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Rare-earth-metal—semiconductor interfacial reactions: Thermodynamic aspects

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Chemical reactions at rare-earth-metal—semiconductor interfaces are discussed based on heats of formation of bulk compounds and estimated heats of adsorption. Photoemission results for rare-earth-metal overlayers on the Si(111), Ge(111), and GaAs(110) surfaces, which have shown valence changes with chemical reactions and clustering of metal atoms, were used to estimate the heats of adsorption. The heats of adsorption of rare-earth metals on the Si surface were found to be considerably reduced as compared to bond strengths in bulk rare-earth silicides. This weak bond is attributed to an effectively zero-valent ($6s^2$) or monovalent ($5d^16s^2$) valence-electron configuration of the rare-earth adatom on the Si surface. The heats of adsorption on the GaAs surface were found to be larger and somewhat closer to bond strengths in bulk rare-earth compounds than in the rare-earth—Si system, probably due to significant ionic contribution to the rare-earth—As bond. The fact that the surface disruption is observed in the initial stage of Ce adsorption on the GaAs surface but not for Sm on GaAs is explained by the larger heat of adsorption for Ce than for Sm (by ~50 kcal/mol). The heats of formation of bulk rare-earth compounds were estimated from their valence behaviors, photoemission core-level shifts, and the heats of formation of related compounds. They are found to be only weakly dependent on the valence and the atomic number of the rare-earth metals, consistent with experimental photoemission results for multiple-layer coverages of these metals on semiconductor substrates.

I. INTRODUCTION

There has been considerable interest in modeling the formation of the Schottky barrier at metal-semiconductor interfaces.[1-5] In contrast to what was orginially thought, recent spectroscopic studies of metal overlayers deposited onto semiconductor surfaces prepared under ultrahigh vacuum[5] have revealed reactive atomic intermixing. These interfacial chemical interactions are now known to be generally complex and different from those found in the bulk. Unfortunately, the energetics of these chemical reactions are quite difficult to determine experimentally, but are extremely important factors in modeling both the morphology of the interface and the formation of the Schottky barrier.

Room-temperature chemical reactions at representative rare-earth-metal-semiconductor interfaces [Ce/Si (Refs. 6 and 7) Ce/Ge (Ref. 8), Ce/GaAs (Ref. 9) Sm/Si (Refs. 10 and 11), Sm/Ge (Ref. 11), Sm/GaAs (Ref. 12), Eu/Si (Ref. 13), Gd/Si (Ref. 14), Tm/Si (Ref. 15), and Yb/Si (Ref. 16)] have recently been studied by using synchrotron radiation photoemission. Changes in emission from the quasi-core-like $4f$ shells and from the Si core levels have given clear evidence of changes in the chemical state of the rare-earth atoms as a function of metal coverage. These include valence changes for Sm and binding-energy shifts for Ce and Yb associated with chemical interactions during chemisorption and interfacial compound formation. In particular, it has been shown that Ce atoms form clusters on the Si(111) surface and that these interact only weakly with the substrate—strong chemical reaction is initiated by disruption of the clusters.[6] In contrast, Ce atoms react more strongly with Ge(111) and GaAs(110) surfaces from the initial adsorption stage.[8,9] Sm exhibits a valence change at a critical coverage of 0.3—1 monolayer (ML) on the Si, Ge, and GaAs surfaces.[10-12] On the other hand, there is no evidence for valence change for trivalent Ce (Refs. 6,7, and 17) and Tm (Ref. 15), and divalent Yb (Ref. 16) and Eu (Ref. 13) at room temperature, although heat treatment results in formation of a mixed-valent Yb silicide.[18] These results are summarized in Table I and provide the systematics necessary for modeling rare-earth-metal—semiconductor interfaces.

In the present paper, these experimental results are used to evaluate various interface energetics based on thermodynamic principles of the lanthanide elements. In particular, we make use of the fact that the electronic, structural, and thermochemical properties are smooth functions of the atomic number within the lanthanide series for the same valence (divalent or trivalent). Irregularities occur in cases where the valence (or the number of atomiclike $4f$ electrons) changes when the rare-earth atom is converted between free atom, adsorbed atom, metal, bulk compound, and interfacial compound.[19-21] Combining the experimental results with these principles make it possible to estimate the heats of adsorption for the initial adsorption stage and the heats of formation for bulk rare-earth compounds. Using the heats of formation and the heats of adsorption thus obtained, the various experimental results are discussed.

In Sec. II, relations between thermochemical quantities are given for the rare-earth elements—including cohesive energies, heats of formation of bulk compounds, heat of adsorption, and hypothetical transition energies between divalent and trivalent metallic states. Energetics of the initial-stage adsorption and metal-atom clustering are

TABLE I. Summary of photoemission results for room-temperature reactions of rare-earth-metal overlayers on cleaved Si(111), Ge(111), and GaAs(110) surfaces. Thicknesses are given in monolayers (ML), referenced to the atomic density of the semiconductor surface.

	Θ_c[a]	Θ_R[b]	Valence[c]	Ref.
Ce/Si	0.6	2.5	III	6,7
Ce/Ge			III	8
Ce/GaAs	<0.1	3.2	III	9
Sm/Si	1	4–5	II→III	10,11
Sm/Ge	1	3–4	II→III	11
Sm/GaAs	0.3	1.5–2	II→III	12
Tm/Si[d]			III	15
Eu/Si			II	13
Gd/Si	<0.5	3–5	III	14
Yb/Si	1.5–2	2–3	II	16
Ca/Si	0.3	3.5	II	38

[a] Critical coverage for the onset of intermixing or valence change (ML).

[b] Thickness of reacted interface layers (ML).

[c] "II→III" means that a divalent to trivalent change occurs at $\Theta \simeq \Theta_c$.

[d] Results for an annealed Si(111)-7×7 surface.

studied in Sec. III. Chemical interactions for fully reacted stages are discussed, based on bulk thermodynamics, in Sec. IV. In Sec. V we discuss the electronic nature of a rare-earth-adatom—substrate bond and propose a mechanism for cluster-induced chemical reactions. Finally, conclusions are given in Sec. VI. Estimates of unknown heats of formation for bulk rare-earth silicides, germanides, and arsenides are given in Appendix A. Bond strengths of rare-earth atoms in these bulk compounds are evaluated in Appendix B.

The important conclusions drawn from the present analyses are the following: (i) The heats of adsorption of rare-earth atoms are considerably reduced from bond strengths in bulk rare-earth compounds, particularly for rare-earth—Si systems, (ii) the large heat of adsorption for Ce atoms compared to Sm is responsible for the disruption of the GaAs surface from the initial adsorption stage, and (iii) chemical reactions for several-monolayer coverages can be interpreted by using bulk heats of formation of rare-earth compounds estimated in the present work.

