃	+88.582	GdSi _{1.89}	24, 25, 27
Tb ₂ O ₃	b	TbSi ₂	...
TbO _{1.72}	b	TbSi ₂	...
Dy ₂ O ₃	b	DySi _{1.4}	...
Ho ₂ O ₃	b	HoSi ₂	...
Er ₂ O ₃	b	ErSi ₂	...
Tm ₂ O ₃	b	TmSi _{2-x}	...
Yb ₂ O ₃	b	YbSi _{2-x}	...
Lu ₂ O ₃	b	Lu ₂ Si ₃	...
ThO ₂ ^d	b	ThSi ₂	...
UO ₂ ^d	+12.066	USi ₃	24, 25
TiO	-12.693	TiSi ₂	24, 25
Ti ₂ O ₃	-25.651	TiSi ₂	24, 25
TiO ₂	-23.014	TiSi ₂	24, 25
ZrO ₂	+5.914	ZrSi ₂	24, 25
HfO ₂	b	HfSi ₂	...
Al ₂ O ₃	c	c	29

^aSee Refs. 27 and 29.

^bFree energy data for the silicide(s) were unavailable.

^cNo known silicides.

^dRadioactive, but still considered since thermodynamic data exist.

phases. The values of ΔG_{1000}° for reactions involving Li₂O, CaO, and BaO were negative. However, for the reactions involving Li₂O and CaO, the magnitude of the negative ΔG_{1000}° is within the uncertainty of the thermodynamic data. Hence the results allowed only BaO to be eliminated from consideration. In most cases these calculations could not be completed due to the lack of free energy data for pertinent ternary phases or silicides.

For three of the systems under consideration, the data for the relevant known ternary phases were available and the calculations were completed. The results of these thermodynamic calculations indicated that BeO,

MgO, and ZrO₂ are thermodynamically stable in contact with silicon at 1000 K, as summarized in Table VII. Beyers' thermodynamic calculations¹⁶ previously showed ZrO₂ to have a stable tie-line with silicon at 1000 K; the calculations of the present study confirm Beyers' findings.

IV. COMPARISON TO EXPERIMENTAL OBSERVATIONS

Both the growth of binary oxides on silicon as well as silicon on binary oxides have been reported. Most of the recent work with the aim of integrating oxides, other than SiO₂, with silicon technology has focused on the integration of oxide superconductors with silicon. Due to the extensive reaction that accompanies direct integration,^{1,2,4,5} many researchers have been working to fabricate superconducting thin films on silicon by depositing a nonreactive epitaxial buffer layer between the silicon substrate and the superconducting oxide.^{7,9} In order to preserve the crystalline template of silicon, the growth of binary oxides on silicon is usually initiated in a vacuum or oxygen-deficient atmosphere.⁴²⁻⁴⁹ Following nucleation of the binary oxide, growth of the binary oxide is continued in an oxygen-rich atmosphere. The excess-oxygen environment may lead to the oxidation of the silicon (or of the silicides or other interfacial reaction products) underlying the binary oxide, if the binary oxide is sufficiently permeable to oxygen. Although the effects of this additional oxidation are not considered in our thermodynamic reactivity analysis, the stability of the initial binary oxide/silicon interface is. The stability of this interface is an important consideration for epitaxial growth. In addition to the recent efforts to integrate oxide superconductors with silicon, the effort (primarily in the 1960s) to develop an epitaxial silicon-on-insulator (SOI) technology has also led to the experimental investigation of silicon deposited on binary oxides.^{50,51} Below we compare these experimental observations with the thermodynamic stability of each binary oxide/silicon interface.

The results of this study are remarkably consistent with experimental reports. With the possible exception of BaO, PrO₂, and IrO₂, for which detailed analysis of the interface with silicon is lacking as described below, the only binary oxides found to be free of reaction layers with silicon are all among the list of candidate materials identified in this study. The integration of several of the candidate materials with silicon, i.e., Li₂O, Sc₂O₃, most of the Re_2O_3 oxides, and HfO₂,⁵² has not been experimentally reported and warrants investigation. Below we compare the experimental observations of all reported binary oxide/silicon couples, both the growth of the binary oxide on silicon, as well as the growth of silicon on the binary oxide, with the results of our thermodynamic analysis.

TABLE IV. Gibbs free energy change at 1000 K (ΔG_{1000}°) for the reactions [Eqs. (3) and (4)] involving multiple MO_x binary oxides for each of the binary oxides in Table III that had a positive ΔG_{1000}° for the reaction $Si + MO_x \rightarrow MSi_2 + SiO_2$ (balanced appropriately) and multiple MO_x binary oxides.

Binary oxide (MO_x or MO_w)	ΔG_{1000}° per MO_x for $Si + MO_x \rightarrow MO_w + SiO_2$ (balanced appropriately) (kcal/mol)	ΔG_{1000}° per MO_w for $Si + MO_w \rightarrow MO_x + MSi_2$ (balanced appropriately) (kcal/mol)	Reference(s)
Ce_2O_3	...	+29.758	24, 25
Pr_2O_3	...	a	...
PrO_2	-39.325
EuO	...	a	24, 25
Eu_2O_3	-4.575
Tb_2O_3	...	a	26
$TbO_{1.72}$	-19.108
		...	24, 25

^aFree energy data for the silicide(s) were unavailable.

A. Reported binary oxide/silicon reactions

Relatively few examples of reactions of binary oxides with silicon have been reported. This may at first seem surprising considering that the vast majority of binary oxides are thermodynamically unstable in contact with silicon at 1000 K, but a nonreactive barrier layer is clearly more newsworthy than a reactive one. What few reports exist are often relegated to brief remarks or footnotes in the description of an otherwise successful experiment.

Reaction between silicon and Gd_2O_3 (at T_{sub} between 923 K and 1023 K),⁹ SnO_2 (at T_{sub} above 1273 K),⁵⁰ and PbO (at $T_{sub} = 783$ K)³ have been noted. All of these, except Gd_2O_3 , are expected from our thermodynamic calculations. Although we were unable to complete our thermodynamic calculations for Gd_2O_3 due to the lack of thermodynamic data, Gd_2O_3 passed ($\Delta G > 0$) the two reactions for which sufficient data were available [Eqs. (1) and (2)]. Tarsa *et al.*⁹ suggested that Gd_2O_3 reacts with silicon to form GdO_2 . Unfortunately, we were unable to assess if this reaction is thermodynamically favored due to the absence of thermodynamic data for GdO_2 .

An equivalent means of showing that a MO_x/Si interface is thermodynamically unstable is to demonstrate the stability of another interface in the $M-Si-O$ phase diagram that would necessarily cross the $Si-MO_x$ tie-line. For example, the stability of M/SiO_2 interfaces has been experimentally (and thermodynamically) studied.⁵³ A stable M/SiO_2 interface in a given $M-Si-O$ system implies that the MO_x/Si interface in that system must be thermodynamically unstable, since the crossing of tie-lines is forbidden. The experiments of Pretorius *et al.*⁵³ showed the metals Cr, Mn, Fe, Co, Ni, Pd, Pt, and Cu to be stable in contact with SiO_2 at 1073 K signifying that the corresponding metal-oxides are all thermodynamically unstable in contact with silicon. Similarly, experiments showing the stability of molybdenum and tungsten in contact with SiO_2 at 1273 K to 1573 K,⁵⁴ the stability of $TiSi$ and $TiSi_2$ in contact with SiO_2 at

1273 K,^{13,55} the stability of V_3Si in contact with SiO_2 at 1273 K,⁵⁶ and the stability of $TaSi_2$ in contact with SiO_2 at temperatures between 1173 K and 1323 K,^{55,57} indicate that the corresponding metal-oxides are all thermodynamically unstable in contact with silicon. These results are all in agreement with our thermodynamic calculations.

B. Reported nonreactive binary oxide-silicon interfaces

1. BeO/Si

Our thermodynamic calculations indicate that BeO is stable in contact with silicon at 1000 K. This is consistent with the experimental observations of Manasevit *et al.*⁵⁸ who reported the epitaxial growth of silicon on several faces of BeO single crystals at substrate temperatures near 1450 K.

2. MgO/Si

Based on the thermodynamic calculations of this study, MgO and silicon are stable in contact with each other at 1000 K. Reports of reaction-free MgO/Si interfaces confirm our thermodynamic calculations.^{59,60} In particular, Fork *et al.*⁵⁹ have examined an epitaxial MgO/Si interface of a film grown at a substrate temperature of 773 K by high-resolution cross-sectional transmission electron microscopy (TEM) and show that it is abrupt and free from reaction layers or noticeable interdiffusion. Cross-sectional TEM studies of polycrystalline MgO films grown on silicon have revealed either no interfacial reaction ($T_{sub} = 923$ K)⁶⁰ or a thin amorphous interfacial layer ($T_{sub} = 673$ K to 773 K).⁶¹ In light of the absence of an interfacial layer in the epitaxial MgO films,⁵⁹ the latter observation of an amorphous interlayer⁶¹ is more likely attributed to incomplete removal of the native oxide on the silicon substrate prior to growth or oxidation of the silicon by O^{2-} ion transport through the polycrystalline

TABLE V. Ternary phases present in the metal-silicon-oxygen systems for each of the binary oxides in Table III that had a positive ΔG_{1000}° for the reaction $\text{Si} + \text{MO}_x \rightarrow \text{MSi}_z + \text{SiO}_2$ (balanced appropriately). The known free energies of formation at 1000 K ($G_{f,1000}^{\circ}$) for these phases are also given. The relevant ternary phases for Eqs. (5) and (6) are shown in bold.