II. THERMODYNAMIC PRINCIPLES OF RARE-EARTH ELEMENTS

We denote the heats of formation[22] ΔH_f of the divalent (II) and trivalent (III) rare-earth bulk silicides $M\text{Si}_x$ or germanides $M\text{Ge}_x$ per mole metal atoms by ΔH_f^{II} and ΔH_f^{III}, respectively, when there is no valence change during the compound formation

$$M(\text{II metal})+x\text{Si}\rightarrow M(\text{II})\text{Si}_x,\quad \Delta H_f=\Delta H_f^{\text{II}}\ , \tag{1}$$

$$M(\text{III metal})\ x\text{Si}\rightarrow M(\text{III})\text{Si}_x,\quad \Delta H_f=\Delta H_f^{\text{III}}\ . \tag{2}$$

These quantities depend on the valence, but are smooth, weakly varying functions of the atomic number within the lanthanide series. Because the variation within the same valence is small and also because there are insufficient thermochemical data to determine the variation,[23] we assume the ΔH_f^{II} and ΔH_f^{III} values to be constant and independent of the atomic number. Similarly, the heats of reaction ΔH_R per mole metal atom, namely, the energy change in a reaction at the rare-earth-metal—GaAs interface defined in Ref. 4, can also be regarded to be constant (ΔH_R^{II} or ΔH_R^{III}) within the lanthanide series if there is no valence change during the reaction

$$M(\text{II metal})+\tfrac{2}{3}\text{GaAs}\rightarrow\tfrac{1}{3}M(\text{II})_3\text{As}_2+\tfrac{2}{3}\ \text{Ga}\ ,\qquad \Delta H_R=\Delta H_R^{\text{II}}\ , \tag{3}$$

$$M(\text{III metal})+\text{GaAs}\rightarrow M(\text{III})\text{As}+\text{Ga},\quad \Delta H_R=\Delta H_R^{\text{III}}\ . \tag{4}$$

In cases where a valence change from a divalent to a trivalent state occurs in going from the metal to the compound, we have to consider an additional term in ΔH_f or ΔH_R of Eqs. (1)–(4). For a divalent to trivalent change, an energy $\Delta H_{\text{II,III}}$ is required to convert the divalent metal to hypothetical trivalent metal; for a trivalent to divalent change, $-\Delta H_{\text{II,III}}$ is required. As shown in Fig. 1, $\Delta H_{\text{II,III}}$, unlike ΔH_f^{II}, ΔH_f^{III}, ΔH_R^{II}, and ΔH_R^{III}, exhibits a strong, irregular variation as a function of the atomic number.[24] Therefore, the valence of the compound is determined by a condition

$$\Delta H_{\text{II},III} \gtrless \Delta H_f^{\text{II}}-\Delta H_f^{\text{III}}\ , \tag{5}$$

as shown in Fig. 1. By using values obtained in Appendix A and listed in Table II for ΔH_f^{II} and ΔH_f^{III} (or ΔH_R^{II} and ΔH_R^{III}), ΔH_f's (or ΔH_R's) for the divalent and trivalent reaction products have been calculated for the rare-earth—Si, —Ge, and —GaAs systems. These are shown in

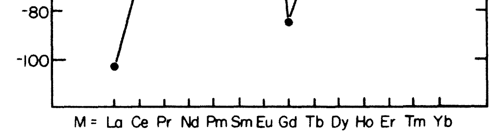

FIG. 1. Energy required to convert a divalent rare-earth metal to a trivalent one $\Delta H_{\text{II,III}}$ (from Ref. 24). $\Delta H_f^{\text{II}}-\Delta H_f^{\text{III}}$ for the rare-earth disilicide and digermanide and $\Delta H_R^{\text{II}}-\Delta H_R^{\text{III}}$ for the rare-earth—GaAs interface are shown by horizontal lines. If $\Delta H_{\text{II,III}} > \Delta H_f^{\text{II}}-\Delta H_f^{\text{III}}$, the rare-earth atom in $M\text{Si}_2$ or $M\text{Ge}_2$ is divalent. If $\Delta H_{\text{II,III}} > \Delta H_R^{\text{II}}-\Delta H_R^{\text{III}}$, the rare-earth—As reaction product is divalent $M_3\text{As}_2$. Estimated error bars are indicated by vertical bars.

TABLE II. Values for ΔH_f^i (or ΔH_R^i for M/GaAs) and E_b^i (i=II,III,IV) obtained in Appendixes A and B. The units are kcal/mol.

	M/Si	M/Ge	M/GaAs
ΔH_f^{II} or ΔH_R^{II}	-36 ± 2	-21 ± 5	-45 ± 7
$\Delta H_f^{\mathrm{III}}$ or $\Delta H_R^{\mathrm{III}}$	-46 ± 3	-34 ± 5	-56 ± 2
ΔH_f^{IV} or ΔH_R^{IV}	-39 ± 2	-28 ± 2	-54 ± 2
E_b^{II}	150	160	145
E_b^{III}	224	235	245
E_b^{IV}	256	269	285

Fig. 2. Note that in the metal, the divalent state is stable in Eu and Yb and the trivalent state is stable in the others.

We can also assume that the heat of adsorption ΔH_{ad} depends strongly on the valence but not on the atomic number in cases where there is no valence change upon adsorption.[25] We denote the heats of adsorption of the divalent and trivalent atoms without valence change during adsorption by $\Delta H_{\mathrm{ad}}^{\mathrm{II}}$ and $\Delta H_{\mathrm{ad}}^{\mathrm{III}}$, i.e.,

$$M(\text{II atom}) \rightarrow M(\text{II ads}),\quad \Delta H_{\mathrm{ad}} = \Delta H_{\mathrm{ad}}^{\mathrm{II}}\ , \tag{6}$$

$$M(\text{III atom}) \rightarrow M(\text{III ads}),\quad \Delta H_{\mathrm{ad}} = \Delta H_{\mathrm{ad}}^{\mathrm{III}}\ . \tag{7}$$

A divalent to trivalent valence change, as for Tm, requires an additional energy $\Delta E_{\mathrm{II,III}}$, namely, a divalent to trivalent ($4f^{n+1}6s^2 \rightarrow 4f^n 5d^1 6s^2$) transition energy of the free atom, as shown in Fig. 3. Therefore, in analogy to Eq. (5), the valence of the adsorbed atom is determined by

$$\Delta E_{\mathrm{II,III}} \gtrless \Delta H_{\mathrm{ad}}^{\mathrm{II}} - \Delta H_{\mathrm{ad}}^{\mathrm{III}}\ , \tag{8}$$

as shown in Fig. 3. $\Delta E_{\mathrm{II,III}}$ is related to $\Delta H_{\mathrm{II,II}}$ by

$$\Delta E_{\mathrm{II,III}} = \Delta H_{\mathrm{II,III}} + E_{\mathrm{coh}}^{\mathrm{III}} - E_{\mathrm{coh}}^{\mathrm{II}}\ , \tag{9}$$

where $E_{\mathrm{coh}}^{\mathrm{II}}$ and $E_{\mathrm{coh}}^{\mathrm{III}}$ are (hypothetical) cohesive energies of divalent and trivalent atoms to divalent and trivalent metals, respectively, and are smooth functions of the atomic number. $E_{\mathrm{coh}}^{\mathrm{II}}$ is interpolated and/or extrapolated smoothly from those of Eu (43 kcal/mol) and Yb (37 kcal/mol) and $E_{\mathrm{coh}}^{\mathrm{III}}$ is interpolated between La (103 kcal/mol) and Lu (102 kcal/mol).[26,27] Note that the free rare-earth atoms are divalent except for La, Ce, Gd, and Lu.