Ternary phase ^a (MSi_xO_y)	Free energy of formation ($G_{f,1000}^{\circ}$) (kcal/mol)	Ternary phase ^a (MSi_xO_y)	Free energy of formation ($G_{f,1000}^{\circ}$) (kcal/mol) ^b
Li₈SiO₆	c	Eu₃SiO₅	c
Li ₄ SiO ₄	- 605.954	Eu ₂ SiO ₄	c
Li ₆ Si ₂ O ₇	c	Eu ₂ SiO ₅	c
Li ₂ SiO ₃	- 428.439	Eu ₃ Si ₂ O ₇	c
Li ₂ Si ₂ O ₅	- 664.434	EuSiO ₃	c
Li ₂ Si ₃ O ₇	c	Eu ₂ Si ₂ O ₇	c
Be₂SiO₄	- 543.542	Gd₂SiO₅	c
Mg₂SiO₄	- 560.595	Gd ₃ Si ₂ O ₇	c
MgSiO ₃	- 398.377	Tb₂SiO₅	c
Ca₃SiO₅	- 753.050	Tb ₂ Si ₂ O ₇	c
Ca ₂ SiO ₄	- 586.443	Dy₂SiO₅	c
Ca ₈ Si ₅ O ₁₈	c	Dy ₂ Si ₂ O ₇	c
Ca ₃ Si ₂ O ₇	- 1023.100	Ho₂SiO₅	c
CaSiO ₃	- 422.822	Ho ₄ Si ₃ O ₁₂	c
CaSi ₂ O ₅	c	Ho ₂ Si ₂ O ₇	c
Sr₃SiO₅	c	Ho ₂ Si ₃ O ₉	c
Sr ₂ SiO ₄	- 605.164	Ho₂Si₆O₉	c
SrSiO ₃	- 426.295	Er₂SiO₅	c
Ba₃SiO₅	c	Er ₂ Si ₂ O ₇	c
Ba ₂ SiO ₄	- 608.939	Tm₂SiO₅	c
BaSiO ₃	- 427.257	Tm ₂ Si ₂ O ₇	c
Ba ₂ Si ₃ O ₈	c	Yb₃SiO₅	c
Ba ₅ Si ₈ O ₂₁	c	Yb ₃ SiO ₇	c
Ba ₃ Si ₅ O ₁₃	c	Yb ₂ SiO ₄	c
BaSi ₂ O ₅	c	Yb ₂ SiO ₅	c
BaSi ₄ O ₉	c	YbSiO ₃	c
ScSi_{0.02}O_{0.98}	c	Yb ₂ Si ₂ O ₇	c
Sc₂SiO₅	c	Lu₂SiO₅	c
Sc ₂ Si ₂ O ₇	c	Lu ₂ SiO ₇	c
Y₂SiO₅	c	Lu ₂ Si ₂ O ₇	c
Y ₄ Si ₃ O ₁₂	c	ThSiO₄	c
Y ₂ Si ₂ O ₇	c	USiO₄	c
La₂SiO₅	c	USi ₇ O ₁₇	c
La ₂ Si ₂ O ₇	c	ZrSiO₄	- 520.307
Ce₂SiO₅	c	HfSiO₄	c
Ce ₂ Si ₂ O ₇	c	Al_{1.90}Si_{0.05}O_{2.95}	c
Pr₂SiO₅	c	Al _{1.70} Si _{0.15} O _{2.85}	c
Pr ₈ Si ₆ O ₂₄	c	Al _{1.40} Si _{0.30} O _{2.70}	c
Nd₂SiO₅	c	Al ₆ Si ₂ O ₁₃	- 1736.172
Nd ₄ Si ₃ O ₁₂	c	Al ₂ SiO ₅	- 660.925
Nd ₂ Si ₂ O ₇	c	Al _{0.50} Si _{0.75} O _{2.25}	c
Sm₂SiO₄	c	Al₂Si₄O₁₀	c
Sm ₂ SiO ₅	c		
Sm ₄ Si ₃ O ₁₂	c		
SmSiO ₃	c		
Sm ₂ Si ₂ O ₇	c		

^aFree energy data from Refs. 24 and 25.^bTernary phase data from Ref. 29.^cFree energy data not given in Refs. 24 and 25.

MgO film (e.g., along grain boundaries) during growth, than to a reaction between MgO and silicon.

3. CaO/Si

Sufficient data existed to complete the thermodynamic calculations for CaO. The calculations indicated

that CaO and silicon would react at 1000 K ($\Delta G_{1000}^{\circ} < 0$) to form CaSi₂ and Ca₃SiO₅. However, the magnitude of this reaction (-1.519 kcal/mol) is close to the approximate uncertainty of the thermodynamic data (± 1 kcal/mol). Consequently, the instability of the CaO/Si interface cannot be asserted. The growth of CaO

TABLE VI. Gibbs free energy change at 1000 K (ΔG_{1000}°) for the reactions [Eqs. (5) and (6)] involving relevant ternary phases (bold) for which data were available (Table V) for each of the binary oxides in Table III that had a positive ΔG_{1000}° for the reaction $\text{Si} + \text{MO}_x \rightarrow \text{MSi}_z + \text{SiO}_2$ (balanced appropriately).

Ternary phase (MSi_xO_y)	ΔG_{1000}° per MO_x for $\text{Si} + \text{MO}_x \rightarrow \text{MSi}_z + \text{MSi}_x\text{O}_y$ (balanced appropriately) (kcal/mol)	ΔG_{1000}° per MO_x for $\text{Si} + \text{MO}_x \rightarrow \text{M} + \text{MSi}_x\text{O}_y$ (balanced appropriately) (kcal/mol)
Li_4SiO_4	a	- 0.493 ^c (± 0.8) ^d
Li_2SiO_3	a	+ 5.049
$\text{Li}_2\text{Si}_2\text{O}_5$	a	+12.467
Be_2SiO_4	b	+14.414
Mg_2SiO_4	+7.951	+11.544
Ca_3SiO_5	-1.519 ^c (± 1.0) ^d	+10.155
Sr_2SiO_4	a	+ 3.041 (± 1.4) ^d
SrSiO_3	a	+ 4.807 (± 1.4) ^d
Ba_2SiO_4	a	- 4.831 (± 0.8) ^d
BaSiO_3	a	+ 2.359 (± 0.9) ^d
ZrSiO_4	+1.253 ^c (± 2.1) ^d	+19.459
$\text{Al}_6\text{Si}_2\text{O}_{13}$	b	+19.050
Al_2SiO_5	b	+24.443

^aFree energy data for the silicide(s) were unavailable.

^bNo known silicides.

^cThe magnitude of this reaction is close to the approximate uncertainty of the thermodynamic data, making its result inconclusive.

^dThe approximate uncertainty given is a lowerbound on the error; approximate errors were not given in Refs. 24 and 25 for some of the terms involved in the calculation of this ΔG_{1000}° value.

on silicon at a substrate temperature of 673 K has been reported by Soerensen and Gyax.⁶² They used Auger depth profiling to analyze a 50 Å thick CaO film grown on silicon and reported that the CaO/Si interface was on the order of 20 Å wide. This suggests that the CaO/Si interface is free of reaction layers.

4. SrO/Si

Although the thermodynamic calculations for SrO in contact with silicon at 1000 K could not be completed due to the absence of thermodynamic data for SrSi_2 and Sr_3SiO_5 , it is believed that SrO and silicon are thermodynamically stable in contact at 1000 K based on experimental observations. Kado and Arita^{63,64} grew both epitaxial SrO films on silicon and epitaxial silicon films on SrO by molecular beam epitaxy (MBE) at substrate temperatures between 923 K and 1053 K. They used Auger electron spectroscopy (AES) to depth-profile the SrO/Si interface(s) and reported both the absence of noticeable interdiffusion at the interface(s) and the absence of Auger peaks due to SiO_2 . Similarly, Soerensen and Gyax⁶² also reported reaction-free SrO/Si interfaces for films grown at $T_{\text{sub}} = 673$ K. It has also been shown that it is not necessary to completely remove the thin native oxide (SiO_2) layer from the silicon substrate in order to achieve an epitaxial SrO layer.⁴² The

residual SiO_2 may be reduced (to Si or volatile SiO) and the excess strontium metal oxidized (to SrO) by initiating the growth with strontium metal in an oxygen-deficient atmosphere.⁴² This observation is consistent with the absence of a stable tie-line between strontium metal and SiO_2 [e.g., the SiO_2 dominant system shown in Fig. 1(a)], and together with the other experimental observations is consistent with the presence of a stable tie-line between silicon and SrO.