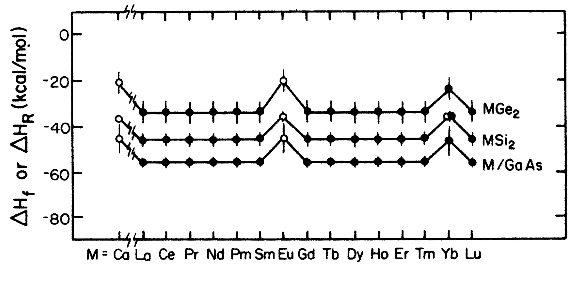

FIG. 2. Heats of formation ΔH_f for the rare-earth disilicides and digermanides and heats of reaction ΔH_R for the rare-earth–GaAs system. We have assumed ΔH_f^{II} and $\Delta H_f^{\mathrm{III}}$ (ΔH_R^{II} and $\Delta H_R^{\mathrm{III}}$) to be independent of the atomic number. Open circles and solid circles represent, respectively, divalent and trivalent reaction products.

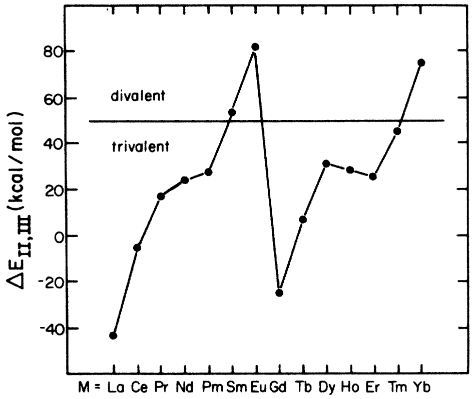

FIG. 3. Energy required to convert a divalent rare-earth free atom to a trivalent one $\Delta E_{\mathrm{II,III}}$. $\Delta H_{\mathrm{ad}}^{\mathrm{II}} - \Delta H_{\mathrm{ad}}^{\mathrm{III}} \simeq 50$ kcal/mol estimated for the Si(111) surface is shown by a horizontal line in the figure. A rare-earth atom with $\Delta E_{\mathrm{II,III}}$ above this line is adsorbed in the divalent state.

III. CHEMISORPTION AND METAL-ATOM CLUSTERING AT ULTRALOW COVERAGES

Although submonolayer metal coverages on semiconductor surfaces have been found to be important for descriptions of band bending at low coverages,[5] little is known about the energetics of the deposition process. In this section, we semiquantitatively estimate the adsorption energies by using the thermochemical principles described in Sec. II and the experimental findings regarding valence changes and metal-atom clustering.

It has been observed by photoemission that Sm and Tm are divalent and trivalent, respectively, at the initial adsorption stage on the Si(111) surface.[10,11,15] The relative stability of the divalent and trivalent adsorbate states is determined by Eq. (8), as illustrated in Fig. 3: $\Delta H_{\mathrm{ad}}^{\mathrm{III}} + \Delta E_{\mathrm{II,III}}(\mathrm{Sm}) > \Delta H_{\mathrm{ad}}^{\mathrm{III}}$ and $\Delta H_{\mathrm{ad}}^{\mathrm{III}} + \Delta E_{\mathrm{II,III}}(\mathrm{Tm}) < \Delta H_{\mathrm{ad}}^{\mathrm{II}}$. Thus, we obtain limits on $\Delta H_{\mathrm{ad}}^{\mathrm{II}}$ and $\Delta H_{\mathrm{ad}}^{\mathrm{III}}$ for the Si surface, namely,

$$47 < \Delta H_{\mathrm{ad}}^{\mathrm{II}} - \Delta H_{\mathrm{ad}}^{\mathrm{III}} < 54 \text{ kcal/mol}\ . \tag{10}$$

For the GaAs(110) and Ge(111) surfaces, only the last inequality in Eq. (10) has been verified because the Tm/GaAs and Tm/Ge surfaces have not been explored, but we do not expect $\Delta H_{\mathrm{ad}}^{\mathrm{II}} - \Delta H_{\mathrm{ad}}^{\mathrm{III}}$ to be much smaller than ~50 kcal/mol.

In the recent combined low-energy–electron-diffraction, angle-resolved Auger, and photoemission study[6] of Ce/Si(111), it was shown that strong chemical reaction between Ce and the substrate occurs only after a critical coverage of ~0.6 ML and that below this coverage Ce atoms are weakly interacting with the substrate in the form of small clusters. Likewise, photoemission results in Sm/Si (Refs. 10 and 11), Sm/Ge (Ref. 11), and Tm/Si (Ref. 15) are also consistent with clustering.

If clustering is to occur, it is necessary that the adatom-substrate bond must be weaker than the metal-

metal bonds in the cluster. A condition for the stability of a metal-atom cluster against transfer of an atom from the cluster to the isolated adatom may be given by

$$\Delta H^{\mathrm{II}}_{\mathrm{ad}} + bE^{\mathrm{II}}_{\mathrm{coh}} > 0 \;, \tag{11}$$

$$\Delta H^{\mathrm{III}}_{\mathrm{ad}} + bE^{\mathrm{III}}_{\mathrm{coh}} > 0 \;, \tag{12}$$

for the divalent and trivalent rare-earth atoms, respectively, when there is no valence change. Here the energy difference between an N-atom cluster plus a free atom and an $(N+1)$-atom cluster is denoted by bE_{coh}. Although the size of the clusters is not known for the rare-earth–semiconductor systems, from the coverage versus cluster-size behavior of various other metals,[28,29] we infer that N would be less than 100 atoms for submonolayer-equivalent coverages. To date, total-energy calculations for rare-earth atom clusters have not been performed but, according to a simple treatment of the cohesive properties of three-dimensional (3D) free-metal atom clusters,[30] b should be ~ 0.8 or less for this cluster size and approaches unity with $N \rightarrow \infty$. Thus, by assuming 3D clusters for Ce/Si, the heats of adsorption should be as small as $\Delta H^{\mathrm{II}}_{\mathrm{ad}} > -30$ kcal/mol and $\Delta H^{\mathrm{III}}_{\mathrm{ad}} > -80$ kcal/mol in order for the metal clusters to be stable against adsorption of isolated atoms, or in order to satisfy Eqs. (11) and (12). We expect further limitation on $\Delta H^{\mathrm{II}}_{\mathrm{ad}}$ and $\Delta H^{\mathrm{III}}_{\mathrm{ad}}$ to smaller values, since the latter limits are derived only from the stability of large $(N \leq 100)$ clusters. [As clusters are formed for Ce/Si, $\Delta H^{\mathrm{III}}_{\mathrm{ad}}$ in Eq. (10) is replaced by $-bE^{\mathrm{III}}_{\mathrm{coh}}$. If clusters are formed also for Sm/Si, $\Delta H^{\mathrm{II}}_{\mathrm{ad}}$ in Eq. (10) should also be replaced by $-bE^{\mathrm{II}}_{\mathrm{coh}}$. This can be shown to be consistent with $b \sim 0.8$.]