5. BaO/Si

Our thermodynamic calculations indicate that it is energetically favorable for BaO to react with silicon [e.g., to form barium metal and Ba_2SiO_4 , Eq. (6)]. However, experimental evidence does not support this conclusion. Kado and Arita⁶⁴ grew epitaxial BaO films on silicon by MBE at a substrate temperature of 1053 K and reported a Rutherford backscattering spectrometry (RBS) channeling yield, χ_{min} , of about 7%. McKee *et al.*⁴³ have also reported the MBE growth of epitaxial BaO layers on silicon substrates by a more involved route, involving the formation of a one monolayer thick BaSi_2 layer on top of the silicon prior to the deposition of BaO. This later result demonstrates the existence of a stable tie-line between BaSi_2 and BaO, which, in the absence of the existence of ternary phases, would mandate a stable tie-line between silicon and BaO [i.e., the metal oxide dominant system shown in Fig. 1(c)]. Analysis of the BaO/ BaSi_2 /silicon interfaces after growth has not been reported, leaving it unclear if the one monolayer thick BaSi_2 layer survives intact or if the final interface is simply between BaO and silicon as the prior work of Kado and Arita⁶⁴ suggests is stable. Such interfacial characterization would help to resolve the discrepancy between our thermodynamic calculations and reported observations. It is possible that interfacial energies favor the BaO/silicon interface due to its more favorable lattice match. Interfacial energies not included in our thermodynamic calculations are likely important in cases where the magnitude of the free energy change of an interfacial reaction is small, as in this case and also for Li_2O /silicon, CaO/silicon, SrO/silicon, and ZrO_2 /silicon (see Table VI).

6. Y_2O_3 /Si

The epitaxial growth of Y_2O_3 on silicon^{44-46,65-67} and silicon on Y_2O_3 ⁶⁸ has been demonstrated at substrate temperatures ranging from 1003 K to 1073 K. Reaction between the silicon and Y_2O_3 has not been reported, despite *in situ* monitoring of the deposition process with reflection high-energy electron diffraction (RHEED) during growth.^{44,65-68} High-resolution cross-sectional TEM micrographs of the Y_2O_3 /Si interface have also been obtained.⁴⁶ Therefore, even though our thermodynamic calculations could not be completed due to the absence

TABLE VII. Summary of the remaining binary oxides that were not able to be eliminated on thermodynamic grounds. These are the only binary oxides that *may* be stable in contact with silicon. Due to the lack of free energy data for relevant silicides, ternary phases, or both, only for a limited number of binary oxides (shown in bold) could thermodynamic stability with silicon be concluded.

Oxide	Magnitude of ΔG_{1000}° per MO_x for Reaction 1 ^a (kcal/mol)	Magnitude of ΔG_{1000}° per MO_x for Reaction 2 ^a (kcal/mol)	Magnitude of ΔG_{1000}° per MO_x for Reaction 5 ^a (kcal/mol)	Magnitude of ΔG_{1000}° per MO_x for Reaction 6 ^a (kcal/mol)
Li ₂ O	+ 24.298	b	b	- 0.493 ^g (± 0.8) ^h
BeO	+ 32.405	c	c	+14.414 ^f
MgO	+ 30.572	+23.385	+7.951 ^f	+11.544 ^f
CaO	+ 39.914	+17.582	-1.519 ^g (± 1.0) ^h	+10.155 ^f
SrO	+ 30.821	b	b	Positive ^e
Sc ₂ O ₃	+123.105	+91.297	d	d
Y ₂ O ₃	+116.823	b	bd	d
La ₂ O ₃	+ 98.470	+66.372	d	d
Ce ₂ O ₃	+104.946	+17.896	d	d
Pr ₂ O ₃	+105.768	b	bd	d
Nd ₂ O ₃	+101.692	+76.974	d	d
Sm ₂ O ₃	+103.941	b	bd	d
EuO	+ 33.238	b	bd	d
Gd ₂ O ₃	+101.549	+88.582	d	d
Tb ₂ O ₃	+114.762	b	bd	d
Dy ₂ O ₃	+112.435	b	bd	d
Ho ₂ O ₃	+118.450	b	bd	d
Er ₂ O ₃	+122.030	b	bd	d
Tm ₂ O ₃	+116.654	b	bd	d
Yb ₂ O ₃	+103.830	b	bd	d
Lu ₂ O ₃	+116.965	b	bd	d
ThO ₂ ⁱ	+ 75.513	b	bd	d
UO ₂ ⁱ	+ 43.670	+12.066	d	d
ZrO₂	+ 42.326	+ 5.914	+1.253 ^g (± 2.1) ^h	+19.459 ^f
HfO ₂	+ 47.648	b	bd	d
Al ₂ O ₃	+ 63.399	c	c	Positive ^e

^aReactions (balanced appropriately)

1: $Si + MO_x \rightarrow M + SiO_2$ at 1000 K (Table II).

2: $Si + MO_x \rightarrow MSi_2 + SiO_2$ at 1000 K (Table III).

5: $Si + MO_x \rightarrow MSi_2 + MSi_xO_y$ at 1000 K (Table VI).

6: $Si + MO_x \rightarrow M + MSi_xO_y$ at 1000 K (Table VI).

^bFree energy data for the silicide(s) were unavailable.

^cNo known silicides.

^dFree energy data for the relevant ternary phase(s) were unavailable.

^eFree energy data for the relevant ternary phase(s) were not available. The free energy change at 1000 K (ΔG_{1000}°) for each of the phases for which data were available was positive.

^fFree energy data for the relevant ternary phase(s) were available and reactions 5 and 6 were positive in all cases.

^gThe magnitude of this reaction is close to the approximate uncertainty of the thermodynamic data, making its result inconclusive.

^hThe approximate uncertainty given is a lowerbound on the error; approximate errors were not given in Refs. 24 and 25 for some of the terms involved in the calculation of this ΔG_{1000}° value.

ⁱRadioactive, but still considered since thermodynamic data exist.

of free energy data for YSi₂ and Y₂SiO₅, it is believed that these calculations, if completed, would confirm the thermodynamic stability of Y₂O₃ in contact with silicon. Analogous to the case of epitaxial SrO/Si growth, it has been shown that it is not necessary to completely remove the thin native oxide (SiO₂) layer from the silicon substrate in order to achieve an epitaxial Y₂O₃ layer.⁴⁴⁻⁴⁶ By initiating growth with the deposition of yttrium metal in an oxygen-deficient atmosphere, the residual SiO₂ may be converted to Y₂O₃ and volatile SiO.⁴⁴ This observation is consistent with the absence of a stable tie-line between

yttrium metal and SiO₂ [e.g., the SiO₂ dominant system shown in Fig. 1(a)].

7. CeO₂/Si

CeO₂ has been epitaxially grown on silicon at temperatures ranging from 293 K to 1123 K.⁶⁹⁻⁷³ This result is unexpected from a thermodynamic standpoint as the calculations presented show that CeO₂ is thermodynamically unstable in contact with silicon [ΔG_{1000}° for Eq. (2) is *negative* for CeO₂]. As the magnitude of

ΔG_{1000}° for Eq. (2) involving CeO_2 , -7.908 kcal/mol, is not appreciably greater than the approximate accuracy of this calculation (approximately ± 2.7 kcal/mol),⁷⁴ Eq. (3) was also applied to see if the thermodynamic instability of CeO_2 with silicon could be more conclusively shown from existing thermodynamic data. The resulting ΔG_{1000}° for Eq. (3) is -16.856 kcal/mol.^{24,25} This result is sufficiently greater than the possible error in the thermodynamic data to rule out the possible thermodynamic stability of CeO_2 in contact with silicon.

Although from a thermodynamic standpoint the calculations presented show that CeO_2 is thermodynamically unstable in contact with silicon, Ce_2O_3 is potentially stable in contact with silicon. This apparent discrepancy between experimental observation and the present thermodynamic calculations would be absent if at the silicon interface the CeO_2 were locally reduced to Ce_2O_3 , yielding a stable $\text{Si/Ce}_2\text{O}_3/\text{CeO}_2$ interface. Indeed both *in situ* x-ray photoelectron spectroscopy (XPS) measurements^{71,72} and *ex situ* cross-sectional TEM investigations⁷³ of epitaxial CeO_2 films deposited on silicon indicate the presence of a mixed-valence^{71,72} (Ce^{4+} and Ce^{3+}), oxygen-deficient⁷³ (CeO_{2-x}) region in the vicinity of the CeO_2/Si interface. Using cross-sectional TEM Chikyow *et al.*⁷³ examined several epitaxial CeO_2/Si interfaces prepared under different conditions, yet nowhere did they find CeO_2 in direct contact with silicon. Similarly, the cross-sectional TEM images of as-grown CeO_2/Si films reported by Inoue *et al.*⁷⁵ do not show CeO_2 in direct contact with silicon. Instead, these TEM studies reveal an amorphous layer between the silicon and overgrown CeO_2 .^{73,75} Inoue *et al.*⁷⁵ attribute this layer to amorphous SiO_2 , while Chikyow *et al.*⁷³ conclude that this amorphous interlayer consists of SiO_2 and oxygen-deficient CeO_{2-x} . The thickness of this layer depends on the growth conditions,⁷⁵ but it is typically a few nanometers in thickness. This suggests, since epitaxy occurs, that the amorphous SiO_2 layer is formed after the initial stages of growth due to O^{2-} ion conduction through the growing CeO_2 (and CeO_{2-x}),⁷⁵ much as the amorphous SiO_2 layer forms at the yttria-stabilized zirconia (YSZ)/Si interface observed by Fenner *et al.*¹

8. PrO_2/Si

Despite our conclusion that PrO_2 is thermodynamically unstable in contact with silicon at 1000 K [ΔG_{1000}° for Eq. (3) is *negative* for PrO_2], Fork *et al.*⁷⁶ have grown epitaxial PrO_2 on silicon at substrate temperatures between 823 K and 923 K. At these lower growth temperatures, ΔG° for Eq. (3) is still negative; in fact, it becomes even more negative than it is at 1000 K. The reported results would be in complete agreement with our thermodynamic analysis if during the initial stages of

growth a stable $\text{PrO}_2/\text{Pr}_2\text{O}_3/\text{Si}$ interface is formed; such a situation is analogous to the thermodynamically unstable CeO_2/Si interface at which interfacial reaction occurs. Unfortunately, cross-sectional TEM studies of PrO_2/Si interfaces have not been reported.