The photoemission experimental results for rare-earth atoms on the GaAs(110) surface[9,12] indicate that the heats of adsorption would be larger on GaAs than on Si. In particular, the Ce/GaAs interface exhibits strong chemical reaction from the initial adsorption stage ($\Theta \sim 0.1$ ML).[9,31] For Sm/GaAs there is no completely unambiguous evidence favoring two-dimensional (2D) over 3D aggregation, although 2D aggregating may be more probable.[12] Therefore, we expect that for the GaAs surface, $\Delta H^{\mathrm{II}}_{\mathrm{ad}}$ and $\Delta H^{\mathrm{III}}_{\mathrm{ad}}$ are close to the above limit and we estimate $\Delta H^{\mathrm{II}}_{\mathrm{ad}}$ and $\Delta H^{\mathrm{III}}_{\mathrm{ad}}$ (which are equal to ΔH_{ad}'s for Sm and Ce, respectively) to be $-(20–40)$ kcal/mol and $-(70–90)$ kcal/mol, respectively.

Whereas Ce atoms disrupt the GaAs surface from the initial adsorption stage and are in a local structural environment similar to bulk GaAs,[9] the Sm/GaAs interface does not show strong chemical reaction below ~ 0.3 ML, as judged from the absence of trivalent features for the initial adsorption stage.[12] We attribute this difference to the heat of adsorption of Sm (either for the divalent or trivalent adsorption state, see Fig. 4), which is smaller than that of Ce by ~ 50 kcal/mol. (From Fig. 4, large heats of adsorption are also expected for Gd, Lu, and Tb, while Tm, Yb, and Eu are expected to have smaller heats of adsorption.) At higher coverages the surface is disrupted as Sm is fully coordinated by As atoms and becomes trivalent.

The fact that the disruption occurs from the initial adsorption stage for Ce/GaAs but not for Ce/Si would suggest that $\Delta H^{\mathrm{III}}_{\mathrm{ad}}$ (which is equal to ΔH_{ad} of Ce) is significantly larger for Ce/GaAs than for Ce/Si. As we estimated $\Delta H^{\mathrm{II}}_{\mathrm{ad}} = -(20–40)$ kcal/mol and $\Delta H^{\mathrm{III}}_{\mathrm{ad}} = -(70–90)$ kcal/mol for rare-earth–GaAs interfaces, it would be reasonable to assume $\Delta H^{\mathrm{II}}_{\mathrm{ad}} = -(0–20)$ kcal/mol and $\Delta H^{\mathrm{III}}_{\mathrm{ad}} = -(50–70)$ kcal/mol for rare-earth–Si interfaces to be consistent with experimental results. (Note that $\Delta H^{\mathrm{II}}_{\mathrm{ad}} - \Delta H^{\mathrm{III}}_{\mathrm{ad}}$ should be $\lesssim 50$ kcal/mol for any estimate.) On the other hand, the strong chemical reaction occurring from the initial adsorption stage of the Ce/Ge(111) interface[8] and the probable metal-atom clustering at the Sm/Ge(111) interface[11] would suggest that the adsorption energies for Ge(111) are intermediate between Si(111) and GaAs(110).

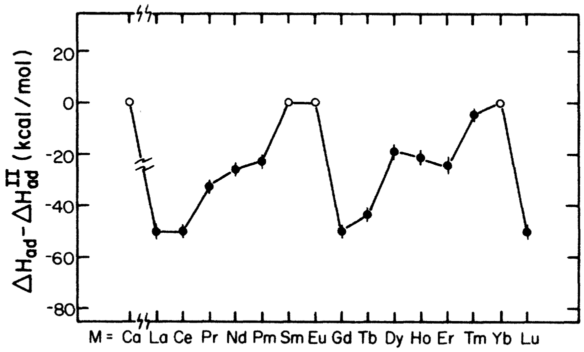

FIG. 4. Heats of adsorption ΔH_{ad} for the rare-earth-metal–semiconductor systems. We have assumed $\Delta H^{\mathrm{II}}_{\mathrm{ad}}$ and $\Delta H^{\mathrm{III}}_{\mathrm{ad}}$ to be constant and $\Delta H^{\mathrm{II}}_{\mathrm{ad}} - \Delta H^{\mathrm{III}}_{\mathrm{ad}} = 50(\pm 3)$ kcal/mol. Open circles and solid circles represent, respectively, divalent and trivalent adsorbed atomic states. $\Delta H^{\mathrm{II}}_{\mathrm{ad}}$ is estimated between 0 and -40 kcal/mol, depending on the substrate.

The above estimated adsorption energies are much smaller than what would be expected from bond strengths in bulk rare-earth Si, Ge, and As compounds (see binding energies of divalent and trivalent rare-earth atoms E^{II}_b and E^{III}_b, listed in Table II for these compounds). Furthermore, $\Delta H^{\mathrm{II}}_{\mathrm{ad}} / \Delta H^{\mathrm{III}}_{\mathrm{ad}}$ is considerably smaller than the value of $\frac{2}{3}$ expected from the divalent and trivalent behaviors of rare-earth atoms (note that $E^{\mathrm{II}}_b / E^{\mathrm{III}}_b \sim \frac{2}{3}$ in Table II). The electronic origin of these weak chemisorption bonds will be discussed in Sec. V A.

IV. CHEMICAL REACTIONS AT MULTIPLE-LAYER COVERAGES

All the rare-earth–Si, –Ge, and –GaAs interfaces studied to date exhibit strong chemical interactions or intermixing between the metal overlayers and the substrate for coverages exceeding several monolayers. We discuss in this section the interfacial reaction chemistry of these thick metal coverages based on the thermochemical data of bulk rare-earth compounds, as reaction products for these thick coverages are expected to some extent to show physical and chemical properties similar to the bulk compounds.

The heats of formation of bulk rare-earth disilicides and digermanides have been calculated by using the values for ΔH^{II}_f ad $\Delta H^{\mathrm{III}}_f$ listed in Table II and are illustrated in

Fig. 2. The means by which the values of ΔH_f^{II} and $\Delta H_f^{\mathrm{III}}$ have been estimated are discussed in Appendix A. For every rare-earth element the observed valence is consistent with the predicted relative stability of the divalent and trivalent compounds shown in Fig. 1, with the stable valences giving large, negative values of ΔH_f indicative of reactive interfaces. Because $\Delta H_f^{\mathrm{II}} - \Delta H_f^{\mathrm{III}} \simeq 10$ kcal/mol, the trivalent configuration will be stabilized relative to the divalent configuration in the silicide by about 10 kcal/mol more than in the metal. This makes $\mathrm{YbSi}_{\sim 2}$ mixed valent.[32] For $\mathrm{EuSi}_{\sim 2}$, the divalent state is still more stable than the trivalent state[33] by 12 kcal/mol.

One can notice in Fig. 2 that the variation of ΔH_f as a function of the atomic number is small in the rare-earth—Si, —Ge, or —GaAs system, suggesting almost identical reaction energetics for several-monolayer coverage of trivalent rare-earth metals and only a small deviation from this for divalent systems. (There is, however, a slight decrease of ~ 10 kcal/mol in the absolute value for Eu and Yb compounds formed from divalent metals.) In fact, experimental results in this higher-coverage region are similar for the different rare-earth metals—in contrast to the variety of behaviors for low coverages discussed above.

The stabilization of the trivalent configuration in the silicide and germanide is supported by the photoemission spectra of the Sm/Si and Sm/Ge interfaces,[10,11] according to which the trivalent $4f$ signal is the most intense for $\Theta \sim 4$ ML where emission from the intermixed region should be a maximum. Since $\mathrm{Sm(III)Si_2}$ is predicted to be more stable than $\mathrm{Sm(II)Si_2}$ by as much as 16 kcal/mol, one would not expect a divalent surface layer on the silicide of the kind observed for a Sm metal,[34] where the divalent state is more stable only by kcal/mol in the bulk.[24,35,36] We conclude, therefore, that the divalent signal observed experimentally for ~ 4 ML is probably due to unreacted metal aggregates on the substrate and/or a Sm skin growing on the fully reacted silicide product. This conclusion supports the model of heterogeneous chemical reactions, as recently discussed for the Ce/Si (Ref. 7) interface.

While the trivalent rare-earth silicides seem to have disilicide stoichiometry at the interface, the room-temperature reaction products of divalent rare-earth—Si interfaces appear to be more metal rich. For instance, the interfacial Yb silicide has been found to remain divalent from the lowest to highest coverages at room temperature and not to show the mixed-valence behavior observed for $\mathrm{YbSi}_{\sim 2}$. As Yb metal-rich compounds tend to be divalent,[37] this reaction product would be assigned to the metal-rich Yb-Si compound(s). Since quite similar thermodynamics should be applicable to multiple-layer coverage Yb/Si and Ca/Si (Fig. 2), we can attribute the Ca-Si reaction products to metal-rich silicides such as $\mathrm{Ca_2Si}$. This is consistent with the observed low emission near E_F (Ref. 38), since $\mathrm{Ca_2Si}$ is a semiconductor. These different chemical behaviors between the divalent and trivalent metal overlayers may be due to the smaller heats of formation for the divalent metals, as shown in Fig. 2, resulting in insufficient heat release during the intermixing reaction. The chemical behavior of the rare-earth-metal—Ge interface for several-monolayer coverages is similar to that of the rare-earth-metal—Si interface,[11] consistent with the similar or slightly smaller ΔH_f's compared to the silicides (Fig. 2).

The relative stability of the divalent and trivalent M-As reaction products on rare-earth—GaAs interfaces and their heats of reaction have also been calculated using the formalism described above. $\Delta H_R^{\mathrm{III}}$ [Eq. (4)] is given by $\Delta H_R^{\mathrm{III}} = \Delta H_f^{\mathrm{III}}(M\mathrm{As}) - \Delta H_f(\mathrm{GaAs}) \simeq -56$ kcal/mol, where $\Delta H_f^{\mathrm{III}}(M\mathrm{As})$ is the heat of formation of M(III)As from the trivalent metal, i.e., -73 kcal/mol (Appendix A). Likewise, ΔH_R^{II} [Eq. (3)] is given by $\Delta H_R^{\mathrm{II}} = \frac{1}{3}\Delta H_f^{\mathrm{II}}(M_3\mathrm{As}_2) - \frac{2}{3}\Delta H_f(\mathrm{GaAs}) \simeq -45$ kcal/mol, where $\Delta H_f^{\mathrm{II}}(M_3\mathrm{As}_3) \simeq -170$ kcal/mol is the heat of formation of $M(\mathrm{II})_3\mathrm{As}_2$ from the divalent metal given in Appendix A. The calculated heats of reaction based on these values are given in Fig. 2. As can be seen, they are negative and are larger than the heats of formation for the corresponding silicides and germanides. The same valence behavior is therefore predicted for the GaAs interfaces as for the rare-earth—Si and —Ge, in agreement with experimental results.[9,12] We expect that a divalent surface layer on the SmAs-like reaction product is less probable than one the $\mathrm{SmSi_2}$ surface because of the very large stability of Sm(III)As relative to Sm(II)As in the bulk (Appendix A), unless As is deficient on the surface. This fact combined with the experimental results on Sm/GaAs (Ref. 12) supports heterogeneous reaction for this interface analogously to the Sm/Si interface discussed above.

V. DISCUSSION

A. Chemisorption bonds between rare-earth atoms and semiconductor surfaces

The heats of adsorption derived in Sec. III are considerably smaller than those expected when two and three valence electrons, respectively, of the divalent and trivalent metal atom are involved in chemisorption (cf. E_b^{II} and E_b^{III} in Table II). Furthermore, the ratio $\Delta H_{\mathrm{ad}}^{\mathrm{II}}/\Delta H_{\mathrm{ad}}^{\mathrm{III}}$ is smaller than the value of $\frac{2}{3}$ expected for the divalent and trivalent chemical bonds.[39] If we used this ratio and the empirical limits defined in Eq. (10), we obtain large values $\Delta H_{\mathrm{ad}}^{\mathrm{II}} \sim -100$ kcal/mol and $\Delta H_{\mathrm{ad}}^{\mathrm{III}} \sim -150$ kcal/mol (for GaAs or Ge, $\Delta H_{\mathrm{ad}}^{\mathrm{II}} \gtrsim -100$ kcal/mol and $\Delta H_{\mathrm{ad}}^{\mathrm{III}} \gtrsim -150$ kcal/mol). This $\Delta H_{\mathrm{ad}}^{\mathrm{III}}$ value is comparable to the adsorption energy of an Al atom on Si(111), ~ -130 kcal/mol, calculated using the first-principle pseudopotential method[40] [or ~ -200 kcal/mol with reference to a trivalent atomic configuration $(3s\,3p^2)$ if the $3s^2 3p$ to $3s\,3p^2$ excitation energy[41] is added].