9. $\text{Pr}_2\text{O}_3/\text{Si}$

Without thermodynamic data for PrSi_2 and Pr_2SiO_5 it is not possible to determine the thermodynamic stability of Pr_2O_3 in contact with silicon. However, Tarsa *et al.*⁷⁷ have grown epitaxial Pr_2O_3 films on silicon and epitaxial silicon films on Pr_2O_3 at a substrate temperature of 873 K. Their study, which includes *in situ* RHEED analysis during growth and *ex situ* cross-sectional TEM analysis, contains no evidence suggestive of reaction at the $\text{Pr}_2\text{O}_3/\text{Si}$ interfaces. It is thus believed that Pr_2O_3 is thermodynamically stable in contact with silicon.

10. $\text{Nd}_2\text{O}_3/\text{Si}$

Due to the lack of thermodynamic data for Nd_2SiO_5 , we were unable to complete our thermodynamic analysis of the stability of Nd_2O_3 in contact with silicon at 1000 K. Nagata *et al.*⁷¹ have reported the epitaxial growth of Nd_2O_3 films on silicon at substrate temperatures between 873 K and 973 K, which would be consistent with the thermodynamic stability of Nd_2O_3 in contact with silicon.

11. ThO_2/Si

Although the thermodynamic calculations for ThO_2 could not be completed due to the absence of thermodynamic data for ThSi_2 and ThSiO_4 , it is believed that ThO_2 and silicon are thermodynamically stable in contact at 1000 K based on experimental observations. The cube-on-cube epitaxial growth of silicon on ThO_2 single crystals has been reported for substrate temperatures between 1373 K and 1423 K.^{50,78} Although it appears that the ThO_2/Si interface is stable, the practicality of using ThO_2 as a buffer layer is unlikely because of its radioactive nature.

12. ZrO_2/Si

There are many reports of the epitaxial growth of ZrO_2 films on silicon at substrate temperatures ranging from 923 K to 1153 K,^{47,66,79-81} but no reports of interfacial reaction between ZrO_2 and silicon. These results are in agreement with the thermodynamic calculations presented in this study in which we find the ZrO_2/Si interface to be stable at 1000 K.

Although the successful integration of yttria-stabilized cubic zirconia ($\text{Y}_2\text{O}_3\text{-ZrO}_2$) with silicon has been widely demonstrated (both the epitaxial growth of silicon on $\text{Y}_2\text{O}_3\text{-ZrO}_2$ ^{66,68,82} and vice versa^{1,44-46,48,65,66,68,80,83-86}), calculating the thermodynamic stability of this ternary

oxide is beyond the scope of the calculations that we present here for binary oxides. Just as it has been shown possible to grow epitaxial SrO and epitaxial Y_2O_3 films on silicon without first removing the thin native oxide (SiO_2) from the silicon substrate,^{42,44-46} epitaxial ZrO_2 ⁴⁷ and $Y_2O_3-ZrO_2$ ^{44-46,48,49} films have been grown on silicon by initiating growth in an oxygen-deficient atmosphere. This results in the reduction of the residual SiO_2 (to Si or volatile SiO) and oxidation of the excess metallic zirconium and yttrium. Additionally, the $Y_2O_3-ZrO_2/Si$ interface is one of the few thermodynamically compatible oxide/Si interfaces for which interdiffusion has been studied. Zirconium diffusion into the silicon was observed to have a decay length of 20 nm per decade of concentration decrease and silicon diffusion into the $Y_2O_3-ZrO_2$ was observed to have a decay length of 7 nm per decade.⁸⁶

13. HfO_2/Si

Although there are no reports characterizing the HfO_2/Si interface,⁵² the oxidation of $HfSi_2$ has been studied.⁸⁷ When $HfSi_2$ undergoes oxidation at temperatures between 773 K and 1273 K, SiO_2 is not found in contact with it,⁸⁷ implying the absence of a tie-line between $HfSi_2$ and SiO_2 . This implies that silicon is stable in contact with either HfO_2 or $HfSiO_4$. This is consistent with the results of our thermodynamic calculations, which could not be completed due to the absence of thermodynamic data for $HfSi_2$ and $HfSiO_4$.

14. RuO_2/Si

In contrast to our calculations indicating that silicon is *not* thermodynamically stable in contact with RuO_2 , initial experimental studies came to the opposite conclusion. Green *et al.*⁸⁸ reported stable RuO_2/Si interfaces for polycrystalline RuO_2 films grown on silicon wafers at substrate temperatures ranging from 848 to 873 K. AES depth-profiling and (low-resolution) TEM gave no indication of reaction or interdiffusion at the interface. This reaction-free result was also concluded by others using AES depth-profiling⁸⁹ or RBS^{90,91} to characterize the RuO_2/Si interface. The reportedly stable RuO_2/Si interface is, however, contrary to other experimental results presented in one of these same initial studies⁸⁸ and to more recent high-resolution TEM investigations.^{92,93} In addition to studying the RuO_2/Si interface, Green *et al.*⁸⁸ analyzed Ru/SiO_2 interfaces by AES depth-profiling, TEM, and RBS and reported that they were also reaction-free. These two experimental results are contradictory in that they simultaneously imply stable RuO_2-Si and $Ru-SiO_2$ tie-lines, an impossibility since it would require the crossing of tie-lines and thus violate the Gibbs phase rule. In contrast to the above experimental results, a thin (~ 3 nm) SiO_2 layer, undetected by the comparatively

low-resolution interface characterization methods mentioned above, was revealed by high-resolution TEM at the RuO_2/Si interface.^{92,93} It was present in the as-deposited polycrystalline RuO_2 films grown on silicon substrates and did not change appreciably in thickness after annealing these samples at temperatures between 723 K and 973 K.^{92,93} In addition to the thin SiO_2 layer, Charai *et al.*⁹³ also observed Ru_2Si precipitates at the RuO_2/Si interface and interpreted their results to indicate that the reaction $3Si + 2RuO_2 \rightarrow Ru_2Si + 2SiO_2$ [i.e., Eq. (2)] is favorable at 773 K. The presence of this reaction layer is in agreement with our thermodynamic calculations as well as prior thermodynamic calculations predicting $Ru-SiO_2$ to be the stable tie-line⁵³ in this system.

The reason that early experimental investigations did not reveal the presence of reaction products is due to the small size of the reaction products compared to the resolution of the interface analysis techniques utilized. At the relatively low reaction temperatures used, the interface reaction is not extensive.

15. IrO_2/Si

Using secondary ion mass spectrometry (SIMS) and x-ray diffraction, Nakamura *et al.*⁹⁴ concluded that the interface between polycrystalline silicon and polycrystalline IrO_2 is nonreactive at processing temperatures up to 1073 K. Our thermodynamic calculations lead to the opposite conclusion; IrO_2 fails ($\Delta G < 0$) Eq. (1). Unfortunately, in the SIMS analysis presented by Nakamura *et al.*⁹⁴ the IrO_2/Si interface occurred at about $0.6 \mu m$ below the sample surface, lowering the resolution at which the interface was chemically profiled. They also reported electrical continuity between the IrO_2 layer and underlying silicon layer. However, interfacial reaction does not preclude electrical continuity. For example, if one of the reaction products forms a conductive percolation path between the underlying silicon and IrO_2 , or if the thickness of the insulating reactant(s) (e.g., SiO_2) is very thin (increasing the probability of electron tunneling), continuity will still be observed. Prior thermodynamic calculations predict the Ir/SiO_2 interface to be stable,⁵³ which implies, in agreement with our calculations, that the IrO_2/Si interface is thermodynamically unstable. Further experimental investigation, e.g., high-resolution TEM, is needed to resolve this discrepancy. Such studies would be enhanced by using higher reaction temperatures to increase the extent of the reaction layer, if one, and facilitate its detection and analysis.