We attribute the apparently much weaker chemisorption bonds of the rare-earth atoms on the semiconductor surfaces to their quite different electronic configuration relative to atoms in fully coordinated solid-state or molecular environments. Indeed, Zunger[41] has shown for Al/GaAs(110) that the bond between an adsorbed Al atom and a substrate As (or Ga) atom (~ 10 kcal/mol) is much weaker than that expected from the bond strength in bulk AlAs. He explained this weak bond by an effectively monovalent $(3s^2 3p^1)$ configuration of the adsorbed

Al atom—in contrast to the trivalent ($3s^13p^2$) configuration in bulk solids such as Al metal, AlAs, and trivalent free molecules. Indeed, the free-atom ground state of Al is monovalent, but $3s \rightarrow 3p$ charge redistribution occurs and the Al atom becomes trivalent when the atomic volume is compressed in a fully coordinated solid-state or molecular environment. For rare-earth elements which have zero-valent ($6s^2$) or monovalent ($5d^16s^2$) free atomic configuration, substantial $6s \rightarrow 5d$ redistribution occurs and the rare-earth atom behaves as a divalent $(5d6s)^2$ or a trivalent $(5d6s)^3$. When a rare-earth atom adsorbs *above* the surface layer of a solid, the atomic volume remains almost uncompressed and an insufficient $6s \rightarrow 5d$ transfer occurs. The bond with the substrate then involves the chemically inert, closed 6*s* shell, resulting in the weak bond. The small values for $\Delta H_{\mathrm{ad}}^{\mathrm{II}}$ and $\Delta H_{\mathrm{ad}}^{\mathrm{III}}$ and the small $\Delta H_{\mathrm{ad}}^{\mathrm{II}}/\Delta H_{\mathrm{ad}}^{\mathrm{III}}$ ratio are consistent with this picture. By analogy to the Al/GaAs system,[41] we expect that the adatom-to-substrate-atom bond lengths are then larger than those in corresponding bulk rare-earth compounds.[42]

The stronger chemical interaction for the low-coverage rare-earth–GaAs interfaces than for rare-earth–Si or–Ge can probably be attributed to the larger electronegativity difference between rare earths and As (0.8–0.9, compared to 0.5 between Al and As or 0.6–0.7 between rare earths and Si or Ge). Hence, a larger rare-earth-to-As charge transfer is expected to occur, resulting in a substantial ionic character in the chemisorption bond by losing relatively inert 6*s* electrons, and the chemisorption bond becomes more similar to a normal divalent (Sm^{2+}) or trivalent (Ce^{3+}, Sm^{3+}) ionic bond.

We expect that the weak rare-earth–semiconductor bond is metastable, since heat treatment (500–800 °C) converts the Ce clusters on Si(111) to ordered chemisorbed arrays for submonolayer coverages.[43] As a result, the Ce atoms on the annealed surface form stronger bonds with Si atoms than in the initial adsorption stage after overcoming an activation barrier. This new chemisorption bond would be more similar to that of the trivalent rare earths. In the case of Ce/GaAs, the activation barrier is overcome at room temperature because of the large heat of adsorption and/or the low barrier energy. For Ce/Ge we postulate that the barrier is smaller than for Ce/Si because the Ge—Ge bond is weaker than the Si—Si bond (Appendix B). This should result in an easier atomic rearrangement of the Ge surface upon Ce adsorption, leading to the lower activation barrier and/or stronger chemisorption.

B. Cluster-induced chemical reaction

In order to intiate strong chemical reaction from the weakly interacting cluster state, an energy of the order of a few electron volts is generally necessary to overcome an activation barrier. For Al/GaAs(110), Zunger[41] has argued that the energy liberated when adsorbed atoms from clusters is sufficient to trigger strong chemical reaction. However, in the present case, condition (11) or (12) is satisfied only by a small excess energy (at most by ~30 kcal/mol for both divalent and trivalent rare earths and probably ~10 kcal/mol or less) and therefore only a small amount of energy is released when an *N*-atom cluster plus an adatom form an $(N+1)$-atom cluster.

We propose that another likely energy source is the coalescing of small clusters into larger ones. The amount of energy liberated can then become quite large. For example, if two 25-atom clusters were to fuse into a 50-atom cluster, an energy of the order of 10 eV would be liberated, according to the theory of Ref. 30. Once the reaction were initiated, heat released in forming bulklike compounds would be large enough to promote further reactions for all the rare-earth–semiconductor interfaces.

To estimate the energy available upon cluster coalescing of this kind, we have calculated the energy change ΔH_t when an adatom is converted to an atom in a bulk reaction product by using, for example,

$$\Delta H_t = -\Delta H_{\mathrm{ad}}^{\mathrm{II}} - E_{\mathrm{coh}}^{\mathrm{II}} + \Delta H_f^{\mathrm{II}} \tag{13}$$

for a divalent adsorbate to a divalent bulk compound. The results are shown in Fig. 5. As can be seen, ΔH_t would be large enough [~ -100 kcal/mol $-\Delta H_{\mathrm{ad}}^{\mathrm{II}} = -(60-100)$ kcal/mol] to promote further reaction for trivalent metal overlayers but is somewhat smaller [~ -80 kcal/mol$-\Delta H_{\mathrm{ad}}^{\mathrm{II}} = -(40-80)$ kcal/mol] for divalent Yb, Eu, and Ca. The insufficient (metal-rich) silicide formation for divalent metals on Si may be due to the small ΔH_t, as well as to the small ΔH_f compared to trivalent rare-earth metals.

If the reaction is triggered by cluster coalescing, the critical coverage Θ_c for the strong reaction would then be dependent on E_{coh}, namely, on the valence of metal atoms in the clusters for a certain substrate. Higher Θ_c would therefore be required for divalent metals than for the trivalent metals because of the smaller E_{coh}. In fact, the Θ_c value for trivalent Ce clusters on Si is smaller than those for divalent Sm and Yb clusters on Si (Table I). The heterogeneous reaction observed for the Ce/Si(111) interface[7] and suggested for Sm/Si(111) in Sec. IV gives support to the present cluster-induced reaction mechanism because the cluster size is distributed statistically and the

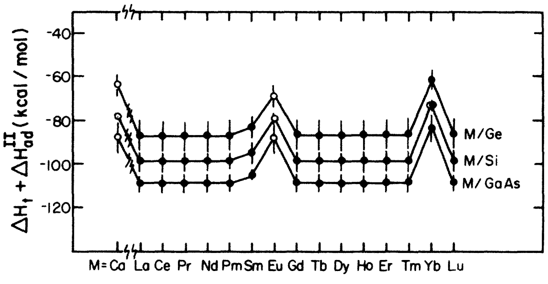

FIG. 5. Energy change ΔH_t when an adsorbed atom is converted to an atom in a bulk reaction product. We have assumed ΔH_f^{II}, $\Delta H_f^{\mathrm{III}}$ (ΔH_R^{II}, $\Delta H_R^{\mathrm{III}}$), $\Delta H_{\mathrm{ad}}^{\mathrm{II}}$, and $\Delta H_{\mathrm{ad}}^{\mathrm{III}}$ to be independent of the atomic number and $\Delta H_{\mathrm{ad}}^{\mathrm{II}} - \Delta H_{\mathrm{ad}}^{\mathrm{III}} = 50(\pm 3)$ kcal/mol. Open circles and solid circles represent, respectively, divalent and trivalent reaction products. As for the valence of the initial (adatom) state, only the experimentally observed one or theoretically predicted one is considered for each lanthanide. $\Delta H_{\mathrm{ad}}^{\mathrm{II}}$ is estimated between 0 and -40 kcal/mol, depending on the substrate (see text).

critical energy needed to trigger chemical reaction would be released at sites where coalescing of large enough clusters occurs.

VI. CONCLUSION

We have discussed chemical interactions taking place for rare-earth-metal overlayers on the Si(111), Ge(111), and GaAs(110) surfaces, based on heats of formation of bulk compounds and estimated heats of adsorption in the initial adsorption stage. We have suggested that the adsorption energies of rare-earth atoms on semiconductor surfaces [particularly Si(111)] are considerably smaller than those estimated from bonding in bulk rare-earth compounds. This was necessary in order to explain metal-atom clustering observed for low coverages. We have attributed the weak chemisorption bond to effectively zero-valent ($6s^2$) or monovalent ($5d^1 6s^2$) valence electron distribution of the rare-earth atom interacting with the Si surface at low coverages. The initial heat of adsorption of a Ce atom is shown to be larger than Sm by ~ 50 kcal/mol. This explains why the initial adsorption of a Ce atom disrupts the surface of GaAs while Sm does not. A cluster-induced reaction is proposed to be initiated by the coalescing of two metal-atom clusters which can provide sufficient energy to overcome an activation barrier and to trigger strong chemical reactions.

We have discussed the energetics of various chemical reactions occurring at rare-earth-metal—semiconductor interfaces. Other important factors in the chemical reactions may be kinetic processes, including activation barrier heights and diffusion processes.[44] Defects on the surface may play a role in the onset of chemical reaction[41] and band bending.[45] These are beyond the scope of the present thermochemical treatment, although the energetics discussed here seem to govern many important aspects of the rare-earth—semiconductor interfaces.

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APPENDIX A: ESTIMATE OF HEATS OF FORMATION FOR BULK SILICIDES AND GERMANIDES

To our knowledge there exist no thermochemical data for rare-earth silicides and germanides. As a result, we have estimated them as follows. We have assumed that ΔH_f^{II} for rare-earth silicides is equal to the heat of formation of a Ca silicide: $\Delta H_f^{\mathrm{II}} \simeq \Delta H_f(\mathrm{CaSi_2}) = -36$ kcal/mol.[46] This is justified because the heats of formation of divalent rare-earth compounds (either insulating or metallic) and those of Ca compounds with the same composition usually agree to within a few (or ~ 2) kcal/mol.[46,47] Different crystal structures usually do not affect the heat of formation significantly.

$\Delta H_f^{\mathrm{III}}$ can be estimated in two different ways. From each of the methods, we obtained the result $\Delta H_f^{\mathrm{III}} \simeq -45$ kcal/mol. In the first, the equivalent core approximation for the final state of $4f$-electron photoemission was used to obtain $\Delta H_f^{\mathrm{III}}$ from the binding-energy shift of trivalent $4f$ features between a Sm metal and a Sm silicide[11] and the heat of formation of a tetravalent Th disilicide, $\Delta H_f^{\mathrm{IV}} = -39$ kcal/mol.[46,47] For the Sm silicide produced at the interface, core-level studies[10,11] suggested a single phase and this has best been assumed to be $\mathrm{SmSi}_{\sim 2}$.[6,48,49] The $4f$ multiplet of the trivalent component is shifted by about 0.2 eV to higher binding energies relative to the metal. We expect that the binding-energy shift reflects different energy changes between metal and silicide when a trivalent Sm atom in the bulk is converted to a tetravalent (e.g., Th) atom. Thus, we consider a reaction cycle described in Fig. 6 where the reaction on the left involves an energy change $\Delta H_f^{\mathrm{III}}$ and that on the right involves ΔH_f^{IV}. A Sm atom with a photoproduced $4f$ hole is approximated by a substitution of a Th atom according to the equivalent-core approximation with complete screening of the $4f$ hole (largely by Sm $5d6s$ electrons) both in the metal and the silicide. Here we have neglected the impurity contribution (heats of solution of Th in Sm and $\mathrm{ThSi_2}$ in $\mathrm{SmSi_2}$, which are of the order of a few tenths of an eV) (Ref. 50), by assuming it to be balanced between the metal and the silicide (Fig. 6). Thus, the binding-energy shift is equal to the difference between the heats of formation of trivalent and tetravalent silicides: $\Delta H_f^{\mathrm{IV}} - \Delta H_f^{\mathrm{III}} \simeq 0.02$ eV $\simeq 5$ kcal/mol. The result is that $\Delta H_f^{\mathrm{III}} \simeq -44$ kcal/mol by the first method.

A second estimate of $\Delta H_f^{\mathrm{III}}$ made use of the fact that $\mathrm{YbSi}_{\sim 2}$ is a homogeneous mixed-valence material,[32] such that the divalent and trivalent forms are energetically degenerate. When forming trivalent $\mathrm{YbSi}_{\sim 2}$ from a divalent Yb metal, the heat of formation is $\Delta H_{\mathrm{II,III}} + \Delta H_f^{\mathrm{III}}$, which should be equal to ΔH_f^{II} in order to be mixed valent. Thus, we get $\Delta H_f^{\mathrm{III}} = \Delta H_f^{\mathrm{II}} - \Delta H_{\mathrm{II,III}}(\mathrm{Yb}) \simeq -46$ kcal/mol, which is in good agreement with the above estimate. We

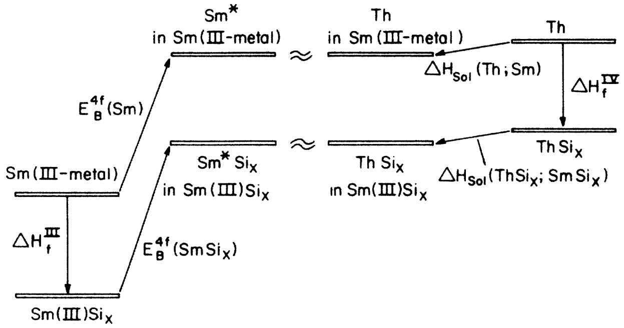

FIG. 6. Thermodynamic cycle for the equivalent-core approximation applied for the $4f$-level binding-energy shift between Sm(III) metal and Sm(III)Si_x. The $4f$-ionized trivalent Sm atom with complete screening (denoted by Sm*) can be replaced by a tetravalent Th atom. E_B^{4f} is the binding energy of the $4f$ level with respect to the Fermi energy, and $\Delta H_{\mathrm{sol}}(X;Y)$ is the heat of solution of X in the Y host.

have employed this value throughout this paper.

Thermochemical and photoemission data for metal germanides are less abundant than those for silicides. Therefore, as $M{\rm Si}_2$ and $M{\rm Ge}_2$ are isoelectronic, we assumed that ratios $E_b^{\rm II}:E_b^{\rm III}:E_b^{\rm IV}$ are the same for $M{\rm Si}_2$ and $M{\rm Ge}_2$, where $E_b^{\rm II}$, $E_b^{\rm III}$, and $E_b^{\rm IV}$ are the binding energies of the divalent, trivalent, and tetravalent metal atoms in the $M{\rm Si}_2$ or $M{\rm Ge}_2$ lattice. By using ΔH_f ($\equiv \Delta H_f^{\rm IV}$) of ThGe$_2$ [-28 kcal/mol (Ref. 46)] to obtain $E_b^{\rm IV}$, we get $\Delta H_f^{\rm III} = -34$ kcal/mol and $\Delta H_f^{\rm II} = -21$ kcal/mol.