16. Al_2O_3/Si

Silicon-on-sapphire is an extensively studied system.^{50,51,95} Among other techniques, high-resolution

TEM has been used to probe the Si/Al₂O₃ interface, revealing it to be abrupt and free of reaction layers.⁹⁶ Epitaxial Al₂O₃ films on silicon substrates have also been prepared,^{97,98} as have epitaxial Si/Al₂O₃/Si heterostructures.⁹⁹ The substrate temperatures used for the synthesis of these epitaxial interfaces range from 723 K to about 1423 K.^{50,97} Although the thermodynamic calculations of this study could not be completed due to the lack of free energy data for Al_{1.90}Si_{0.05}O_{2.95} and Al₂Si₄O₁₀, the success by the above researchers in establishing reaction-free Al₂O₃/Si interfaces suggests that they are indeed thermodynamically compatible materials. Note that the well-known reaction between silicon and Al₂O₃, Al₂O₃ + 2Si → 2SiO + Al₂O,^{95,100} is not relevant to this study because it involves gaseous products.

17. In₂O₃/Si

Although our thermodynamic calculations indicate that the In₂O₃/Si interface is thermodynamically unstable at 1000 K, initial studies of the interface between polycrystalline In₂O₃ films and the underlying silicon substrate reported it to be reaction-free after processing at temperatures of 873 K¹⁰¹ and 923 K.¹⁰² This was likely due to the relatively low resolution of the AES depth-profiling,¹⁰² RBS interface analysis,¹⁰² and scanning transmission electron microscopy (STEM)¹⁰¹ methods employed and the relatively low reaction temperatures. In contrast to these initial results, a high-resolution TEM study revealed the presence of a thin (3.5 nm to 5 nm) SiO₂ layer at the In₂O₃/Si interface both in as-deposited polycrystalline In₂O₃ films on silicon and after annealing these films at 873 K.¹⁰³ This result is in agreement with our thermodynamic calculations.

C. Discussion

An important practical result of our calculations is that there are not any conducting binary oxides that are thermodynamically stable in contact with silicon at 1000 K. In applications where it is desired to provide a stable electrical contact between an oxide electrode and the underlying silicon (e.g., in DRAM's incorporating high ϵ_r materials), the most straightforward and processing-tolerant method for achieving such a contact would be to use a conductive oxide that is stable in contact with silicon. Since no such binary oxides exist, integration routes other than Si/conducting MO_x/insulator will probably be needed to provide reliable conducting contacts. Potential examples include Si/MSi₂/conducting MO_x/insulator [where *M* is chosen from an appropriate "no phase dominant" system of the type shown in Fig. 1(b)] or Si/MSi_z/MSi_y/M/conducting MO_x/insulator. This latter route involves moving from Si to MO_x along the edges of the Si-M-O phase diagram triangle, a path

that traverses only conducting elements, silicides, and oxides. A thermodynamically stable contact scheme involves a sequence of layers, between each of which a tie-line exists; i.e., each interface is thermodynamically stable. Of course, even if reaction occurs, it is possible to maintain electrical conduction between the silicon overlying conducting oxide if, for example, one of the reaction products is conductive and forms a conductive path between the silicon and conductive oxide or if the thickness of the insulating reactants is thin enough to allow sufficient conduction by electron tunneling. But obtaining such a conductive path is very dependent on reaction kinetics, and puts limits on the tolerable processing conditions.

In those cases where the thermodynamic stability of a particular binary oxide in contact with silicon could not be assessed due to insufficient thermodynamic data, an alternative to determining the free energy of the relevant phase(s) is to perform bulk or thin-film experiments to determine key tie-lines in the M-Si-O phase diagram.¹³⁻¹⁶ Conceptually the MO_x/Si interface itself is the most relevant to study. However, experimental difficulties associated with this interface may make other interfaces more tractable. For example, the MO_x/Si interface must be prepared using experimental conditions yielding silicon that is free of even a thin native oxide layer (i.e., SiO₂) being brought into initial contact with the binary oxide. Another potential complication is that excess oxygen during the fabrication process can lead to oxidation of the silicon surface, even though the MO_x/Si interface is stable, as has been observed for the CeO_{2-x}/Si and YSZ/Si interfaces by TEM.^{1,75}

For these reasons it is often experimentally more convenient to select a potential reaction other than that between MO_x and silicon to determine the key tie-lines in the M-Si-O phase diagram. Regardless if one is using thermodynamic data or experimental methods, the relevant reaction to test is one lying at the crossing of two potential tie-lines. The thermodynamic stability of all of the binary oxides, except Sc₂O₃, remaining in Table VII in contact with silicon could be established if Eqs. (2), (5), and (6) were evaluated. A simple bulk or thin-film means to experimentally evaluate the tie-line addressed by Eqs. (2) and (5) is to see if MSi_x is stable in contact with SiO₂ or MSi_xO_y. For example, MSi_z could be oxidized and the interface examined to see if MSi_z exists in contact with either SiO₂ or MSi_xO_y. Such an observation, as has been experimentally noted between SiO₂ and TiSi₂,^{13,55} V₃Si,⁵⁶ and TaSi₂,^{55,57} indicates the existence of a stable tie-line between MSi_z and SiO₂, and consequently implies the absence of a stable Si-MO_x tie-line. Similarly, Eq. (6) can be experimentally probed by depositing the metal *M* on the silicate MSi_xO_y and heating to see if a reaction takes place between these materials.

V. EXTENSION OF APPROACH TO TERNARY OXIDES

A thermodynamic analysis of the type used here to test the stability of binary oxides in contact with silicon can be readily extended to ternary oxides. Below we apply it to the case of SrTiO₃ in contact with silicon. Not only does sufficient data exist to show that SrTiO₃ is thermodynamically unstable in contact with silicon at 1000 K, but this interface has also been extensively studied experimentally. However, the use of this method to comprehensively investigate ternary oxides with the goal of identifying candidate buffer layers for use between silicon and overlying oxides is precluded by the lack of thermodynamic data.

Any reaction between SrTiO₃ and silicon with $\Delta G < 0$ is sufficient to show that the SrTiO₃/Si interface is thermodynamically unstable. One such reaction is



with $\Delta G_{1000}^\circ = -19.133$ kcal/mol.^{24,25} Although this reaction may not be the most favorable of all possible reactions, its existence indicates that the SrTiO₃/Si interface is thermodynamically unstable at 1000 K. Several researchers have noted a reaction at the SrTiO₃/Si interface at substrate temperatures ranging from 473 K to 873 K.¹⁰⁴⁻¹⁰⁶ This reaction interferes with the direct epitaxial growth of SrTiO₃ on silicon.¹⁰⁶⁻¹⁰⁸ One route leading to epitaxial SrTiO₃ films on silicon substrates has employed an intermediate epitaxial SrO buffer layer.¹⁰⁸ This is an excellent example of how a stable binary oxide buffer layer can enable the successful integration of oxides with silicon, i.e., SrTiO₃/SrO/Si.

A rule of thumb for choosing potential ternary or higher multicomponent oxides for direct integration with silicon is to choose those made of combinations of binary oxides that are all thermodynamically compatible with silicon.¹⁰⁹ Examples that follow this simple guide that have been experimentally demonstrated to be compatible with silicon are yttria-stabilized cubic zirconia (Y₂O₃-ZrO₂),^{1,44-46,48,49,65,66,68,80,82-86} (Ba,Sr)O,^{64,110} LaAlO₃,^{50,78} ZrSiO₄,^{50,78} Al₂BeO₄,⁵⁸ and MgAl₂O₄,^{50,51,111-113} whereas SrTiO₃ is not since TiO₂ is thermodynamically unstable in contact with silicon, as shown above.

VI. CONCLUSIONS

Thermodynamic data indicate that BeO, MgO, and ZrO₂ are thermodynamically stable in contact with silicon at 1000 K. There are no thermodynamic data available to show that Li₂O, most of the alkaline earth oxides (BeO, MgO, CaO, and SrO), the column IIIB oxides (Sc₂O₃, Y₂O₃, and Re₂O₃, where Re is a rare earth), ThO₂, UO₂, ZrO₂, HfO₂, and Al₂O₃ are not thermodynamically stable in contact with silicon. Of these materials, BeO, MgO,

CaO, SrO, Y₂O₃, Pr₂O₃, Nd₂O₃, ThO₂, ZrO₂, and Al₂O₃ have been integrated with silicon and appear to be free of reaction layers. The remaining materials (Li₂O, Sc₂O₃, most of the Re₂O₃ oxides, and HfO₂) are candidates for future experimental investigations. Note that all of these remaining binary oxides (both those determined to be compatible and those that are potentially compatible) are insulating materials, with ϵ_r value ranging from 3.0 for CaO to 21 for La₂O₃.³¹

For the successful integration of oxide overlayers (e.g., high T_c superconductors, ferroelectrics, etc.) on top of the binary oxides identified in this study as being stable or potentially stable in contact with silicon, compatibility between the overlayer and the binary oxide is also necessary. Although such stability was not the subject of this study, the limited number of binary oxides identified as being compatible or potentially compatible with silicon greatly limits the possibilities for a single binary oxide interlayer between the desired overlayer and a silicon substrate.

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REFERENCES

1. D. B. Fenner, A. M. Viano, D. K. Fork, G. A. N. Connell, J. B. Boyce, F. A. Ponce, and J. C. Tramontana, *J. Appl. Phys.* **69**, 2176 (1991).
2. C. Ziegler, F. Baudenbacher, H. Karl, H. Kinder, and W. Göpel, *Fresenius J. Anal. Chem.* **341**, 308 (1991).
3. Y. Shichi, S. Tanimoto, T. Goto, K. Kuroiwa, and Y. Tarui, *Jpn. J. Appl. Phys.* **33**, 5172 (1994).
4. M. Scheib, H. Goebel, L. Hofmann, B. Lengeler, H. Oechsner, and G. Zorn, *Thin Solid Films* **174**, 5 (1989).
5. J. K. G. Panitz and C. C. Hu, *J. Vac. Sci. Technol.* **16**, 315 (1979).
6. V. S. Dharmadhikari and W. W. Grannemann, *J. Vac. Sci. Technol. A* **1**, 483 (1983).
7. A. Mogro-Campero, *Supercond. Sci. Technol.* **3**, 155 (1990).
8. D. K. Fork, in *Pulsed Laser Deposition of Thin Films*, edited by D. B. Chrisey and G. K. Hubler (Wiley, New York, 1994), p. 393.
9. E. J. Tarsa, K. L. McCormick, and J. S. Speck, in *Epitaxial Oxide Thin Films and Heterostructures*, edited by D. K. Fork, J. M. Phillips, R. Ramesh, and R. M. Wolf (Mater. Res. Soc. Symp. Proc. **341**, Pittsburgh, PA, 1994), p. 73.
10. J. M. Phillips, *MRS Bulletin* **20**, 35 (April 1995); J. M. Phillips, to be published in *Processing and Properties of High T_c Superconductors, Volume 2: Thin Films*, edited by S. Jin and D. K. Christen (World Scientific).
11. M. Gurvitch and A. T. Fiory, *Appl. Phys. Lett.* **51**, 1027 (1987).
12. Q. X. Jia, K. L. Jiao, and W. A. Anderson, *J. Appl. Phys.* **70**, 3364 (1991).
13. R. Beyers, *J. Appl. Phys.* **56**, 147 (1984).
14. R. Beyers, R. Sinclair, and M. E. Thomas, *J. Vac. Sci. Technol. B* **2**, 781 (1984).

15. R. Beyers, K. B. Kim, and R. Sinclair, *J. Appl. Phys.* **61**, 2195 (1987).
16. R. Beyers, Ph.D. Thesis, Stanford University, 1989, pp. 38–76.
17. K. J. Hubbard, B.S. Thesis, The Pennsylvania State University, 1993.
18. Note that is the M - Si - O system contains more than one metal-silicide phase, there will be several phase diagram possibilities within the "no phase dominant" type; if the system contains no metal-silicide phases, there will not be a "no phase dominant" type.
19. Of all the silicides, only the most silicon-rich (MSi_z) lies on a tie-line between MSi_z and SiO_2 in all of the possible no phase dominant phase diagrams, making the preference of this tie-line or the one between silicon and MO_x , Eq. (2), the critical test of metal oxide dominant versus no phase dominant.
20. Of all the silicides, only the most silicon-rich (MSi_z) lies on a tie-line between MSi_z and MO_x in all of the possible MO_x dominant type (see Fig. 3) phase diagrams, making the preference of this tie-line or the one between silicon and MO_w , Eq. (4), the critical test of MO_x and MO_w dominant versus MO_x dominant.
21. Note that if the M - Si - O system contains more than one metal-silicide phase, there will be several phase diagram possibilities within the MO_x dominant type (see Fig. 3); if the system contains no metal-silicide phases, there will not be a MO_x dominant type.
22. These are the potential compatibility triangles that would accompany a tie-line between silicon and MO_x . The ternary phases lying on these compatibility triangles are the only ones relevant to the existence of the tie-line being tested by Eqs. (5), (6), and (7).
23. If a tie-line between silicon and MO_x does not exist, a tie-line from the relevant MSi_xO_y phase(s) that crosses the silicon- MO_x tie-line position must exist. Such a tie-line must connect with either M or MSi_z since a MSi_z - SiO_2 tie-line is known not to exist [in order to reach Eq. (5), ΔG had to be positive for Eq. (2)].
24. I. Barin and O. Knacke, *Thermochemical Properties of Inorganic Substances* (Springer-Verlag, Berlin, 1973).
25. I. Barin, O. Knacke, and O. Kubaschewski, *Thermochemical Properties of Inorganic Substances, Supplement* (Springer-Verlag, Berlin, 1977).
26. *Thermodynamic Properties of Elements and Oxides* (United States Bureau of Mines Bulletin 672, U.S. Government Printing Office, Washington, DC, 1982).
27. G. M. Lukashenko, R. I. Polotskaya, and V. R. Sidorko, *J. Alloys Compd.* **179**, 299 (1992).
28. See, for example, R. E. Dickerson, *Molecular Thermodynamics* (Benjamin/Cummings, Menlo Park, 1969).
29. *Powder Diffraction File: Inorganic Phases* (JCPDS International Centre for Diffraction Data, Swarthmore, PA, 1992).
30. *CRC Handbook of Chemistry and Physics*, 71st ed. (CRC Press, Cleveland, OH, 1990/91).
31. *The Oxide Handbook*, 2nd ed., edited by G. V. Samsonov (IFI/Plenum, New York, 1982).
32. *Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology, New Series, Group III, Vol. 7b*, edited by K-H. Hellwege (Springer-Verlag, Berlin, 1975), p. 456.
33. W. J. Kramers and J. R. Smith, *Trans. Brit. Ceram. Soc.* **56**, 590 (1957).
34. *Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology, New Series, Group III, Vol. 27g*, edited by O. Madelung (Springer-Verlag, Berlin, 1992), p. 4.
35. G. Brauer, H. Reuther, H. Walz, and K. H. Zapp, *Z. Anorg. Allg. Chem.* **369**, 144 (1969).
36. G. Natta and M. Strada, *Gazzetta Chimica Italiana* **58**, 419 (1928).
37. O. Muller and R. Roy, *J. Less-Common Met.* **16**, 129 (1968).
38. A. Ourmazd, D. W. Taylor, J. A. Rentschler, and J. Bevk, *Phys. Rev. Lett.* **59**, 213 (1987).
39. E. I. Givargizov, *Oriented Crystallization on Amorphous Substrates* (Plenum Press, New York, 1991).
40. R. P. Reade, P. Berdahl, R. E. Russo, and L. W. Schaper, *Appl. Phys. Lett.* **66**, 2001 (1995).
41. H. J. Goldschmidt, *Interstitial Alloys* (Plenum Press, New York, 1967), p. 296.
42. H. Mori and H. Ishiwara, *Jpn. J. Appl. Phys.* **30**, L1415 (1991); H. Ishiwara, H. Mori, K. Jyokyu, and S. Ueno, in *Silicon Molecular Beam Epitaxy*, edited by J. C. Bean, S. S. Iyer, and K. L. Wang (Mater. Res. Soc. Symp. Proc. **220**, Pittsburgh, PA, 1991), p. 595; H. Ishiwara, N. Tsuji, H. Mori, and H. Nohira, *Appl. Phys. Lett.* **61**, 1459 (1992).
43. R. A. McKee, F. J. Walker, J. R. Conner, E. D. Specht, and D. E. Zelmon, *Appl. Phys. Lett.* **59**, 782 (1991); R. A. McKee, F. J. Walker, J. R. Conner, and R. Raj, *Appl. Phys. Lett.* **63**, 2818 (1993).
44. H. Behner, J. Wecker, Th. Matthée, and K. Samwer, *Surf. Interface Anal.* **18**, 685 (1992).
45. Th. Matthée, J. Wecker, H. Behner, G. Friedl, O. Eibl, and K. Samwer, *Appl. Phys. Lett.* **61**, 1240 (1992).
46. A. Bardal, O. Eibl, Th. Matthée, G. Friedl, and J. Wecker, *J. Mater. Res.* **8**, 2112 (1993).
47. S. I. Krasnosvobodtsev and E. V. Pechen, *Physica C* **185–189**, 2097 (1991).
48. H. Behner, J. Wecker, and B. Heines, in *High T_c Superconductor Thin Films*, edited by L. Corraera (North-Holland, Amsterdam, 1992), p. 623.
49. E. V. Pechen, R. Schoenberger, B. Brunner, S. Ritzinger, K. F. Renk, M. V. Sidorov, and S. R. Oktyabrsky, *J. Appl. Phys.* **74**, 3614 (1993).
50. J. D. Filby and S. Nielsen, *Br. J. Appl. Phys.* **18**, 1357 (1967).
51. H. M. Manasevit, *J. Cryst. Growth* **22**, 125 (1974).
52. The growth of HfO_2 layers on silicon has been reported by R. de Reus, F. W. Saris, G. J. van der Kolk, C. Witmer, B. Dam, D. H. A. Blank, D. J. Adelerhof, and J. Flokstra, *Mater. Sci. Engr. B* **7**, 135 (1990). From RBS analyses, these researchers report HfO_2 to be inert in contact with silicon at temperatures up to 1073 K. However, as in many reports of the deposition of oxides on silicon, no mention is given in this work of the method used to remove the native oxide from the (100) Si wafer prior to growth. It is thus likely that the stable interfaces studied were actually $HfO_2/SiO_2/Si$, which does not indicate whether the HfO_2/Si interface is stable or unstable. It is for this same reason that other reports of the growth of binary oxides on silicon, in which the removal of the native oxide prior to growth is unclear, are not considered in our comparisons.
53. R. Pretorius, J. M. Harris, and M-A. Nicolet, *Solid-State Electron.* **21**, 667 (1978).
54. D. M. Brown, W. E. Engeler, M. Garfinkel, and P. V. Gray, *Solid-State Electron.* **11**, 1105 (1968).
55. S. P. Murarka, *J. Vac. Sci. Technol.* **17**, 775 (1980); S. P. Murarka, *Silicides for VLSI Applications* (Academic Press, New York, 1983), pp. 138–140.
56. K. E. Spear, P. W. Gilles, and H. Schäfer, *J. Less-Common Met.* **14**, 69 (1968).
57. S. P. Murarka, D. B. Fraser, W. S. Lindenberger, and A. K. Sinha, *J. Appl. Phys.* **51**, 3241 (1980).
58. H. M. Manasevit, D. H. Forbes, and I. B. Cadoff, *Trans. Metall. Soc. AIME* **236**, 275 (1966).
59. D. K. Fork, F. A. Ponce, J. C. Tramontana, and T. H. Geballe, *Appl. Phys. Lett.* **58**, 2294 (1991).
60. P. Tiwari, S. Sharan, and J. Narayan, *J. Appl. Phys.* **69**, 8358 (1991).
61. S. H. Rou, T. M. Graettinger, A. F. Chow, C. N. Soble, II, D. J. Lichtenwalner, O. Auciello, and A. I. Kingon, in *Ferroelectric*