The heats of formation of monoarsenides have been reported for some trivalent rare earths.[46] As most of these values fall in the range between -72 and -75 kcal/mol, we employ $\Delta H_f^{\rm III}(M{\rm As}) = -73$ kcal/mol. $\Delta H_f^{\rm II}(M_3{\rm As}_2)$ was obtained from a rough interpolation of the heats of formation[46] for Ca$_3$P$_2$, Ca$_3$Sb$_2$, and Ca$_3$Bi$_2$ to be $-170(\pm 20)$ kcal/mol. We have not considered divalent M(II)As or trivalent M(III)$_2$As$_3$ because they are expected to be energetically unfavorable since they are not observed under ambient conditions. In particular, M(II)As should be very unstable because in going from M(III)As to M(II)As, an electron from the As p level must be transferred to the rare-earth $4f$ shell.

APPENDIX B: ESTIMATE OF BINDING ENERGIES OF RARE-EARTH ATOMS IN BULK COMPOUNDS

The cohesive energy of the trivalent rare-earth disilicide relative to trivalent rare-earth atoms plus Si atoms,

$$E_{\rm coh}^{\rm III}(M{\rm Si}_2) = -\Delta H_f^{\rm III} + E_{\rm coh}^{\rm III} + 2E_{\rm coh}({\rm Si}) = 367 \text{ kcal/mol} , \tag{14}$$

with $E_{\rm coh}({\rm Si}) = 109$ kcal/mol, was assumed to be built by nearest-neighbor binding energies. The rare-earth disilicides crystallize in the β-ThSi$_2$ structure and the AlB$_2$ structure (or their modifications) where there are three covalent bonds between Si atoms and 12 rare-earth-metal—Si nearest-neighbor bonds per unit formula. The binding energy of a trivalent rare-earth atom in the disilicide lattice $E_b^{\rm III}$ may then be defined as the energy required to break the 12 metal—Si bonds. The Si—Si bond energy, including the π bond as well as the σ bond, was calculated according to the bond orbital theory of Harrison to be 48 kcal/mol,[51] and thus we estimated $E_b^{\rm III} \simeq 224$ kcal/mol. Similarly, for the divalent rare-earth and Ca disilicides (CaSi$_2$ crystallizes in a layer structure having the same number of Si—Si covalent bonds and metal-Si nearest neighbors), we considered

$$E_{\rm coh}^{\rm II}(M{\rm Si}_2) = -\Delta H_f^{\rm II} + E_{\rm coh}^{\rm II} + 2E_{\rm coh}({\rm Si}) \simeq 295 \text{ kcal/mol} , \tag{15}$$

and obtained $E_b^{\rm II} \simeq 150$ kcal/mol.

For the rare-earth germanides, we assumed that the ratios $E_b^{\rm II}:E_b^{\rm III}:E_b^{\rm IV}$ are the same for the silicides and germanides and evaluated $E_b^{\rm IV}$ to be 256 and 269 kcal/mol for ThSi$_2$ and ThGe$_2$, respectively, from published heats of formation[46] of -39 kcal/mol for ThSi$_2$ and -28 kcal/mol for ThGe$_2$. Hence, $E_b^{\rm II} \simeq 160$ kcal/mol and $E_b^{\rm III} \simeq 235$ kcal/mol. These values are a little larger than those for silicides in spite of the smaller heats of formation because more energy is needed to break Si—Si bonds than Ge—Ge bonds in a reaction $M + x{\rm Si} \rightarrow M{\rm Si}_x$ or $M + x{\rm Ge} \rightarrow M{\rm Ge}_x$. These values have been used to estimate $\Delta H_f^{\rm II}$ and $\Delta H_f^{\rm III}$ of the germanides in Appendix A.

The binding energies of rare earths in rare-earth arsenides can be approximated in the same manner from

$$E_{\rm coh}^{\rm III}(M{\rm As}) = -\Delta H_f^{\rm II}(M{\rm As}) + E_{\rm coh}^{\rm II} + E_{\rm coh}({\rm As}) \simeq 435 \text{ kcal/mol} , \tag{16}$$

$$E_{\rm coh}^{\rm III}(M_3{\rm As}_2) = -\Delta H_f^{\rm III}(M_3{\rm As}_2) + 3E_{\rm coh}^{\rm III} + E_{\rm coh}({\rm As}) \simeq 245 \text{ kcal/mol} , \tag{17}$$

where $E_{\rm coh}({\rm As}) = 72$ kcal/mol. Since these arsenides have crystal structures of ionic compounds, the cohesive energies (16) and (17) were decomposed into only nearest-neighbor rare-earth—As bonds. Therefore, $E_b^{\rm II}$ and $E_b^{\rm III}$ were approximated by the cohesive energies per mole metal atoms, namely, $\simeq 145$ $\simeq 245$ kcal/mol, respectively. These values are of similar magnitude to those for the silicides and germanides. All the values obtained in Appendixes A and B are listed in Table II.

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[23] For monosulfides, dihydrides, or dicarbides of lanthanide elements [R. Kieffer and F. Benesovsky, *Hartstoffe* (Springer, Vienna, 1963)], ΔH_f typically differs between divalent and trivalent compounds by ~ 10 kcal/mol. Within the divalent or trivalent compound series, it differs by only a few (or ~ 2) kcal/mol.

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[26] $E_{\rm coh}^{\rm III}$ can be obtained as $E_{\rm coh}^{\rm III} = E_{\rm coh} + \Delta E_{\rm II,III}$ but is a smooth function of the atomic number only with 10 kcal/mol (ranging from 93 kcal/mol to 103 kcal/mol). For the same reason as for $\Delta H_{\rm ad}^{\rm III}$ stated in Ref. 25, we use the barycenter of the $4f^n(X)5d^1$ multiplet as the reference atomic state. Therefore, the interpolated $E_{\rm coh}^{\rm III}$ is generally larger than the true $E_{\rm coh}^{\rm III}$ by 0–10 kcal/mol. However, for present purposes the true $E_{\rm coh}^{\rm III}$ and the linearly interpolated $E_{\rm coh}^{\rm III}$ make little difference and we employ the latter values for simplicity.

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$$\tfrac{3}{2}E_{\text{bond}}(\text{Si—Si}) = -(\epsilon_p - \epsilon_s) + 3V_2^h - \tfrac{3}{2}E_{\text{overlap}} + (4/\pi)V_{pp\pi} ,$$

where the second (σ-σ hybridization energy) and last (π-π hybridization energy) terms are scaled by $1/d^2$ ($d=$Si—Si bond length).