- Thin Films II*, edited by A. I. Kingon, E. R. Myers, and B. Tuttle (Mater. Res. Soc. Symp. Proc. **243**, Pittsburgh, PA, 1992), p. 81.
62. G. Soerensen and S. Gygax, *Physica B*, **169**, 673 (1991).
 63. Y. Kado and Y. Arita, *J. Appl. Phys.* **61**, 2398 (1987); Y. Kado and Y. Arita, in *Extended Abstracts of the 18th (1986 International) Conference on Solid State Devices and Materials* (Tokyo, 1986), p. 45.
 64. Y. Kado and Y. Arita, in *Extended Abstracts of the 20th (1988 International) Conference on Solid State Devices and Materials* (Tokyo, 1988), p. 181.
 65. H. Fukumoto, T. Imura, and Y. Osaka, *Appl. Phys. Lett.* **55**, 360 (1989).
 66. H. Fukumoto, M. Yamamoto, and Y. Osaka, *Proc. Electrochem. Soc.* **90**, 239 (1990).
 67. K. Harada, H. Nakanishi, H. Itozaki, and S. Yazu, *Jpn. J. Appl. Phys.* **30**, 934 (1991).
 68. M. Yamamoto, H. Fukumoto, and Y. Osaka, in *Heteroepitaxy of Dissimilar Materials*, edited by R. F. C. Farrow, J. P. Harbison, P. S. Peercy, and A. Zangwill (Mater. Res. Soc. Symp. Proc. **221**, Pittsburgh, PA, 1991), p. 35.
 69. T. Inoue, Y. Yamamoto, S. Koyama, S. Suzuki, and Y. Ueda, *Appl. Phys. Lett.* **56**, 1332 (1990); T. Inoue, M. Osonoe, H. Tohda, M. Hiramatsu, Y. Yamamoto, A. Yamanaka, and T. Nakayama, *J. Appl. Phys.* **69**, 8313 (1991); L. Luo, X. D. Wu, R. C. Dye, R. E. Muenchausen, S. R. Foltyn, Y. Coulter, C. J. Maggiore, and T. Inoue, *Appl. Phys. Lett.* **59**, 2043 (1991); T. Inoue, T. Ohsuna, L. Luo, X. D. Wu, C. J. Maggiore, Y. Yamamoto, Y. Sakurai, and J. H. Chang, *Appl. Phys. Lett.* **59**, 3604 (1991); T. Inoue, T. Ohsuna, Y. Yamada, K. Wakamatsu, Y. Itoh, T. Nozawa, E. Sasaki, Y. Yamamoto, and Y. Sakurai, *Jpn. J. Appl. Phys.* **31**, L1736 (1992); Y. Yamamoto, M. Satoh, Y. Sakurai, S. Nakajima, T. Inoue, and T. Ohsuna, *Jpn. J. Appl. Phys.* **32**, L620 (1993).
 70. M. Yoshimoto, H. Nagata, T. Tsukahara, and H. Koinuma, *Jpn. J. Appl. Phys.* **29**, L1199 (1990); H. Nagata, M. Yoshimoto, H. Koinuma, E. Min, and N. Haga, *J. Cryst. Growth* **123**, 1 (1992); M. Yoshimoto, K. Shimozono, T. Maeda, T. Ohnishi, M. Kumagai, T. Chikyow, O. Ishiyama, M. Shinohara, and H. Koinuma, *Jpn. J. Appl. Phys.* **34**, L688 (1995).
 71. H. Nagata, M. Yoshimoto, T. Tsukahara, S. Gonda, and H. Koinuma, in *Evolution of Thin-Film and Surface Microstructure*, edited by C. V. Thompson, J. Y. Tsao, and D. J. Srolovitz (Mater. Res. Soc. Symp. Proc. **202**, Pittsburgh, PA, 1991), p. 445.
 72. H. Koinuma, H. Nagata, T. Tsukahara, S. Gonda, and M. Yoshimoto, *Appl. Phys. Lett.* **58**, 2027 (1991).
 73. T. Chikyow, S. M. Bedair, L. Tye, and N. A. El-Masry, *Appl. Phys. Lett.* **65**, 1030 (1994); L. Tye, T. Chikyow, N. A. El-Masry, and S. M. Bedair, in *Epitaxial Oxide Thin Films and Heterostructures*, edited by D. K. Fork, J. M. Phillips, R. Ramesh, and R. M. Wolf (Mater. Res. Soc. Symp. Proc. **341**, Pittsburgh, PA, 1994), p. 107; L. Tye, N. A. El-Masry, T. Chikyow, P. McLarty, and S. M. Bedair, *Appl. Phys. Lett.* **65**, 3081 (1994).
 74. The approximate error stated is calculated from the "B" quality data for SiO₂, the "B-C" quality data for CeO₂, and the "C" quality data for CeSi₂ given in Ref. 24 and 25.
 75. T. Inoue, T. Ohsuna, Y. Obara, Y. Yamamoto, M. Satoh, and Y. Sakurai, *Jpn. J. Appl. Phys.* **32**, 1765 (1993).
 76. D. K. Fork, D. B. Fenner, and T. H. Geballe, *J. Appl. Phys.* **68**, 4316 (1990).
 77. E. J. Tarsa, J. S. Speck, and McD. Robinson, *Appl. Phys. Lett.* **63**, 539 (1993).
 78. T. L. Chu, M. H. Francombe, G. A. Gruber, J. J. Oberly, and R. L. Tallman, *Deposition of Silicon on Insulating Substrates*, Report No. AFCRL-65-574 (Westinghouse Research Laboratories, Pittsburgh, PA, 1965). See especially pp. 31–34 and pp. 41–44. (NTIS ID No. AD-619 992).
 79. M. Morita, H. Fukumoto, T. Imura, Y. Osaka, and M. Ichihara, *J. Appl. Phys.* **58**, 2407 (1985); Y. Osaka, T. Imura, Y. Nishibayashi, and F. Nishiyama, *J. Appl. Phys.* **63**, 581 (1988).
 80. H. Myoren, Y. Nishiyama, H. Fukumoto, H. Nasu, and Y. Osaka, *Jpn. J. Appl. Phys.* **28**, 351 (1989).
 81. A. Lubig, Ch. Buchal, J. Schubert, C. Copetti, D. Guggi, C. L. Jia, and B. Stritzker, *J. Appl. Phys.* **71**, 5560 (1992); A. Lubig, Ch. Buchal, D. Guggi, C. L. Jia, and B. Stritzker, *Thin Solid Films* **217**, 125 (1992).
 82. I. Golecki, H. M. Manasevit, L. A. Moudy, J. J. Yang, and J. E. Mee, *Appl. Phys. Lett.* **42**, 501 (1983); H. M. Manasevit, I. Golecki, L. A. Moudy, J. J. Yang, and J. E. Mee, *J. Electrochem. Soc.* **130**, 1752 (1983); A. L. Lin, and I. Golecki, *J. Electrochem. Soc.* **132**, 239 (1985).
 83. P. Legagneux, G. Garry, D. Dieumegard, C. Schwebel, C. Pellet, G. Gautherin, and J. Siejka, *Appl. Phys. Lett.* **53**, 1506 (1988).
 84. H. Fukumoto, T. Imura, and Y. Osaka, *Jpn. J. Appl. Phys.* **27**, L1404 (1988); H. Fukumoto, M. Yamamoto, Y. Osaka, and F. Nishiyama, *J. Appl. Phys.* **67**, 2447 (1990); H. Fukumoto, M. Yamamoto, and Y. Osaka, *J. Appl. Phys.* **69**, 8130 (1991).
 85. D. K. Fork, D. B. Fenner, G. A. N. Connell, J. M. Phillips, and T. H. Geballe, *Appl. Phys. Lett.* **57**, 1137 (1990); D. K. Fork, D. B. Fenner, R. W. Barton, J. M. Phillips, G. A. N. Connell, J. B. Boyce, and T. H. Geballe, *Appl. Phys. Lett.* **57**, 1161 (1990); D. K. Fork, F. A. Ponce, J. C. Tramontana, N. Newman, J. M. Phillips, and T. H. Geballe, *Appl. Phys. Lett.* **58**, 2432 (1991).
 86. W. Pursseit, S. Corsépius, M. Zwerger, P. Berberich, H. Kinder, O. Eibl, C. Jaekel, U. Breuer, and H. Kurz, *Physica C* **201**, 249 (1992).
 87. S. P. Murarka and C. C. Chang, *Appl. Phys. Lett.* **37**, 639 (1980).
 88. M. L. Green, M. E. Gross, L. E. Papa, K. J. Schnoes, and D. Brasen, *J. Electrochem. Soc.* **132**, 2677 (1985).
 89. Q. X. Jia and W. A. Anderson, *Appl. Phys. Lett.* **57**, 304 (1990).
 90. E. Kolawa, F. C. T. So, E. T-S. Pan, and M-A. Nicolet, *Appl. Phys. Lett.* **50**, 854 (1987).
 91. L. Krusin-Elbaum, M. Wittmer, and D. S. Yee, *Appl. Phys. Lett.* **50**, 1879 (1987).
 92. C. W. Nieh, E. Kolawa, F. C. T. So, and M-A. Nicolet, *Mater. Lett.* **6**, 177 (1988).
 93. A. Charai, S. E. Hörnström, O. Thomas, P. M. Fryer, and J. M. E. Harper, *J. Vac. Sci. Technol. A* **7**, 784 (1989).
 94. T. Nakamura, Y. Nakao, A. Kamisawa, and H. Takasu, *Appl. Phys. Lett.* **65**, 1522 (1994); T. Nakamura, Y. Nakao, A. Kamisawa, and H. Takasu, *Jpn. J. Appl. Phys.* **33**, 5207 (1994).
 95. H. M. Manasevit and W. J. Simpson, *J. Appl. Phys.* **35**, 1349 (1964); H. M. Manasevit, A. Miller, F. L. Morritz, and R. Nolder, *Trans. Metall. Soc. AIME* **233**, 540 (1965).
 96. F. A. Ponce, *Appl. Phys. Lett.* **41**, 371 (1982).
 97. M. Ishida, I. Katakabe, T. Nakamura, and N. Ohtake, *Appl. Phys. Lett.* **52**, 1326 (1988); K. Sawada, M. Ishida, T. Nakamura, and N. Ohtake, *Appl. Phys. Lett.* **52**, 1672 (1988); K. Sawada, M. Ishida, T. Nakamura, and T. Suzaki, *J. Cryst. Growth* **95**, 494 (1989).
 98. H. Iizuka, K. Yokoo, and S. Ono, *Appl. Phys. Lett.* **61**, 2978 (1992).
 99. M. Ishida, K. Sawada, S. Yamaguchi, T. Nakamura, and T. Suzaki, *Appl. Phys. Lett.* **55**, 556 (1989); M. Ishida, S. Yamaguchi, Y. Masa, T. Nakamura, and Y. Hikita, *J. Appl. Phys.* **69**, 8408 (1991).
 100. G. Grube, A. Schneider, U. Esch, and M. Flad, *Z. Anorg. Chem.* **260**, 120 (1949).

101. E. Kolawa, C. Garland, L. Tran, C.W. Nieh, J.M. Molarius, W. Flick, M-A. Nicolet, and J. Wei, *Appl. Phys. Lett.* **53**, 2644 (1988).
102. Y. Zeng, Z. Zhang, W. Luo, N. Yang, Y. Cai, Z. Hua, and X. Shen, *Thin Solid Films* **214**, 235 (1992); Z. Zhang, Y. Zeng, W. Lou, Y. Cai, Y. Sun, Z-Y. Hua, and X. Shen, *Vacuum* **43**, 1033 (1992).
103. E. Kolawa, C.W. Nieh, J.M. Molarius, L. Tran, C. Garland, W. Flick, M-A. Nicolet, F.C.T. So, and J.C.S. Wei, *Thin Solid Films* **166**, 15 (1988).
104. W.B. Pennebaker, *IBM J. Res. Develop.* **13**, 686 (Nov. 1969).
105. S. Matsubara, T. Sakuma, S. Yamamichi, H. Yamaguchi, and Y. Miyasaka, in *Ferroelectric Thin Films*, edited by E.R. Myers and A.I. Kingon (*Mater. Res. Soc. Symp. Proc.* **200**, Pittsburgh, PA, 1990), p. 243; T. Sakuma, S. Yamamichi, S. Matsubara, H. Yamaguchi, and Y. Miyasaka, *Appl. Phys. Lett.* **57**, 2431 (1990); H. Yamaguchi, S. Matsubara, and Y. Miyasaka, *Jpn. J. Appl. Phys.* **30**, 2197 (1991).
106. H. Nagata, T. Tsukahara, S. Gonda, M. Yoshimoto, and H. Koizumi, *Jpn. J. Appl. Phys.* **30**, L1136 (1991).
107. H. Ishiwara and K. Azuma, in *Heteroepitaxy on Silicon: Fundamentals, Structure, and Devices*, edited by H.K. Choi, R. Hull, H. Ishiwara, and R.J. Nemanich (*Mater. Res. Soc. Symp. Proc.* **116**, Pittsburgh, PA, 1988), p. 369.
108. H. Mori, and H. Ishiwara, *Jpn. J. Appl. Phys.* **30**, L1415 (1991); H. Ishiwara, H. Mori, K. Jyokyu, and S. Ueno, in *Silicon Molecular Beam Epitaxy*, edited by J.C. Bean, S.S. Iyer, and K.L. Wang (*Mater. Res. Soc. Symp. Proc.* **220**, Pittsburgh, PA, 1991), p. 595.
109. Since the free energy of the ternary or higher, multicomponent oxide must be lower than its binary constituents in order for it to form, and the binary constituents selected are individually compatible with silicon, the only potential reactions with silicon (i.e., where $\Delta G < 0$) involve ternary or higher, multicomponent products (e.g., MM'_xO_z , MM'_xSi_y , or $MM'_xSi_yO_z$ phases). Although this greatly reduces the number of reactions that need to be tested to establish thermodynamic stability, thermodynamic data for these relevant multicomponent materials are often lacking.
110. Y. Kado and Y. Arita, in *Extended Abstracts of the 21st Conference on Solid State Devices and Materials* (Tokyo, 1989), p. 45.
111. H.M. Manasevit and D.H. Forbes, *J. Appl. Phys.* **37**, 734 (1966).
112. H. Seiter and Ch. Zaminer, *Z. Angew. Phys.* **20**, 158 (1965).
113. M. Ihara, Y. Arimoto, M. Jifuku, T. Kimura, S. Kodama, H. Yamawaki, and T. Yamaoka, *J. Electrochem. Soc.* **129**, 2569 (1982); M. Ihara, *Microelectron. Eng.* **1**, 161 (1983).

APPENDIX: TERNARY PHASE DIAGRAMS

The construction of phase diagrams must be in accordance with the Gibbs phase rule:²⁸

$$f = c + 2 - p, \quad (11)$$

where f is the number of degrees of freedom (number of independent intensive variables), c is the number of components in the system (i.e., the minimum number of independent constituents sufficient to form all the phases in the phase diagram), and p is the number of phases in equilibrium. This phase rule is readily deduced by subtracting the total number of independent equations involving the intensive variables from the total number of intensive variables.

The three-component phase diagrams, M -Si-O, considered in this paper are all at fixed temperature and pressure. With these two intensive variables fixed, the Gibbs phase rule implies that the maximum number (i.e., when $f = 0$) of phases that can coexist in equilibrium is three. Consequently, M -Si-O phase diagrams are constrained to contain only one, two, and at most three-phase regions. A one-phase region exists at the vertex of any of the triangles within the phase diagram; a two-phase region exists on any tie-line; and the interior to any triangle is a three-phase region. Crossing tie-lines are not allowed because at the point of their intersection the simultaneous coexistence of four phases (two from each tie-line) would be implied, whereas a maximum of three phases in coexistence is mandated by the Gibbs phase rule.